ENVIRONNENTAL PROTECTION AGENCY

40 CFR Parts 260, 261, 264, 265, 266, 270, and 271

[EPA/OSW-FR-91- SWH-FRL-39689]

Burning of Hazardous Waste in Boilers and Industrial Furnaces

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule: corrections; technical amendments.

SUMMARY: On February 21, 1991, the Environmental Protection Agency (EPA) published a final rule to regulate air emissions from the burning of hazardous waste in boilers and industrial furnaces (56 FR 7134). Today's notice corrects typographical and editorial errors that appeared in the regulatory text, including corrections to appendices II and III, and adds two appendices, appendix IX and appendix X, to part 266. Appendices IX and X were not ready at the time of publication; therefore, a note was placed in the appropriate location in the rule to inform readers that these appendices were to be published at a later date. Copies of these appendices were, however, made available to the public through the RCRA Docket maintained at EPA and through the National Technical Information Service (NTIS).

EFFECTIVE DATE: The effective date of the rule remains August 21, 1991.

FOR FURTHER INFORMATION CONTACT: For general information, contact the RCRA Hotline at (800) 424-9346 (toll-free) or (703) 920-9810. For more specific aspects of the final rule, contact Shiva Garg, Office of Solid Waste (OS-322), U.S. Environmental Protection Agency, 401 M Street, SW., Washington, DC 20460 (703) 308-8460.

SUPPLEMENTARY INFORMATION: On February 21, 1991, EPA promulgated a rule regulating the burning of hazardous waste in boilers and industrial furnaces (56 FR 7134). Based upon EPA's review of the notice, and comments received from the public, a number of editorial and typographical errors were found. This notice corrects errors found in the rule.[1]

In addition, appendices II and III to part 266 are being revised to address a number of problems that were identified by the Agency. First, the title of appendix II is being renamed because the use of words total chlorine and

chloride in the title (as published on February 21) is duplicative because total chlorine includes chloride. Second, the values in appendices II and III were erroneously calculated using a reference air concentration (RAC) for free chlorine of 0.04 $\mu g/m^3$ instead of 0.4 $\mu g/m^3$. This resulted in Tier I limits for total chlorine and Tier II limits for free chlorine that were too low by an order of magnitude. Third, the units used in appendices II and III were inadvertently different than the units used in appendix I and are being converted to g/hr to be consistent.

Also, two appendices to part 266, IX and X, are being added because they were not ready for publication when the final rule was promulgated, although they were available to the public through the RCRA Docket and through the National Technical Information Service (NTIS). Appendix IX is the Methods Manual for Compliance with the BIF Regulations, U.S. E.P.A., December 1990, document number PB 91-120-006. Appendix X is the Guideline on Air Quality Models (Revised) (1986), U.S. EPA, and includes Supplement A (1987); document numbers PB 86-245-248 and PB 88-150-958. These documents are available from NTIS, 5285 Port Royal Road, Springfield, Virginia 22161, phone number (703) 487-4600.

Finally, the rule deleted subpart D of part 266 and replaced it with new subpart H. However, references to subpart D at other locations in the CFR were inadvertently not revised. Today's notice makes conforming corrections at four locations: §§ 261.6(a)(2), 261.6(a)(2)(ii), 266.40 (c) and (d). A few other conforming corrections have also been made.

List of Subjects in 40 CFR Parts 260, 261, 264, 265, 266, 270, and 271

Administrative practices and procedures, Confidential business information, Hazardous materials transportation, Hazardous waste, Indian lands, Insurance, Incorporation by reference, Intergovernmental relations, Packaging and containers, Penalties, Recycling, Reporting and recordkeeping requirements, Security measures, Security bonds, Water pollution control, Water supply.

Dated: June 24, 1991.

Don R. Clay,

Assistant Administrator for Solid Waste and Emergency Response.

A. Technical Corrections

In rule document number 91-2667, beginning on page 7134 in the **Federal Register** published on Thursday,

February 21, 1991, make the following corrections:

PART 261—[AMENDED]

1. On page 7206, third column, in amendment 2 to part 261, add the following at the beginning of line 3 of the amendatory language of § 261.2: ", paragraph (d)(3) as (d)(4) and paragraph (d)(4) as (d)(5)". The corrected amendatory language will read as follows:

"2. Section 261.2 is amended by redesignating paragraph (d)(2) as (d)(3), paragraph (d)(3) as (d)(4), and paragraph (d)(4) as (d)(5), and adding a new paragraph (d)(2) to read as follows:"

PART 266—[AMENDED]

§ 266.100 [Corrected]

2. On page 7208, second column, in § 266.100(b)(2), line 3, replace the period after "recovery" with a semicolon.

3. On page 7208, second column, in § 266.100(b)(3), line 7, change "§ 261.5 of this chapter." to "§ 261.5 of this chapter; and ".

§ 266.102 [Corrected]

4. On page 7209, second column, in § 266.102(b)(1), line 12, change "for the Evaluation of Solid Waste" to "for Evaluating Solid Waste".

5. On page 7210, first column, in § 266.102, the paragraph designated as "(d)(4)(iii)(D)" should be designated as "(d)(4)(iv)".

6. On page 7210, third column, in § 266.102(e)(4)(i)(C), line 1, insert "A" between "(C)" and "sampling".

7. On page 7211, second column, in § 266.102(e)(6) heading, line 1, change "paramenters" to "parameters".

8. On page 7211, third column, in § 266.102(e)(6)(i)(B)(*1*)(*ii*), line 2, change "means" to "mean".

9. On page 7211, third column, at two locations: In lines 30 and 59, the number "2" in each subparagraph (2) heading of § 266.102(e)(6)(i)(B) and § 266.102(e)(6)(ii)(B), respectively, should be italicized.

10. On page 7211, third column, in § 266.102(e)(6)(ii), line 10, change "opeator" to "operator".

11. On page 7211, third column, in § 266.102(e)(6)(ii)(B)(*2*), lines 3 and 4, change "arithmetic mean of the most recent one hour block average for the average period" to "arithmetic mean of one hour block averages for the averaging period".

12. On page 7212, first column, in § 266.102(e)(6)(iv)(B), line 15, delete the comma between "§ 266.106(f)" and "need".

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[1] The Agency expects to promulgate another technical corrections notice later this summer that addresses other concerns identified since the promulgation of the rule on February 21, 1991.

§ 266.103 [Corrected]

13. On page 7213, first column, in § 266.103(a)(1)(ii), line 7, insert "or" between "burn" and "to".

14. On page 7214, first column, in § 266.103(b)(2)(ii)(A), line 4, insert "and" between "silver" and "thallium".

15 On page 7214, first column, in § 266.103(b)(2)(ii)(B), line 3, the reference to "(b)(ii)(A)" should read "(b)(2)(ii)(A)".

16. On page 7214, first column, in § 266.103(b)(2)(ii)(D), line 4, the reference to "(b)(ii)(B) or (b)(ii)(C)" should read "(b)(2)(ii)(B) or (b)(2)(ii)(C)".

17. On page 7214, second column, line 3, in § 266.103(b)(2)(iv), change "paticulate" to "particulate".

18. On page 7214, second column, in § 266.103(b)(2)(v)(A)(5), line 2, change "eqivalent" to "equivalent".

19. On page 7214, second column, in § 266.103(b)(2)(v)(A)(5), line 4, replace the period after "facility" with a semicolon.

20. On page 7214, second column, in § 266.103(b)(2)(vi), line 3, change "HC1" to "HCl".

21. On page 7214, third column, in § 266.103(b)(3)(ii), line 2, replace the semicolon after "streams" with a colon.

22. On page 7215, first column, in § 266.103(b)(5)(ii)(B), line 1, change "meat" to "meet".

23. On page 7215, first column, at two locations: in lines 38 and 66, the number "1" in each subparagraph (1) heading of § 266.103(b)(5)(i)(B) and § 266.103(b)(5)(ii)(B), respectively, should be italicized.

24. On page 7215, first column, line 46, the number "2" in the subparagraph (2) heading of § 266.103(b)(5)(i)(B) should be italicized.

25. On page 7215, second column, line 4, the number "2" in the subparagraph (2) heading of § 266.103(b)(5)(ii)(B) should be italicized.

26. On page 7215, second column, in § 266.103(b)(5)(ii)(B)(2), line 3 and 4, change "arithmetic mean of the most recent one hour block averages" to "arithmetic mean of one hour block averages".

27. On page 7215, second column, in § 266.103(b)(6) introductory text, lines 2 and 3, change "[the effective date of this rule]" to "August 21, 1991".

28. On page 7216, first column, in § 266.103(c), lines 1 and 2, delete "On or before August 21, 1992", capitalize the "t" in "the", and insert "on or before August 21, 1992" in line 12 between "Director" and "a".

29. On page 7216, first column, in § 266.103(c)(1), line 10, add "and all applicable emissions standards" after "limits".

30. On page 7216, second column, in § 266.103(c)(1)(iv), line 3, change "light-weighted" to "light-weight".

31. On page 7216, second column, in § 266.103(c)(1)(ix), line 8, replace the semicolon after "(e))" with a colon.

32. On page 7216, third column, in § 266.103(c)(1)(xi), lines 1, change "system" to "systems", and in line 7, replace the semicolon after "(e))" with a colon.

33. On page 7216, third column, in § 266.103(c)(1)(xii), line 8, replace the semicolon after "(e))" with a colon.

34. On page 7217, third column, in § 266.103(c)(4)(i)(C), line 2, change "test" to "testing".

35. On page 7217, third column, in § 266.103(c)(4)(ii)(B)(5), line 3, change "averge" to "average".

36. On page 7218, second column, in § 266.103(c)(4)(iv)(C)(2)(ii), lines 3 and 4, change "the arithmetic mean of the most recent one hour block averages for the averaging period" to "arithmetic mean of one hour block averages for the averaging period".

37. On page 7218, third column, in § 266.103(c)(7)(i)(A), line 3, change "(1)" (one) to "(1)" (lower case "el").

38. On page 7218, third column, in § 266.103(c)(7)(i)(B), delete the last word "to" in line 1 and replace by "only for purposes of compliance testing (and pretesting to prepare for compliance testing)".

39. On page 7219, first column, in § 266.103(c)(7)(ii)(B)(1)(ii), line 7, insert a period after "HCl/Cl₂".

40. On page 7219, first column, line 18, the number "2" in the subparagraph (2) heading of § 266.103(c)(7)(ii)(B) should be italicized.

41. On page 7219, third column, in § 266.103(g)(1), line 1, change "or" to "of".

§ 266.104 [Corrected]

42. On page 7220, second column, in § 266.104(a)(1), change the equation:

$$DRE = \left[\frac{1 - W_{out}}{W_{in}} \right] \times 100$$

to:

$$DRE = \left[1 - \frac{W_{out}}{W_{in}} \right] \times 100$$

43. On page 7220, third column, in § 266.104(a)(3), in line 12, change "tetrra-," to "tetra-," and in line 16, the reference to "paragraph (a)" should read "paragraph (a)(1)".

44. On page 7220, third column, in § 266.104(b)(2), lines 5 through 7, change

"in Hazardous Waste Incinerators, Boilers, and Industrial Furnaces" to "for Incinerators, Boilers, and Industrial Furnaces Burning Hazardous Waste".

45. On page 7221, first column, in § 266.104(c)(3), lines 3 through 6, change "Performance Specifications for Continuous Emission Monitoring of Hydrocarbons for Incinerators, Boilers and Industrial Furnaces" to "Performance Specifications for Continuous Emission Monitoring of Hydrocarbons for Incinerators, Boilers, and Industrial Furnaces Burning Hazardous Waste"; and in line 7, insert "and" between "CO" and "oxygen".

46. On page 7221, second column, line 3, in § 266.104(e)(1), insert "(PCDDs)" after "Dibenzo-p-Dioxins", and in line 6, replace the period at the end of the sentence after "part" with a semicolon.

47. On page 7221, second column, in § 266.104(e)(2), line 13, replace the period at the end of the sentence after "TCDD" with a semicolon.

48. On page 7221, second column, in § 266.104(e)(4), line 6, insert a before "2.2".

49. On page 7221, third column, in § 266.104(f)(3)(iii), line 4, change "conducts" to "conduct".

50. On page 7222, first column, the paragraph designated as "(g)2." of § 266.104, should be designated as "(g)(2)".

§ 266.106 [Corrected]

51. On page 7222, second column, in § 266.106(a), line 9, change "for Evaluation Solid Waste" to "for Evaluating Solid Waste".

52. On page 7222, third column, in the equation after line 3, in § 266.106(b)(2)(i), change "<1.0" to "≤1.0", and change "n = numer of carcinogenic metals" to "n = number of carcinogenic metals".

53. On page 7222, third column, in § 266.106(b)(2)(ii)(B), line 2, insert "as defined in § 266.102(e)(6)(ii)" between "hours" and "with".

54. On page 7222, third column, in § 266.106(b)(5), line 7, insert "shall be used" at the end of the sentence before the period.

55. On page 7223, first column, in § 266.106(b)(6), in the equation after line 15, change lines 5 and 6 of the equation that read "K=physical stack height (meters); K=stack gas flow rate (m³/second); and" to read: "H=physical stack height (meters); V=stack gas flow rate (m³/second); and".

56. On page 7223, second column, in § 266.106(c)(2), in the equation after line 12, delete the minus sign after "AER(i)".

57. On page 7223, third column, the equation in § 266.106(d)(3) is revised to read as below:

$$\frac{\sum_{i=1}^{n} \text{Predicted Ambient Concentration}_{(i)}}{\text{Risk-Specific Dose}_{(i)}} \leq 1.0$$

58. On page 7224, first column, in § 266.106(e), in line 8, change "each" to "a", and in line 10, change "levels" to "level".

59. On page 7224, first column, in § 266.106(f)(2)(ii) introductory text, delete the semicolon after "metal".

60. On page 7224, second column, line 3, in § 266.106(f)(2)(ii)(B), change "ratio" to "ratios".

§ 266.107 [Corrected]

61. On page 7224, second column, in § 266.107(a), line 4, change "provided by paragraphs (b), (c), or (d) of" to "provided by paragraph (b) or (c) of".

62. On page 7224, third column, in § 266.107(b)(2) heading, line 1, change "screen" to "screening".

63. On page 7224, third column, in § 266.107(b)(3), line 9, change "screen" to "screening".

64. On page 7225, first column, in § 266.107(d), change the paragraphs designated as "(i)" and "(ii)" to "(1)" and "(2)".

65. On page 7225, first column, in § 266.107(e), in line 3, insert "limit" between "screening" and "provided",

and in line 4, the reference to "Appendix I" should read "Appendix II".

66. On page 7225, first column, in § 266.107(h), line 5, change "his" to "this".

§ 266.108 [Corrected]

67. On page 7225, first column, in § 266.108(a), in the heading, line 1, change "Exemption" to "Exempt", and in the introductory text, line 5, change "section" to "subpart".

68. On page 7225, second column, first column of the table entitled "Exempt Quantities for Small Quantity Burner Exemption" in § 266.108(a)(1), insert "to" between "10.0" and "11.9".

69. On page 7225, second column, in § 266.108(c), in the equation after line 7, change "<1.0" to "≤ 1.0", and in the line after the equation that reads "Allowable Quantity Burned, means the", delete the comma after "Burned".

§ 266.109 [Corrected]

70. On page 7225, third column, in § 266.109(a)(1)(i), in line 4, change "of" to "on", and in line 8, delete the apostrophe after "fuel" and replace it with an end quotation mark.

71. On page 7226, first column, in § 266.109(a)(2)(iv) introductory text, line 3, change the reference to "(a)(iii)" to "(a)(2)(iii)".

72. On page 7226, first column, in § 266.109(a)(2)(iv)(A), line 2, change "componds" to "compounds".

73. On page 7226, first column, in § 266.109(b)(2), line 2, add "or adjusted Tier I" between "I" and "metals".

§ 266.110 [Corrected]

74. On page 7226, third column, line 4, in § 266.110(f)(3), insert "the" between "of" and "fuel".

75. On page 7227, third column, line 11, "§ 266.122" should correctly be designated as "§ 266.112".

Part 266, Appendix I [Amended]

76. On page 7228, in appendix I to part 266, in the title for Table I-A, change "Carcinogenic" to "Noncarcinogenic".

77. On page 7230, in appendix I to part 266, Table I-D: under "Values for use in rural areas", the first column "Beryllium" is moved so that it appears as the fifth column under "Values for use in urban areas". Also under "Values for use in urban areas", in second column under "Arsenic g/hr", change "9.6E+01" corresponding to a terrain adjusted eff. stack ht. of 16 meters to "9.6E-01".

78. On page 7230, in appendix I to part 266, Table I-E, in column 2, change "4.3-01" corresponding to "Terrain adjusted eff. stack ht. (m)" of 12 meters in the first column to "4.3E-01".

79. On page 7231, appendix II to part 266 is corrected to read as follows:

APPENDIX II.—TIER I FEED RATE SCREENING LIMITS FOR TOTAL CHLORINE

Terrain-adjusted effective stack height (m)	Noncomplex Terrain		Complex Terrain
	Urban (g/hr)	Rural (g/hr)	(g/hr)
4	8.2E+01	4.2E+01	1.9E+01
6	9.1E+01	4.8E+01	2.8E+01
8	1.0E+02	5.3E+01	4.1E+01
10	1.2E+02	6.2E+01	5.8E+01
12	1.3E+02	7.7E+01	7.2E+01
14	1.5E+02	9.1E+01	9.1E+01
16	1.7E+02	1.2E+02	1.1E+02
18	1.9E+02	1.4E+02	1.2E+02
20	2.1E+02	1.8E+02	1.3E+02
22	2.4E+02	2.3E+02	1.4E+02
24	2.7E+02	2.9E+02	1.6E+02
26	3.1E+02	3.7E+02	1.7E+02
28	3.5E+02	4.7E+02	1.9E+02
30	3.9E+02	5.8E+02	2.1E+02
35	5.3E+02	9.6E+02	2.6E+02
40	6.2E+02	1.4E+03	3.3E+02
45	8.2E+02	2.0E+03	4.0E+02
50	1.1E+03	2.6E+03	4.8E+02
55	1.3E+03	3.5E+03	6.2E+02
60	1.6E+03	4.6E+03	7.7E+02
65	2.0E+03	6.2E+03	9.1E+02
70	2.3E+03	7.2E+03	1.1E+03
75	2.5E+03	8.6E+03	1.2E+03
80	2.9E+03	1.0E+04	1.3E+03
85	3.3E+03	1.2E+04	1.4E+03
90	3.7E+03	1.4E+04	1.6E+03
95	4.2E+03	1.7E+04	1.8E+03
100	4.6E+03	2.1E+04	2.0E+03
105	5.3E+03	2.4E+04	2.3E+03
110	6.2E+03	2.9E+04	2.5E+03

APPENDIX II.—TIER I FEED RATE SCREENING LIMITS FOR TOTAL CHLORINE—Continued

Terrain-adjusted effective stack height (m)	Noncomplex Terrain		Complex Terrain
	Urban (g/hr)	Rural (g/hr)	(g/hr)
115	7.2E+03	3.5E+04	2.8E+03
120	8.2E+03	4.1E+04	3.2E+03

80. On pages 7231 and 7232, appendix III to part 266 is corrected to read as follows:

APPENDIX III.—Tier II Emission Rate Screening Limits for Free Chlorine and Hydrogen Chloride

Terrain-adjusted effective stack height (m)	Noncomplex terrain				Complex terrain	
	Values for urban areas		Values for rural areas		Values for use in urban and rural areas	
	Cl_2 (g/hr)	HCl (g/hr)	Cl_2 (g/hr)	HCl (g/hr)	Cl_2 (g/hr)	HCl (g/hr)
4	8.2E+01	1.4E+03	4.2E+01	7.3E+02	1.9E+01	3.3E+02
6	9.1E+01	1.6E+03	4.8E+01	8.3E+02	2.8E+01	4.9E+02
8	1.0E+02	1.8E+03	5.3E+01	9.2E+02	4.1E+01	7.1E+02
10	1.2E+02	2.0E+03	6.2E+01	1.1E+03	5.8E+01	1.0E+03
12	1.3E+02	2.3E+03	7.7E+01	1.3E+03	7.2E+01	1.3E+03
14	1.5E+02	2.6E+03	9.1E+01	1.6E+03	9.1E+01	1.6E+03
16	1.7E+02	2.9E+03	1.2E+02	2.0E+03	1.1E+02	1.8E+03
18	1.9E+02	3.3E+03	1.4E+02	2.5E+03	1.2E+02	2.0E+03
20	2.1E+02	3.7E+03	1.8E+02	3.1E+03	1.3E+02	2.3E+03
22	2.4E+02	4.2E+03	2.3E+02	3.9E+03	1.4E+02	2.4E+03
24	2.7E+02	4.8E+03	2.9E+02	5.0E+03	1.6E+02	2.8E+03
26	3.1E+02	5.4E+03	3.7E+02	6.5E+03	1.7E+02	3.0E+03
28	3.5E+02	6.0E+03	4.7E+02	8.1E+03	1.9E+02	3.4E+03
30	3.9E+02	6.9E+03	5.8E+02	1.0E+04	2.1E+02	3.7E+03
35	5.3E+02	9.2E+03	9.6E+02	1.7E+04	2.6E+02	4.6E+03
40	6.2E+02	1.1E+04	1.4E+03	2.5E+04	3.3E+02	5.7E+03
45	8.2E+02	1.4E+04	2.0E+03	3.5E+04	4.0E+02	7.0E+03
50	1.1E+03	1.8E+04	2.6E+03	4.6E+04	4.8E+02	8.4E+03
55	1.3E+03	2.3E+04	3.5E+03	6.1E+04	6.2E+02	1.1E+04
60	1.6E+03	2.9E+04	4.6E+03	8.1E+04	7.7E+02	1.3E+04
65	2.0E+03	3.4E+04	6.2E+03	1.1E+05	9.1E+02	1.6E+04
70	2.3E+03	3.9E+04	7.2E+03	1.3E+05	1.1E+03	1.8E+04
75	2.5E+03	4.5E+04	8.6E+03	1.5E+05	1.2E+03	2.0E+04
80	2.9E+03	5.0E+04	1.0E+04	1.8E+05	1.3E+03	2.3E+04
85	3.3E+03	5.8E+04	1.2E+04	2.2E+05	1.4E+03	2.5E+04
90	3.7E+03	6.6E+04	1.4E+04	2.5E+05	1.6E+03	2.9E+04
95	4.2E+03	7.4E+04	1.7E+04	3.0E+05	1.8E+03	3.2E+04
100	4.8E+03	8.4E+04	2.1E+04	3.6E+05	2.0E+03	3.5E+04
105	5.3E+03	9.2E+04	2.4E+04	4.3E+05	2.3E+03	3.9E+04
110	6.2E+03	1.1E+05	2.9E+04	5.1E+05	2.5E+03	4.5E+04
115	7.2E+03	1.3E+05	3.5E+04	6.1E+05	2.8E+03	5.0E+04
120	8.2E+03	1.4E+05	4.1E+04	7.2E+05	3.2E+03	5.6E+04

Part 266, Appendix IV [Amended]

81. On page 7232, in appendix IV to part 266, first column of the table, change "Methyl Ethyl Katone" to "Methyl Ethyl Ketone", and in line 34, change "Metyl Parathion" to "Methyl Parathion".

Part 266, Appendix VII [Amended]

82. On page 7234, first column, in appendix VII to part 266, in the table entitled "Metals—TCLP Extract Concentration Limits": in the heading in the third column of the table, replace "Concentration limits (mg/kg)" with "Concentration limits (mg/L)"; and add the following at the end of the table:

Thallium | 7440-28-0 | 7×E+00

83. On page 7234, third column, in appendix VII to part 266, in the table entitled "Nonmetals—Residue Concentration Limits—Continued", delete 8 lines beginning with "Thallium" and ending with "Thallium(I) sulfate.

Part 266, Appendix VIII [Amended]

84. On page 7235, in appendix VIII to part 266, first column of the table entitled "PICS Found in Stack Effluents", change "roform" to "chloroform" and "robenzene" to "chlorobenzene".

PART 270—[AMENDED]

§ 270.22 [Corrected]

85. On page 7235, second column, in § 270.22(a)(2)(ii)(B), line 12, change "Test Methods for the Evaluation of" to "Test Methods for Evaluating".

86. On page 7235, second column, in § 270.22(a)(2)(ii)(C), line 5, the reference to "(a)(1)(ii)(B)" should read "(a)(2)(ii)(B)".

87. On page 7236, first column, in § 270.22(a)(5)(vii), line 4, change "feestocks" to "feedstocks".

88. On page 7236, first column, in § 270.22(a)(6), line 1, change "trail" to "trial".

89. On page 7236, second column, in § 270.22(a)(6), line 8, change "from from" to "from" i.e. delete one "from" as it is duplicative.

90. On page 7236, second column, in § 270.22(b)(1), line 2, change "minimze" to "minimize".

§ 270.42 [Corrected]

91. On page 7237, first column, in § 270.42(g)(1) introductory text, line 3, change "wates" to "wastes".

92. On page 7237, first column, in § 270.42(g)(1)(i), line 5, change "effetive" to "effective".

93. On page 7237, second column, in § 270.42(g)(1)(iv), in lines 1 and 2, delete "In the case of Classes 2 and 3 modifications,"; in line 2, capitalize the "t" in "the"; and insert "Class 2 or 3" between "complete" and "modification" so that paragraph (iv) reads as follows: "The permittee also submits a complete Class 2 or 3 modification request within 180 days of the effective date of the rule listing or identifying the waste, or subjecting the unit to RCRA Subtitle C management standards;".

94. On page 7237, in appendix I to § 270.42, in line 1 of "L.5.", replace the period after "requirements" with a colon.

95. On page 7237, third column, in amendment 4 to part 270, the amendatory language is corrected to read as follows: "4. In § 270.42, appendix I is amended by revising the heading of L and items 1 through 4, 5a, 6, 7b, and 8 to read as follows:"

§ 270.66 [Corrected]

96. On page 7237, third column, line 2, in § 270.66(b)(1), change "operation" to "operational".

97. On page 7238, second column, in § 270.66(b)(4), line 8, change "107" to "266.107".

98. On page 7238, at two locations, lines 13, 14, and 15, in § 270.66(c)(2)(i) and in lines 5 and 6 in § 270.66(c)(2)(ii), change "Test Methods for the Evaluation of Solid Waste" to "Test Methods for Evaluating Solid Waste".

99. On page 7238, third column, in § 270.66(c)(3)(vi), line 3, delete "and".

100. On page 7238, third column, in § 270.66(c)(3)(vii), line 1, insert "air" between "any" and "pollution".

101. On page 7239, second column, in § 270.66(f)(3), line 10, replace the period after "standard" with a semicolon.

102. On page 7239, second column, in § 270.66(f)(8), line 5, change "is" to "in".

§ 270.33 [Corrected]

103. On page 7239, third column, in · § 270.73 at two locations, in paragraph (f), line 2, and in paragraph (g), line 3, change "as" to "has".

104. On page 7240, in § 271.1(j), Table 1, third column, replace "[insert FR page numbers]" with "56 FR 7134–7240".

B. Technical Amendments

For the reasons set out in the preamble, 40 CFR part 261 is amended as follows:

PART 261—IDENTIFICATION AND LISTING OF HAZARDOUS WASTE

1. The authority citation for part 261 continues to read as follows:

Authority: 42 U.S.C. 6905, 6912(a), 6921, 6922, and 6938.

§ 261.3 [Amended]

2. In § 261.3(c)(2)(ii)(8), line 3 is amended by replacing "by § 261.6(a)(3) (v) through (ix)" with "by § 261.6(a)(3) (v) through (viii)".

§ 261.6 [Amended]

3. In § 261.6(a)(2), line 4, the letter "G" is amended to read "H". The entire line should now read as: "subparts C through H of part 266 of".

4. In § 261.6(a)(2)(ii), line 5, the reference to "subpart D" should be replaced by "subpart H".

For the reasons set out in the preamble, 40 CFR part 265 is amended as follows:

PART 265—INTERIM STATUS STANDARDS FOR OWNERS AND OPERATORS OF HAZARDOUS WASTE TREATMENT, STORAGE, AND DISPOSAL FACILITIES

1. The authority citation for part 265 continues to read as follows:

Authority: 42 U.S.C. 6905, 6912(a), 6924, 6925, 6935.

§ 265.370 [Amended]

2. § 265.370 is amended by deleting the period (.) at the end and replacing it with the following: ", and subpart H of part 266, if the unit is a boiler or an industrial furnace as defined in · § 260.10.".

For the reasons set out in the preamble, 40 CFR part 270 is amended as follows:

PART 270—EPA ADMINISTERED PERMIT PROGRAMS: THE HAZARDOUS WASTE PERMIT PROGRAM

1. The authority citation for part 270 continues to read as follows:

Authority: 42 U.S.C. 6905, 6912, 6924, 6925, 6927, 6939, 6974.

§ 270.1 [Amended]

2. § 270.1(b) is amended by replacing "40 CFR part 265" in line 44 by "40 CFR parts 265 and 266".

§ 270.42 [Amended]

3. Section 270.42(c)(1)(iv) is revised to read as follows:

(c) * * *

(1) * * *

(iv) Provides the applicable information required by 40 CFR 270.13 through 270.22, 270.62, 270.63, and 270.66.

* * * * *

For the reasons set out in the preamble, 40 CFR part 266 is amended as follows:

PART 266—STANDARDS FOR THE MANAGEMENT OF SPECIFIC HAZARDOUS WASTES AND SPECIFIC TYPES OF HAZARDOUS WASTE MANAGEMENT FACILITIES

1. The authority citation for part 266 continues to read as follows:

Authority: Secs. 1006, 2002(a), 3004, and 3014 of the Solid Waste Disposal Act, as amended (42 U.S.C. 6905, 6912(a), 6924, and 6934).

§ 266.4 [Amended]

2. Section 266.40(c) is amended by replacing "subpart D" in line 6 by "subpart H."

3. Section 266.40(d) is amended by replacing "subpart D" in line 4 by "subpart H".

4. Part 266 is amended by adding two appendices, appendices IX and X as follows:

Appendix IX to Part 266—Methods Manual for Compliance With the BIF Regulations

Burning Hazardous Waste in Boilers and Industrial Furnaces

Table of Contents

Section 1.0 INTRODUCTION

This document presents required methods for demonstrating compliance uith U.S. Environmental Protection Agency regulations for boilers and industrial furnaces (BIFs) burning hazardous waste (see 40 CFR part 266, subpart H). Included in this document are:

1. Performance Specifications for Continuous Emission Monitoring (CEM) of Carbon Monoxide, Oxygen, and Hydrocarbons in Stack Gases.

2. Sampling and Analytical (S&A) Methods for Multiple Metals, Hexavalent Chromium, HCl and Chlorine, Polychlorinated Dibenzo-p-dioxins and Dibenzofurans, and Aldehydes and Ketones.

3. Procedures for Estimating the Toxicity Equivalency of Chlorinated Dibenzo-p-dioxin and Dibenzofuran Congeners.

4. Hazardous Waste Combustion Air Quality Screening Procedures (HWCAQSP).

5. Simplified Land Use Classification Procedure for Compliance vith Tier I and Tier II Limits.

6. Statistical Methodology for Bevill Residue Determinations.

7. Procedures for Determining Default Values for Air Pollution Control System Removal Efficiencies.

8. Procedures for Determining Default Values for Partitioning of Metals, Ash, and Total Chloride/Chlorine.

9. Alternate Methodology for Implementing Metals Controls.

Additional methods referenced in subpart H of part 266 but not included in this document can be found in 40 CFR parts 60 and 61, and "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods" (SW-846).

The CEM performance specifications of section 2.0, the S&A methods of section 3.0 and the toxicity equivalency procedure for dioxins and furans of section 4.0 are required procedures for determining compliance with BIF regulations. The CEM performance specifications and the S&A methods are interim. The finalized CEM performance specifications and methods will be published in SW-846 or 40 CFR parts 60 and 61.

SECTION 2.0 PERFORMANCE SPECIFICATIONS FOR CONTINUOUS EMISSION MONITORING SYSTEMS

2.1 *Performance Specifications for Continuous Emission Monitoring of Carbon Monoxide and Oxygen for Incinerators, Boilers, and Industrial Furnaces Burning Hazardous Waste*

2.1.1 *Applicability and Principle*

2.1.1.1 Applicability. These performance specifications apply to carbon monoxide (CO) and oxygen (O₂) continuous emission monitoring systems (CEMSs) installed on incinerators, boilers, and industrial furnaces burning hazardous waste. The specifications include procedures which are intended to be used to evaluate the acceptability of the CEMS at the time of its installation or whenever specified in regulations or permits. The procedures are not designed to evaluate CEMS performance over an extended period of time. The source owner or operator is responsible for the proper calibration, maintenance, and operation of the CEMS at all times.

2.1.1.2 Principle. Installation and measurement location specifications, performance and equipment specifications, test and data reduction procedures, and brief quality assurance guidelines are included in the specifications. Calibration drift, relative accuracy, calibration error, and response time tests are conducted to determine conformance of the CEMS with the specifications.

2.1.2 *Definitions*

2.1.2.1 Continuous Emission Monitoring System (CEMS). A continuous monitor is one in which the sample to be analyzed passes the measurement section of the analyzer without interruption, and which evaluates the detector response to the sample at least once each 15 seconds and computes and records the results at least every 60 seconds. A CEMS consists of all the equipment used to acquire data and includes the sample extraction and transport hardware, the analyzer(s), and the

data recording/processing hardware and software.

2.1.2.2 Monitoring System Types. The specifications require CEMSs capable of accepting calibration gases. Alternative system designs may be used if approved by the Regional Administrator. There are two basic types of monitoring systems: extractive and in-situ.

2.1.2.2.1 Extractive. Systems that use a pump or other mechanical, pneumatic, or hydraulic means to draw a sample of the stack or flue gas and convey it to a remotely located analyzer.

2.1.2.2.2 In-situ. Systems that perform an analysis without removing a sample from the stack. Point in-situ analyzers place the sensing or detecting element directly in the flue gas stream. Cross-stack in-situ analyzers measure the parameter of interest by placing a source beam on one side of the stack and the detector (in single-pass instruments) or a retroreflector (in double-pass instruments) on the other side, and measuring the parameter of interest (e.g., CO) by the attenuation of the beam by the gas in its path.

2.1.2.3 Instrument Measurement Range. The difference between the minimum and maximum concentration that can be measured by a specific instrument. The minimum is often stated or assumed to be zero and the range expressed only as the maximum.

2.1.2.4 Span or Span Value. Full scale instrument measurement range.

2.1.2.5 Calibration Drift (CD). The difference in the CEMS output readings from the established reference value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment takes place. A CD test is performed to demonstrate the stability of the CEMS calibration over time.

2.1.2.6 Response Time. The time interval between the start of a step change in the system input (e.g., change of calibration gas) and the time when the data recorder displays 95 percent of the final value.

2.1.2.7 Accuracy. A measure of agreement between a measured value and an accepted or true value, expressed as the percentage difference between the true and measured values relative to the true value. For these performance specifications, accuracy is checked by conducting a calibration error (CE) test and a relative accuracy (RA) test. Certain facilities, such as those using solid waste or batch-fed processes, may observe long periods of almost no CO emissions with brief, high-level CO emission spikes. These facilities, as well as facilities whose CO emissions never exceed 5-10 ppm, may need to be exempted from the RA requirement because the RA test procedure cannot ensure acquisition of meaningful test results under these conditions. An alternative procedure for accuracy determination is described in section 2.1.9.

2.1.2.8 Calibration Error (CE). The difference between the concentration indicated by the CEMS and the known concentration of the cylinder gas. A CE test procedure is performed to document the accuracy and linearity of the monitoring

equipment over the entire measurement range.

2.1.2.9 Relative Accuracy (RA). A comparison of the CEMS response to a value measured by a performance test method (PTM). The PA test is used to validate the calibration technique and verify the ability of the CEMS to provide representative and accurate measurements.

2.1.2.10 Performance Test Method (PTM). The sampling and analysis procedure used to obtain reference measurements for comparison to CEMS measurements. The applicable test methods are Method 10, 10A, or 10B (for the determination of CO) and Method 3 or 3A (for the determination of O_2). These methods are found in 40 CFR part 60, appendix A.

2.1.2.11 Performance Specification Test (PST) Period. The period during which CD, CE, response time, and RA tests are conducted.

2.1.2.12 Centroidal Area. A concentric area that is geometrically similar to the stack or duct cross section and is no greater than 1 percent of the stack or duct cross-sectional area.

2.1.3 *Installation and Measurement Location Specifications*

2.1.3.1 CEMS Installation and Measurement Locations. The CEMS shall be installed in a location in which measurements representative of the source's emissions can be obtained. The optimum location of the sample interface for the CEMS is determined by a number of factors, including ease of access for calibration and maintenance, the degree to which sample conditioning will be required, the degree to which it represents total emissions, and the degree to which it represents the combustion situation in the firebox. The location should be as free from in-leakage influences as possible and reasonably free from severe flow disturbances. The sample location should be at least two equivalent duct diameters downstream from the nearest control device, point of pollutant generation, or other point at which a change in the pollutant concentration or emission rate occurs and at least 0.5 diameter upstream from the exhaust or control device. The equivalent duct diameter is calculated as per 40 CFR part 60, appendix A, method 1, section 2.1. If these criteria are not achievable or if the location is otherwise less than optimum, the possibility of stratification should be checked as described in Section 2.1.3.3 to determine whether the location would cause failure of the relative accuracy test.

2.1.3.1.1 For extractive or point in-situ CEMSs, the measurement point should be within or centrally located over the centroidal area of the stack or duct cross section.

2.1.3.1.2 For cross-stack CEMSs, the effective measurement path should (1) have at least 70 percent of the path within the inner 50 percent of the stack or duct cross-sectional area or (2) be centrally located over any part of the centroidal area.

2.1.3.1.3 Both the CO and O_2 monitors should be installed at the same general location. If this is not possible, they may be installed at different locations if the effluent

gases at both sample locations are not stratified and there is no in-leakage of air between sampling locations.

2.1.3.2 Performance Test Method (PTM) Measurement Location and Traverse Points.

2.1.3.2.1 Select an accessible PTM measurement point at least two equivalent diameters downstream from the nearest control device, the point of CO generation, or other point at which a change in the CO concentration may occur, and at least a half equivalent diameter upstream from the effluent exhaust or control device. When pollutant concentration changes are due solely to diluent leakage (e.g., air heater leakages) and CO and O_2 are simultaneously measured at the same location, one half diameter may be used in place of two equivalent diameters. The CEMS and PTM locations need not be the same.

2.1.3.2.2 Select traverse points that ensure acquisition of representative samples over the stack or duct cross section. At a minimum, establish a measurement line that passes through the centroidal area in the direction of any expected stratification. If this line interferes with the CEMS measurements, displace the line up to 30 cm (or 5 percent of the equivalent diameter of the cross section, whichever is less) from the centroidal area. Locate three traverse points at 17, 50, and 83 percent of the measurement line. If the measurement line is no longer than 2.4 meters and pollutant stratification is not expected, the tester may choose to locate the three traverse points on the line at 0.4, 1.2, and 2.0 meters from the stack or duct wall. This option must not be used at a site located within eight equivalent diameters downstream of a flow disturbance. The tester may select other traverse points, provided that they can be shown to the satisfaction of the Administrator to provide a representative sample over the stack or duct cross-section. Conduct all necessary PTM tests within 3 cm of the selected traverse points. Sampling must not be performed within 3 cm of the duct or stack inner wall.

2.1.3.3 Stratification Test Procedure. Stratification is defined as a difference in excess of 10 percent between the average concentration in the duct or stack and the concentration at any point more than 1.0 meter from the duct or stack wall. To determine whether effluent stratification exists, a dual probe system should be used to determine the average effluent concentration while measurements at each traverse point are being made. One probe, located at the stack or duct centroid, is used as a stationary reference point to indicate the change in effluent concentration over time. The second probe is used for sampling at the traverse points specified in method 1, appendix A, 40 CFR part 60. The monitoring system samples sequentially at the reference and traverse points throughout the testing period for five minutes at each point.

2.1.4 *CEMS Performance and Equipment Specifications*

Table 2.1-1 summarizes the performance specifications for the CEMSs. Two sets of standards for CO are given; one for low-range and another for high-range measurements. The high-range specifications relate to measurement and quantification of

short duration high concentration peaks, while the low-range specifications relate to the overall average operating condition of the burning device. The dual-range specifications can be met by using (1) one analyzer for each range, (2) a dual range unit, or (3) a single measurement range instrument capable of meeting both specifications with a single unit. Adjustments cannot be made to the analyzer between determinations of low- and high-level accuracy within the single measurement range. In the second case, when the concentration exceeds the span of the lower range, the data acquisition system recorder shall switch to the high range automatically.

2.1.4.1 CEMS Span Value. In order to measure high and low concentrations with the same or similar degree of accuracy, the maximum ranges (span values) are specified for low and high range analyzers. The span values are listed in Table 2.1-2. Tier I and Tier II format definitions are established in 40 CFR part 266, subpart H.

TABLE 2.1-1—Performance Specifications of CO and O_2 Monitors

Parameter	CO monitors		O_2 monitors
	Low range	High range	
Calibration drift 24 hours.	$\leq$ 6 ppm [1] ...	$\leq$ 90 ppm	$\leq$0.5% O_2
Calibration error.	$\leq$ 10 ppm [1].	$\leq$ 150 ppm..	$\leq$0.5% O_2
Response time.	$\leq$ 2 min........	$\leq$ 2 min........	$\leq$ 2 min
Relative accuracy [2].	([3])..............	([3])..............	(incorporated in CO RA calculation)

[1] For Tier II, CD and CE are $\leq$3% and $\leq$5% of twice the permit limit, respectively.
[2] Expressed as the sum of the mean absolute value plus the 95% confidence interval of a series of measurements.
[3] The greater of 10% of PTM or 10 ppm.

TABLE 2.1-2—CEMS Span Values for CO and O_2 Monitors

	CO monitors		O_2 monitors (percent)
	Low range (ppm)	High range (ppm)	
Tier I rolling average format.	200...............	3,000	25
Tier II rolling average format.	2 × permit limit.	3,000	25

2.1.4.2 Daily Calibration Gas Values. The owner or operator must choose calibration gas concentrations (or calibration filters for in-situ systems) that include zero and high-level calibration values for the daily calibration checks. For a single measurement range monitor, three CO calibration gas concentrations (or calibration filters for in-situ systems) shall be used, i.e., the zero and high-level concentrations of the low-range

CO analyzer and the high-level concentration of the high-range CO analyzer.

2.1.4.2.1 The zero level for the CO or O_2 analyzer may be between zero and 20 percent of the span value, e.g., 0–40 ppm for low-range CO analyzer, 0–600 ppm for the high-range CO analyzer, and 0–5 percent for the O_2 analyzer (for Tier I).

2.1.4.2.2 The high-level concentration for the CO or O_2 analyzer shall be between 50 and 90 percent of the span value, i.e., 100–180 ppm for the low-range CO analyzer, 1500–2700 ppm for the high-range CO analyzer, and 12.5–22.5 percent O_2 for the O_2 analyzer.

2.1.4.3 Data Recorder Scale. The strip chart recorder, computer, or digital recorder must be capable of recording all readings within the CEMS's measurement range and shall have a resolution of 0.5 percent of span value, i.e., 1 ppm CO for low-range CO analyzer, 15 ppm CO for high-range CO analyzer, and 0.1 percent O_2 for the O_2 analyzer.

2.1.4.4 Response Time. The response time for the CO or O_2 monitor shall not exceed 2 minutes to achieve 95 percent of the final stable value.

2.1.4.5 Calibration Drift. The CEMS must allow the determination of CD at the zero and high-level values. The CD must be determined separately for CO and O_2 monitors in terms of concentration. The CO CEMS calibration response must not drift or deviate from the reference value of the calibration gas (or calibration filters for in-situ systems) by more than 3 percent of the span value after each 24-hour period of the 7-day test, i.e., 6 ppm CO for the low-range analyzer (Tier I) and 90 ppm for the high-range analyzer, at both zero and high levels. The O_2 monitor calibration response must not drift or deviate from the reference value by more than 0.5 percent O_2 at both zero and high levels.

2.1.4.6 Relative Accuracy. The result of the PA test of the CO CEMS (which incorporates the O_2 monitor) must be no greater than 10 percent of the mean value of the PTM results or must be within 10 ppm CO of the PTM results, whichever is less restrictive. The ppm CO concentration shall be corrected to 7 percent O_2 before calculating the RA.

2.1.4.7 Calibration Error. The mean difference between the CEMS and reference values at all three test points (see Table 2.1-3) must be no greater than 5 percent of span value for CO monitors (i.e., 10 ppm CO for low range Tier I CO analyzers and 150 ppm CO for high range CO analyzers) and 0.5 percent for O_2 analyzers.

2.1.4.8 Measurement and Recording Frequency. The sample to be analyzed shall pass through the measurement section of the analyzer without interruption. The detector shall measure the sample concentration at least once every 15 seconds. An average

emission rate shall be computed and recorded at least once every 60 seconds.

2.1.4.9 Hourly Rolling Average Calculation. The CEMS shall calculate every minute an hourly rolling average, which is the arithmetic mean of the 60 most recent 1-minute average values.

2.1.4.10 Retest. If the CEMS produces results within the specified criteria, the test is successful. If the CEMS does not meet one or more of the criteria, the necessary corrections must be made and the performance tests repeated.

2.1.5 *Test Periods*

2.1.5.1 Pretest Preparation Period. Install the CEMS, prepare the PTM test site according to the specifications in section 2.1.3, and prepare the CEMS for operation and calibration according to the manufacturer's written instructions. A pretest conditioning period similar to that of the 7-day CD test is recommended to verify the operational status of the CEMS.

2.1.5.2 Calibration Drift Test Period. While the facility is operating under normal conditions, determine the CD at 24-hour intervals for seven consecutive days according to the procedure given in section 2.1.6.1. All CD determinations must be made following a 24-hour period during which no unscheduled maintenance, repair, or adjustment takes place. If the combustion unit is taken out of service during the test period, record the onset and duration of the downtime and continue the calibration drift test when the unit resumes operation.

2.1.5.3 Relative Accuracy Test Period. Conduct the RA test according to the procedure in section 2.1.6.4 while the facility is operating under normal conditions. RA testing for CO and O_2 shall be conducted simultaneously so that the results can be calculated for CO corrected to 7 percent O_2. The RA test shall be conducted during the CD test period. It is emphasized that during the CD test period, no adjustments or repairs may be made to the CEMS other than routine calibration adjustments performed immediately following the daily CD determination.

2.1.5.4 Calibration Error Test and Response Time Test Periods. Conduct the CE and response time tests during the CD test period.

2.1.6 *Performance Specification Test Procedures*

2.1.6.1 Calibration Drift Test.

2.1.6.1.1 Sampling Strategy. Conduct the CD test for all monitors at 24-hour intervals for seven consecutive days using calibration gases at the two (or three, if applicable) concentration levels specified in section 2.1.4.2. Introduce the calibration gases into the sampling system as close to the sampling probe outlet as practical. The gas shall pass

through all filters, scrubbers, conditioners, and other CEMS components used during normal sampling. If periodic automatic or manual adjustments are made to the CEMS zero and calibration settings, conduct the CD test immediately before these adjustments, or conduct it in such a way that the CD can be determined. Record the CEMS response and subtract this value from the reference (calibration gas) value. To meet the specification, none of the differences shall exceed the limits specified in Table 2.1-1.

2.1.6.1.2 Calculations. Summarize the results on a data sheet. An example is shown in Figure 2.1-1. Calculate the differences between the CEMS responses and the reference values.

2.1.6.2 Response Time. Check the entire CEMS including sample extraction and transport, sample conditioning, gas analyses, and the data recording.

2.1.6.2.1 Introduce zero gas into the system. For extractive systems, introduce the calibration gases at the probe as near to the sample location as possible. For in-situ system, introduce the zero gas at a point such that all components active in the analysis are tested. When the system output has stabilized (no change greater than 1 percent of full scale for 30 seconds), switch to monitor stack effluent and wait for a stable value. Record the time (upscale response time) required to reach 95 percent of the final stable value.

2.1.6.2.2 Next, introduce a high-level calibration gas and repeat the above procedure. Repeat the entire procedure three times and determine the mean upscale and downscale response times. The longer of the two means is the system response time.

2.1.6.3 Calibration Error Test Procedure.

2.1.6.3.1 Sampling Strategy. Challenge each monitor (both low- and high-range CO and O_2) with zero gas and EPA Protocol 1 cylinder gases at three measurement points within the ranges specified in Table 2.1-3.

TABLE 2.1–3—CALIBRATION ERROR CONCENTRATION RANGES FOR TIER I

Measurement point	GAS Concentration Ranges		
	CO, ppm		O_2, percent
	Low range [1]	High range	
1	0–40	0–600	0–2
2	60–80	900–1200	8–10
3	140–160	2100–2400	14–16

[1] For Tier II, the CE specifications for the low-range CO CEMS are 0–20%, 30–40%, and 70–80% of twice the permit limit.

BILLING CODE 6560-50-M

SOURCE:	DATE:
MONITOR:	LOCATION:
SERIAL NUMBER:	SPAN:

LOW RANGE	
HIGH RANGE	

	DAY	DATE	TIME	CALIBRATION VALUE	MONITOR RESPONSE	DIFFERENCE	PERCENT OF SPAN*
ZERO/ LOW LEVEL	1						
	2						
	3						
	4						
	5						
	6						
	7						
HIGH LEVEL	1						
	2						
	3						
	4						
	5						
	6						
	7						

*Acceptance Criteria : ≤ 5% of span each day for seven days.

Figure 2.1-1   Calibration Drift Determination

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BILLING CODE 6560-50-C

2.1.6.3.1.1 If a single measurement range is used, the calibration gases used in the daily CD checks (if they are Protocol 1 cylinder gases and meet the criteria in section 2.1.6.3.1) may be used for determining CE.

2.1.6.3.1.2 Operate each monitor in its normal sampling mode as nearly as possible. The calibration gas shall be injected into the sample system as close to the sampling probe outlet as practical and should pass through all CEMS components used during normal sampling. Challenge the CEMS three non-consecutive times at each measurement point and record the responses. The duration of each gas injection should be sufficient to ensure that the CEMS surfaces are conditioned.

2.1.6.3.2 Calculations. Summarize the results on a data sheet. An example data sheet is shown in Figure 2.1-2. Average the differences between the instrument response and the certified cylinder gas value for each gas. Calculate three CE results (five CE results for a single-range CO CEMS) according to Equation 5 (section 2.1.7.5). No confidence coefficient is used in CE calculations.

2.1.6.4 Relative Accuracy Test Procedure.

2.1.6.4.1 Sampling Strategy for PTM tests. Conduct the PTM tests in such a way that they will yield measurements representative of the emissions from the source and can be correlated to the CEMS data. Although it is preferable to conduct the CO, diluent, and moisture (if needed) simultaneously, moisture measurements that are taken within a 60-minute period which includes the simultaneous CO and O_2 measurements may be used to calculate the dry CO concentration.

Note: At times, CEMS RA tests may be conducted during incinerator performance tests. In these cases, PTM results obtained during CEMS RA tests may be used to determine compliance with incinerator emissions limits as long as the source and test conditions are consistent with the applicable regulations.

BILLING CODE 6560-50-M

SOURCE:	DATE:
MONITOR:	LOCATION:
SERIAL NUMBER:	SPAN:

LOW RANGE	
HIGH RANGE	

RUN NUMBER	CALIBRATION VALUE	MONITOR RESPONSE	DIFFERENCE		
			Zero/Low	Mid	High
1 - Zero					
2 - Mid					
3 - High					
4 - Mid					
5 - Zero					
6 - High					
7 - Zero					
8 - Mid					
9 - High					
MEAN DIFFERENCE =					
CALIBRATION ERROR =			%	%	%

Figure 2.1-2   Calibration Error Determination

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2.1.6.4.2 Performance Test Methods.

2.1.6.4.2.1 Unless otherwise specified in the regulations, method 3 or 3A and method 10, 10A, or 10B (40 CFR part 60, appendix A) are the test methods for O_2 and CO, respectively. Make a sample traverse of at least 21 minutes, sampling for 7 minutes at each of three traverse points (see section 3.2).

2.1.6.4.2.2 When the installed CEMS uses a nondispersive infrared (NDIR) analyzer, method 10 shall use the alternative interference trap specified in section 10.1 of the method. An option, which may be approved by the Administrator in certain cases, would allow the test to be conducted using method 10 without the interference trap. Under this option, a laboratory interference test is performed for the analyzer prior to the field test. The laboratory interference test includes the analysis of SO_2, NO, and CO_2 calibration gases over the range of expected effluent concentrations. Acceptable performance is indicated if the CO analyzer response to each of the gases is less than 1 percent of the applicable measurement range of the analyzer.

2.1.6.4.3 Number of PTM Tests. Conduct a minimum of nine sets of all necessary PTM tests. If more than nine sets are conducted, a maximum of three sets may be rejected at the tester's discretion. The total number of sets used to determine the RA must be greater than or equal to nine. All data, including the rejected data, must be reported.

2.1.6.4.4 Correlation of PTM and CEMS Data. The time and duration of each PTM test run and the CEMS response time should be considered in correlating the data. Use the CEMS final output (the one used for reporting) to determine an integrated average CO concentration for each PTM test run. Confirm that the pair of results are on a consistent moisture and O_2 concentration basis. Each integrated CEMS value should then be compared against the corresponding average PTM value. If the CO concentration measured by the CEMS is normalized to a specified diluent concentration, the PTM results shall be normalized to the same value.

2.1.6.4.5 Calculations. Summarize the results on a data sheet. Calculate the mean of the PTM values and calculate the arithmetic differences between the PTM and the CEMS data sets. The mean of the differences, standard deviation, confidence coefficient, and CEMS RA should be calculated using Equations 1 through 4.

2.1.7 Equations

2.1.7.1 Arithmetic Mean ($\bar{d}$). Calculate $\bar{d}$ of the difference of a data set using Equation 1.

$$\bar{d} = \frac{1}{n} \sum_{i=1}^{n} d_i \quad (Eq. 1)$$

where:
n = Number of data points.

$$\sum_{i=1}^{n} d_i = \text{Algebraic sum of the individual difference } d_i.$$

When the mean of the differences of pairs of data is calculated, correct the data for moisture, if applicable.

2.1.7.2 Standard Deviation (S_d). Calculate S_d using Equation 2.

$$S_d = \sqrt{\frac{\sum_{i=1}^{n} d_i^2 - \frac{\left(\sum_{i=1}^{n} d_i\right)^2}{n}}{n-1}}$$

$$(Eq. 2)$$

2.1.7.3 Confidence Coefficient (CC). Calculate the 2.5 percent error CC (one-tailed) using Equation 3.

$$CC = t_{0.975} \frac{S_d}{\sqrt{n}} \quad (Eq. 3)$$

where:
$t_{0.975}$ = t-value (see Table 2.1-4).

TABLE 2.1-4—t-Values

n[a]	$t_{0.975}$	n[a]	$t_{0.975}$	n[a]	$t_{0.975}$
2	12.706	7	2.447	12	2.201
3	4.303	8	2.365	13	2.179
4	3.182	9	2.306	14	2.160
5	2.776	10	2.662	15	2.145
6	2.571	11	2.228	16	2.131

[a] The values in this table are already corrected for n−1 degrees of freedom. Use n equal to the number of individual values.

2.1.7.4 Relative Accuracy. Calculate the RA of a set of data using Equation 4.

$$RA = \frac{|\bar{d}| + |CC|}{PTM} \times 100$$

$$(Eq. 4)$$

where:
$|\bar{d}|$ = Absolute value of the mean of the differences (Equation 1).
$|CC|$ = Absolute value of the confidence coefficient (Equation 3).
PTM = Average reference value.

2.1.7.5 Calibration Error. Calculate CE using Equation 5.

$$CE = \left| \frac{\bar{d}}{FS} \right| \times 100$$

$$(Eq. 5)$$

where:

$\bar{d}$ = Mean difference between CEMS response and the known reference concentration.

2.1.8 Reporting

At a minimum, summarize in tabular form the results of the CD, RA, response time, and CE test, as appropriate. Include all data sheets, calculations, CEMS data records, and cylinder gas or reference material certifications.

2.1.9 Alternative Procedure

2.1.9.1 Alternative RA Procedure Rationale. Under some operating conditions, it may not be possible to obtain meaningful results using the RA test procedure. This includes conditions where consistent, very low CO emissions or low CO emissions interrupted periodically by short duration, high level spikes are observed. It may be appropriate in these circumstances to waive the PTM RA test and substitute the following procedure.

2.1.9.2 Alternative RA Procedure. Conduct a complete CEMS status check following the manufacturer's written instructions. The check should include operation of the light source, signal receiver, timing mechanism functions, data acquisition and data reduction functions, data recorders, mechanically operated functions (mirror movements, calibration gas valve operations, etc.), sample filters, sample line heaters, moisture traps, and other related functions of the CEMS, as applicable. All parts of the CEMS must be functioning properly before the RA requirement can be waived. The instruments must also have successfully passed the CE and CD requirements of the performance specifications. Substitution of the alternative procedure requires approval of the Regional Administrator.

2.1.10 Quality Assurance (QA)

Proper calibration, maintenance, and operation of the CEMS is the responsibility of the owner or operator. The owner or operator must establish a QA program to evaluate and monitor CEMS performance. As a minimum, the QA program must include:

2.1.10.1 A daily calibration check for each monitor. The calibration must be adjusted if the check indicates the instrument's CD exceeds the specification established in section 2.1.4.5. The gases shall be injected as close to the probe as possible to provide a check of the entire sampling system. If an alternative calibration procedure is desired (e.g., direct injections or gas cells), subject to Administrator approval, the adequacy of this alternative procedure may be demonstrated during the initial 7-day CD test. Periodic comparisons of the two procedures are suggested.

2.1.10.2 A daily system audit. The audit must include a review of the calibration check data, an inspection of the recording system, an inspection of the control panel warning lights, and an inspection of the sample transport and interface system (e.g., flowmeters, filters), as appropriate.

2.1.10.3 A quarterly calibration error (CE) test. Quarterly RA tests may be substituted for the CE test when approved by the Director on a case-by-case basis.

2.1.10.4 An annual performance specification test.

2.1.11 *References*

1. Jahnke, James A. and G.J. Aldina, "Handbook: Continuous Air Pollution Source Monitoring Systems," U.S. Environmental Protection Agency Technology Transfer, Cincinnati, Ohio 45268, EPA–625/6–79–005, June 1979.

2. "Gaseous Continuous Emissions Monitoring Systems-Performance Specification Guidelines for SO_2, NO_x, CO_2, O_2, and TRS." U.S. Environmental Protection Agency OAQPS, ESED, Research Triangle Park, North Carolina 27711, EPA–450/3–82–026, October 1982.

3. "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume I. Principles." U.S. Environmental Protection Agency ORD/EMSL, Research Triangle Park, North Carolina, 27711, EPA–600/9–76–006, December 1984.

4. Michie, Raymond, M. Jr., et. al., "Performance Test Results and Comparative Data for Designated Reference Methods for Carbon Monoxide," U.S. Environmental Protection Agency ORD/EMSL, Research Triangle Park, North Carolina, 27711, EPA–600/S4–83–013, September 1982.

5. Ferguson, B.B., R.E. Lester, and W.J. Mitchell, "Field Evaluation of Carbon Monoxide and Hydrogen Sulfide Continuous Emission Monitors at an Oil Refinery," U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 27711, EPA–600/4–82–054, August 1982.

2.2 *Performance Specifications for Continuous Emission Monitoring of Hydrocarbons for Incinerators, Boilers, and Industrial Furnaces Burning Hazardous Waste*

2.2.1 *Applicability and Principle*

2.2.1.1 Applicability. These performance specifications apply to hydrocarbon (HC) continuous emission monitoring systems (CEMSs) installed on incinerators, boilers, and industrial furnaces burning hazardous waste. The specifications include procedures which are intended to be used to evaluate the acceptability of the CEMS at the time of its installation or whenever specified in regulations or permits. The procedures are not designed to evaluate CEMS performance over an extended period of time. The source owner or operator is responsible for the proper calibration, maintenance, and operation of the CEMS at all times.

2.2.1.2 Principle. A gas sample is extracted from the source through a heated sample line and heated filter (except as provided by section 2.2.10) to a flame ionization detector (FID). Results are reported as volume concentration equivalents of propane. Installation and measurement location specifications, performance and equipment specifications, test and data reduction procedures, and brief quality assurance guidelines are included in the specifications. Calibration drift, calibration error, and response time tests are conducted to determine conformance of the CEMS with the specifications.

2.2.2 *Definitions*

2.2.2.1 Continuous Emission Monitoring System (CEMS). The total equipment used to acquire data, which includes sample extraction and transport hardware, analyzer, data recording and processing hardware, and software. The system consists of the following major subsystems:

2.2.2.1.1 Sample Interface. That portion of the system that is used for one or more of the following: Sample acquisition, sample transportation, sample conditioning, or protection of the analyzer from the effects of the stack effluent.

2.2.2.1.2 Organic Analyzer. That portion of the system that senses organic concentration and generates an output proportional to the gas concentration.

2.2.2.1.3 Data Recorder. That portion of the system that records a permanent record of the measurement values. The data recorder may include automatic data reduction capabilities.

2.2.2.2 Instrument Measurement Range. The difference between the minimum and maximum concentration that can be measured by a specific instrument. The minimum is often stated or assumed to be zero and the range expressed only as the maximum.

2.2.2.3 Span or Span Value. Full scale instrument measurement range.

2.2.2.4 Calibration Gas. A known concentration of a gas in an appropriate diluent gas.

2.2.2.5 Calibration Drift (CD). The difference in the CEMS output readings from the established reference value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment takes place. A CD test is performed to demonstrate the stability of the CEMS calibration over time.

2.2.2.6 Response Time. The time interval between the start of a step change in the system input (e.g., change of calibration gas) and the time when the data recorder displays 95 percent of the final value.

2.2.2.7 Accuracy. A measurement of agreement between a measured value and an accepted or true value, expressed as the percentage difference between the true and measured values relative to the true value. For these performance specifications, accuracy is checked by conducting a calibration error (CE) test.

2.2.2.8 Calibration Error (CE). The difference between the concentration indicated by the CEMS and the known concentration of the cylinder gas. A CE test procedure is performed to document the accuracy and linearity of the monitoring equipment over the entire measurement range.

2.2.2.9 Performance Specification Test (PST) Period. The period during which CD, CE, and response time tests are conducted.

2.2.2.10 Centroidal Area. A concentric area that is geometrically similar to the stack or duct cross section and is no greater than 1 percent of the stack or duct cross-sectional area.

2.2.3 *Installation and Measurement Location Specifications*

2.2.3.1 CEMS Installation and Measurement Locations. The CEMS shall be installed in a location in which measurements representative of the source's emissions can be obtained. The optimum location of the sample interface for the CEMS is determined by a number of factors, including ease of access for calibration and maintenance, the degree to which sample conditioning will be required, the degree to which it represents total emissions, and the degree to which it represents the combustion situation in the firebox. The location should be as free from in-leakage influences as possible and reasonably free from severe flow disturbances. The sample location should be at least two equivalent duct diameters downstream from the nearest control device, point of pollutant generation, or other point at which a change in the pollutant concentration or emission rate occurs and at least 0.5 diameter upstream from the exhaust or control device. The equivalent duct diameter is calculated as per 40 CFR part 60, appendix A, method 1, section 2.1. If these criteria are not achievable or if the location is otherwise less than optimum, the possibility of stratification should be investigated as described in section 2.2.3.2. The measurement point shall be within the centroidal area of the stack or duct cross section.

2.2.3.2 Stratification Test Procedure. Stratification is defined as a difference in excess of 10 percent between the average concentration in the duct or stack and the concentration at any point more than 1.0 meter from the duct or stack wall. To determine whether effluent stratification exists, a dual probe system should be used to determine the average effluent concentration while measurements at each traverse point are being made. One probe, located at the stack or duct centroid, is used as a stationary reference point to indicate the change in effluent concentration over time. The second probe is used for sampling at the traverse points specified in 40 CFR Part 60 appendix A, method 1. The monitoring system samples sequentially at the reference and traverse points throughout the testing period for five minutes at each point.

2.2.4 *CEMS Performance and Equipment Specifications*

If this method is applied in highly explosive areas, caution and care shall be exercised in choice of equipment and installation.

2.2.4.1 Flame Ionization Detector (FID) Analyzer. A heated FID analyzer capable of meeting or exceeding the requirements of these specifications. Heated systems shall maintain the temperature of the sample gas between 150 °C (300 °F) and 175 °C (350 °F) throughout the system. This requires all system components such as the probe, calibration valve, filter, sample lines, pump, and the FID to be kept heated at all times such that no moisture is condensed out of the system.

Note: As specified in the regulations, unheated HC CEMs may be considered an acceptable interim alternative monitoring technique. For additional notes, see section 2.2.10. The essential components of the measurement system are described below:

2.2.4.1.1 Sample Probe. Stainless steel, or equivalent, to collect a gas sample from the centroidal area of the stack cross-section.

2.2.4.1.2 Sample Line. Stainless steel or Teflon tubing to transport the sample to the analyzer.

Note: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

2.2.4.1.3 Calibration Valve Assembly. A heated three-way valve assembly to direct the zero and calibration gases to the analyzer is recommended. Other methods, such as quick-connect lines, to route calibration gas to the analyzers are applicable.

2.2.4.1.4 Particulate Filter. An in-stack or out-of-stack sintered stainless steel filter is recommended if exhaust gas particulate loading is significant. An out-of-stack filter must be heated.

2.2.4.1.5 Fuel. The fuel specified by the manufacturer (e.g., 40 percent hydrogen/60 percent helium, 40 percent hydrogen/60 percent nitrogen gas mixtures; or pure hydrogen) should be used.

2.2.4.1.6 Zero Gas. High purity air with less than 0.1 parts per million by volume (ppm) HC as methane or carbon equivalent or less than 0.1 percent of the span value, whichever is greater.

2.2.4.1.7 Calibration Gases. Appropriate concentrations of propane gas (in air or nitrogen). Preparation of the calibration gases should be done according to the procedures in EPA Protocol 1. In addition, the manufacturer of the cylinder gas should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change by more than ±2 percent from the certified value.

2.2.4.2 CEMS Span Value. 100 ppm propane.

2.2.4.3 Daily Calibration Gas Values. The owner or operator must choose calibration gas concentrations that include zero and high-level calibration values.

2.2.4.3.1 The zero level may be between 0 and 20 ppm (zero and 20 percent of the span value).

2.2.4.3.2 The high-level concentration shall be between 50 and 90 ppm (50 and 90 percent of the span value).

2.2.4.4 Data Recorder Scale. The strip chart recorder, computer, or digital recorder must be capable of recording all readings within the CEMS's measurement range and shall have a resolution of 0.5 ppm (0.5 percent of span value).

2.2.4.5 Response Time. The response time for the CEMS must not exceed 2 minutes to achieve 95 percent of the final stable value.

2.2.4.6 Calibration Drift. The CEMS must allow the determination of CD at the zero and high-level values. The CEMS calibration response must not differ by more than ±3 ppm (±3 percent of the span value) after each 24-hour period of the 7-day test at both zero and high levels.

2.2.4.7 Calibration Error. The mean difference between the CEMS and reference values at all three test points listed below shall be no greater than 5 ppm (±5 percent of the span value).

2.2.4.7.1 Zero Level. Zero to 20 ppm (0 to 20 percent of span value).

2.2.4.7.2 Mid-Level. 30 to 40 ppm (30 to 40 percent of span value).

2.2.4.7.3 High-Level. 70 to 80 ppm (70 to 80 percent of span value).

2.2.4.8 Measurement and Recording Frequency. The sample to be analyzed shall pass through the measurement section of the analyzer without interruption. The detector shall measure the sample concentration at least once every 15 seconds. An average emission rate shall be computed and recorded at least once every 60 seconds.

2.2.4.9 Hourly Rolling Average Calculation. The CEMS shall calculate every minute an hourly rolling average, which is the arithmetic mean of the 60 most recent 1-minute average values.

2.2.4.10 Retest. If the CEMS produces results within the specified criteria, the test is successful. If the CEMS does not meet one or more of the criteria, necessary corrections must be made and the performance tests repeated.

2.2.5 *Performance Specification Test (PST) Periods*

2.2.5.1 Pretest Preparation Period. Install the CEMS; prepare the PTM test site according to the specifications in section 2.2.3; and prepare the CEMS for operation and calibration according to the manufacturer's written instructions. A pretest conditioning period similar to that of the 7-day CD test is recommended to verify the operational status of the CEMS.

2.2.5.2 Calibration Drift Test Period. While the facility is operating under normal conditions, determine the magnitude of the CD at 24-hour intervals for seven consecutive days according to the procedure given in section 2.2.6.1. All CD determinations must be made following a 24-hour period during which no unscheduled maintenance, repair, or adjustment takes place. If the combustion unit is taken out of service during the test period, record the onset and duration of the downtime and continue the CD test when the unit resumes operation.

2.2.5.3 Calibration Error Test and Response Time Test Periods. Conduct the CE and response time tests during the CD test period.

2.2.6 *Performance Specification Test Procedures*

2.2.6.1 Calibration Drift Test.

2.2.6.1.1 Sampling Strategy. Conduct the CD test at 24-hour intervals for seven consecutive days using calibration gases at the two daily concentration levels specified in section 2.2.4.3. Introduce the two calibration gases into the sampling system as close to the sampling probe outlet as practical. The gas shall pass through all CEM components used during normal sampling. If periodic automatic or manual adjustments are made to the CEMS zero and calibration settings, conduct the CD test immediately before these adjustments, or conduct it in such a way that the CD can be determined. Record the CEMS response and subtract this value from the reference (calibration gas) value. To meet the specification, none of the differences shall exceed 3 ppm.

2.2.6.1.2 Calculations. Summarize the results on a data sheet. An example is shown in Figure 2.2–1. Calculate the differences between the CEMS responses and the reference values.

2.2.6.2 Response Time. The entire system including sample extraction and transport, sample conditioning, gas analyses, and the data recording is checked with this procedure.

2.2.6.2.1 Introduce the calibration gases at the probe as near to the sample location as possible. Introduce the zero gas into the system. When the system output has stabilized (no change greater than 1 percent of full scale for 30 sec), switch to monitor stack effluent and wait for a stable value. Record the time (upscale response time) required to reach 95 percent of the final stable value.

2.2.6.2.2 Next, introduce a high-level calibration gas and repeat the above procedure. Repeat the entire procedure three times and determine the mean upscale and downscale response times. The longer of the two means is the system response time.

2.2.6.3 Calibration Error Test Procedure.

2.2.6.3.1 Sampling Strategy. Challenge the CEMS with zero gas and EPA Protocol 1 cylinder gases at measurement points within the ranges specified in section 2.2.4.7.

2.2.6.3.1.1 The daily calibration gases, if Protocol 1, may be used for this test.

BILLING CODE 6560-50-M

SOURCE:	DATE:
MONITOR:	LOCATION:
SERIAL NUMBER:	SPAN:

	DAY	DATE	TIME	CALIBRATION VALUE	MONITOR RESPONSE	DIFFERENCE	PERCENT OF SPAN*
ZERO/ LOW LEVEL	1						
	2						
	3						
	4						
	5						
	6						
	7						
HIGH LEVEL	1						
	2						
	3						
	4						
	5						
	6						
	7						

*Acceptance Criteria : ≤ 3% of span each day for seven days.

Figure 2.2-1 Calibration Drift Determination

2.2.6.3.1.2 Operate the CEMS as nearly as possible in its normal sampling mode. The calibration gas should be injected into the sampling system as close to the sampling probe outlet as practical and shall pass through all filters, scrubbers, conditioners, and other monitor components used during normal sampling. Challenge the CEMS three non-consecutive times at each measurement point and record the responses. The duration of each gas injection should be for a sufficient period of time to ensure that the CEMS surfaces are conditioned.

2.2.6.3.2 Calculations. Summarize the results on a data sheet. An example data sheet is shown in Figure 2.2-2. Average the differences between the instrument response and the certified cylinder gas value for each gas. Calculate three CE results according to Equation 1. No confidence coefficient is used in CE calculations.

2.2.7 Equations

2.2.7.1 Calibration Error. Calculate CE using Equation 1.

$$CE = \left| \frac{\bar{d}}{FS} \right| \times 100 \qquad \text{(Eq. 1)}$$

where.

$\bar{d}$ = Mean difference between CEMS response and the known reference concentration.

2.2.8 Reporting

At a minimum, summarize in tabular form the results of the CD, response time, and CE test, as appropriate. Include all data sheets, calculations, CEMS data records, and cylinder gas or reference material certifications.

SOURCE:	DATE:
MONITOR:	LOCATION:
SERIAL NUMBER:	SPAN:

RUN NUMBER	CALIBRATION VALUE	MONITOR RESPONSE	DIFFERENCE		
			Zero/Low	Mid	High
1 - Zero					
2 - Mid					
3 - High					
4 - Mid					
5 - Zero					
6 - High					
7 - Zero					
8 - Mid					
9 - High					
MEAN DIFFERENCE =					
CALIBRATION ERROR =			%	%	%

Figure 2.2-2 Calibration Error Determination

2.2.9 *Quality Assurance (QA)*

Proper calibration, maintenance, and operation of the CEMS is the responsibility of the owner or operator. The owner or operator must establish a QA program to evaluate and monitor CEMS performance. As a minimum, the QA program must include:

2.2.9.1 A daily calibration check for each monitor. The calibration must be adjusted if the check indicates the instrument's CD exceeds 3 ppm. The gases shall be injected as close to the probe as possible to provide a check of the entire sampling system. If an alternative calibration procedure is desired (e.g., direct injections or gas cells), subject to Administrator approval, the adequacy of this alternative procedure may be demonstrated during the initial 7-day CD test. Periodic comparisons of the two procedures are suggested.

2.2.9.2 A daily system audit. The audit must include a review of the calibration check data, an inspection of the recording system, an inspection of the control panel warning lights, and an inspection of the sample transport and interface system (e.g., flowmeters, filters), as appropriate.

2.2.9.3 A quarterly CE test. Quarterly RA tests may be substituted for the CE test when approved by the Director on a case-by-case basis.

2.2.9.4 An annual performance specification test.

2.2.10 *Alternative Measurement Technique*

The regulations allow gas conditioning systems to be used In conjunction with unheated HC CEMs during an interim period. This gas conditioning may include cooling to not less than 40 °F and the use of condensate traps to reduce the moisture content of sample gas entering the FID to less than 2 percent. The gas conditioning system, however, must not allow the sample gas to bubble through the condensate as this would remove water soluble organic compounds. All components upstream of the conditioning system should be heated as described in section 2.2.4 to minimize operating and maintenance problems.

2.2.11 *References*

1. Measurement of Volatile Organic Compounds-Guideline Series. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 27711, EPA-450/2-78-041, June 1978.

2. Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Continuous Source Emission Monitors (Protocol No. 1). U.S. Environmental Protection Agency ORD/EMSL, Research Triangle Park, North Carolina, 27711, June 1978.

3. Gasoline Vapor Emission Laboratory Evaluation-Part 2. U.S. Environmental Protection Agency, OAQPS, Research Triangle Park, North Carolina, 27711, EMB Report No. 76-GAS-6, August 1975.

Section 3.0 SAMPLING AND ANALYTICAL METHODS

3.1 *Methodology for the Determination of Metals Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes*

3.1.1 *Applicability and Principle*

3.1.1.1 Applicability. This method is being developed for the determination of total chromium (Cr), cadmium (Cd), arsenic (As), nickel (Ni), manganese (Mn), beryllium (Be), copper (Cu), zinc (Zn), lead (Pb), selenium (Se), phosphorus (P), thallium (Tl), silver (Ag), antimony (Sb), barium (Ba), and mercury (Hg) stack emissions from hazardous waste incinerators and similar combustion processes. This method may also be used for the determination of particulate emissions following the procedures and precautions described. Modifications to the sample recovery and analysis procedures described in this protocol for the purpose of determining particulate emissions may potentially impact the front-half mercury determination. Mercury emissions should be determined using EPA method 101A given in 40 CFR part 61.

3.1.1.2 Principle. The stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in a series of chilled impingers containing an aqueous solution of dilute nitric acid combined with dilute hydrogen peroxide in each of two impingers, and acidic potassium permanganate solution in each of two impingers. Sampling train components are recovered and digested in separate front- and back-half fractions. Materials collected in the sampling train are digested with acid solutions to dissolve organics and to remove organic constituents that may create analytical interferences. Acid digestion is performed using conventional Parr® Bomb or microwave digestion techniques. The nitric acid and hydrogen peroxide impinger solution, the acidic potassium permanganate impinger solution, the HCl rinse solution, and the probe rinse and digested filter solutions are analyzed for mercury by cold vapor atomic absorption spectroscopy (CVAAS). The nitric acid and hydrogen peroxide solution and the probe rinse and digested filter solutions of the train catches are analyzed for Cr, Cd, Ni, Mn, Be, Cu, Zn, Pb, Se, P, Tl, Ag, Sb, Ba, and As by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of antimony, arsenic, cadmium, lead, selenium, and thallium, if these elements require greater analytical sensitivity than can be obtained by ICAP. Additionally, if desired, the tester may use AAS for analyses of all metals if the resulting in-stack method detection limits meet the goal of the testing program. For convenience, aliquots of each digested sample Fraction 1A plus Fraction 2A can be combined proportionally with respect to the original Fraction 1 (normally diluted to 300 ml following digestion and prior to analysis) section 3.1.5.3.3; and concentrated Fraction 2A (normally diluted to 150 ml following digestion and prior to analysis)

section 3.1.5.3.4.1 or 3.1.5.3.4.2 for a single analytical determination. The efficiency of the analytical procedure is quantified by the analysis of spiked quality control samples containing each of the target metals and/or other quality assurance measures, as necessary, including actual sample matrix effects checks.

3.1.2 *Range, Sensitivity, Precision, and Interferences*

3.1.2.1 Range. For the analyses described in this methodology and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per milliliter (ng/ml) to micrograms per milliliter (μg/ml) range in the analytical finish solution can be analyzed using this technique. Samples containing greater than approximately 50 μg/ml of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 μg/ml of cadmium should be diluted to that level before analysis.

3.1.2.2 Analytical Sensitivity. ICAP analytical detection limits for the sample solutions (based on SW-846, method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). The actual method detection limits are sample dependent and may vary as the sample matrix may affect the limits. The analytical detection limits for analysis by direct aspiration AAS (based on SW-846, Method 7000 series) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml). The detection limit for mercury by CVAAS is approximately 0.2 ng/ml). The use of GFAAS can give added sensitivity compared to the use of direct aspiration AAS for the following metals: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

Using (1) the procedures described in this method, (2) the analytical detection limits described in the previous paragraph, (3) a volume of 300 ml, Fraction 1, for the front half and 150 ml, Fraction 2A, for the back-half samples, and (4) a stack gas sample volume of 1.25 m³, the corresponding instack method detection limits are presented in Table A-1 and calculated as shown:

$$\frac{A \times B}{C} = D$$

where:
A = analytical detection limit, μg/ml.
B = volume of sample prior to aliquot for analysis, ml.
C = stack sample volume, dscm (dsm³).
D = in-stack detection limit, μg/m³.

Values in Table 3.1-1 are calculated for the front and back half and/or the total train.

To ensure optimum sensitivity in obtaining the measurements, the concentrations of target metals in the solutions are suggested to be at least ten times the analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, this concentration can be as low as approximately three times the analytical detection limit. In all cases, on at least one sample (run) in the source test and for each metal analyzed, repetitive analyses, method of standard additions (MSA), serial dilution, or matrix spike addition, etc., shall be used to establish the quality of the data.

Actual in-stack method detection limits will be determined based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be made more sensitive than those shown in Table A–I for a specific test by using one or more of the following options:

• A 1-hour sampling run may collect a stack gas sampling volume of about 1.25 m³. If the sampling time is increased and 5 m³ are collected, the in-stack method detection limits would be one fourth of the values shown in Table A–I (this means that with this change, the method is four times more sensitive than a 1-hour run. Larger sample volumes (longer runs) would make it even more sensitive).

• The in-stack detection limits assume that all of the sample is digested (with exception of the aliquot for mercury) and the final liquid volumes for analysis are 300 ml, Fraction 1 for the front half and 150 ml, Fraction 2A, for the back-half sample. If the front-half volume is reduced from 300 ml to 30 ml, the front-half in-stack detection limits would be one tenth of the values shown above (ten times more sensitive). If the back-half volume is reduced from 150 ml to 25 ml, the in-stack detection limits would be one sixth of the above values. Matrix effects checks are necessary on analyses of samples and typically are of greater significance for samples that have been concentrated to less than the normal original sample volume. Reduction to a volume of less than 25 ml may not allow redissolving of the residue and may increase interference by other compounds.

• When both of the above two improvements are used on one sample at the same time, the resultant improvements are multiplicative. For example, where stack gas volume is increased by a factor of five and the total liquid sample digested volume of both the front and back halves is reduced by a factor of six, the in-stack method detection limit is reduced by a factor of thirty (the method is thirty times more sensitive).

TABLE 3. 1–1—IN-STACK METHOD DETECTION LIMITS (ug/m³) FOR TRAIN FRACTIONS USING ICAP AND AAS

Metal	Front-half fraction 1 probe and filter	Back-half fraction 2 impingers 1–3	Back-half fractions "Hg, only" impingers 4–8	Total train
Antimony	7.7 (0.7)*	3.8 (0.4)*		11.5 (1.1)*
Arsenic	12.7 (0.3)*	6.4 (0.1)*		19.1 (0.4)*
Barium	0.5	0.3		0.8
Beryllium	0.07 (0.05)*	0.04 (0.03)*		0.11 (0.08)*
Cadmium	1.0 (0.02)*	0.5 (0.01)*		1.5 (0.03)*
Chromium	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Copper	1.4	0.7		2.1
Lead	10.1 (0.2)*	5.0 (0.1)*		15.1 (0.3)*
Manganese	0.5 (0.2)*	0.2 (0.1)*		0.7 (0.3*)
Mercury	0.6**	3.0**	2.0**	5.6**
Nickel	3.6	1.8		5.4
Phosphorus	18	9		27
Selenium	18 (0.5)*	9 (0.3)*		27 (0.8)*
Silver	1.7	0.9		2.6
Thallium	9.6 (0.2)*	4.8 (0.1)*		14.4 (0.3)*
Zinc	0.5	0.3		0.8

( )* Detection limit when analyzed by GFAAS.
** Detection limit when analyzed by CVAAS, estimated for Back Half and Total Train.
NOTE: Actual method in-stack detection limits will be determined based on actual source sampling parameters and analytical results as described earlier in this section.

• Conversely, reducing stack gas sample volume and increasing sample liquid volume will increase in-stack detection limits (the method would then be less sensitive). The front-half and back-half samples (Fractions 1A plus and 2A) can be combined proportionally (see section 3.1.1.2 of this methodology) prior to analysis. The resultant liquid volume (excluding the mercury fractions, which must be analyzed separately) is recorded. Combining the sample as described does not allow determination (whether front or back half) of where in the train the sample was captured. The in-stack method detection limit then becomes a single value for all metals except mercury, for which the contribution of the mercury fractions must be considered.

• The above discussion assumes no blank correction. Blank corrections are discussed later in this method.

3.1.2.3 Precision. The precisions (relative standard deviation) for each metal detected in a method development test at a sewage sludge incinerator, are as follows: Sb (12.7%), As (13.5%), Ba (20.6%), Cd (11.5%), Cr (11.2%), Cu (11.5%), Pb (11.6%), P (14.6%), Se (15.3%), Tl (12.3%), and Zn (11.8%). The precision for nickel was 7.7% for another test conducted at a source simulator. Beryllium, manganese, and silver were not detected in the tests; however, based on the analytical sensitivity of the ICAP for these metals, it is assumed that their precisions should be similar to those for the other metals, when detected at similar levels.

3.1.2.4 Interferences. Iron can be a spectral interference during the analysis of arsenic, chromium, and cadmium by ICAP. Aluminum can be a spectral interference during the analysis of arsenic and lead by ICAP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit (in-stack detection limit). Refer to EPA method 6010 (SW–846) or the other analytical methods used for details on potential interferences for this method. The analyst must eliminate or reduce interferences to acceptable levels. For all GFAAS analyses, matrix modifiers should be used to limit interferences, and standards should be matrix matched.

3.1.3 Apparatus

3.1.3.1 Sampling Train. A schematic of the sampling train is shown in Figure 3.1–1. It is similar to the 40 CFR part 60, appendix A method 5 train. The sampling train consists of the following components:

3.1.3.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as method 5, sections 2.1.1 and 2.1.2, except that glass nozzles are required unless an alternate probe tip prevents the possibility of contamination or interference of the sample with its materials of construction. If a probe tip other than glass is used, no correction (because of any effect on the

sample by the probe tip) of the stack sample test results can be made.

3.1.3.1.2 Pitot Tube and Differential Pressure Gauge. Same as method 2, sections 2.1 and 2.2, respectively.

3.1.3.1.3 Filter Holder. Glass, same as method 5, section 2.1.5, except that a Teflon filter support or other non-metallic, non–contaminating support must be used to replace the glass frit.

3.1.3.1.4 Filter Heating System. Same as method 5, section 2.1.6.

3.1.3.1.5 Condenser. The following system shall be used for the condensation and collection of gaseous metals and for determining the moisture content of the stack gas. The condensing system should consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. The first impinger is optional and is recommended as a moisture knockout trap for use during test conditions which require such a trap. The first impinger shall be appropriately-sized, if necessary, for an expected large moisture catch and generally constructed as described for the first impinger in method 5, paragraph 2.1.7. The second impinger (or the first HNO_3/ H_2O_2 impinger) shall also be constructed as described for the first impinger in method 5. The third impinger (or the second HNO_3/ H_2O_2 impinger) shall be the same as the Greenburg Smith impinger with the standard tip described as the second impinger in method 5, paragraph 2.1.7. All other impingers used in the methods train are the same as the first HNO_3/H_2O_2 impinger described in this paragraph. In summary, the first impinger which may be optional as described in this methodology shall be empty, the second and third shall contain known quantities of a nitric acid/hydrogen peroxide solution (section 3.1.4.2.1), the fourth shall be empty, the fifth and sixth shall contain a known quantity of acidic potassium permanganate solution (section 3.1.4.2.2), and the last impinger shall contain a known quantity of silica gel. A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger. When the moisture knockout impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not to be performed, the potassium permanganate impingers and the empty impinger preceding them are removed.
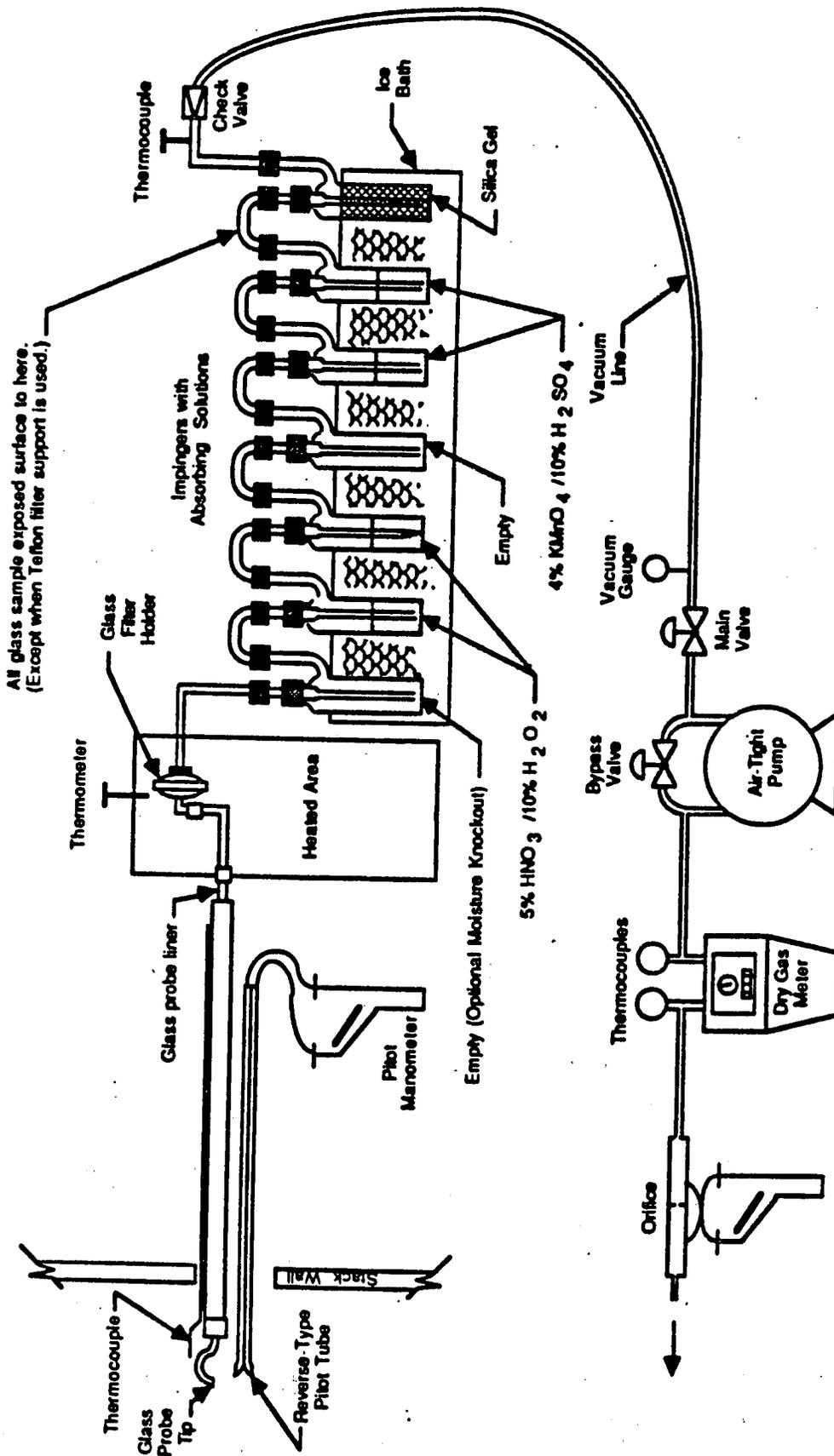
BILLING CODE 6560-50-M

Figure 3.1-1 Schematic of multiple metals sampling train configuration.

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3.1.3.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as method 5, sections 2.1.8 through 2.1.10, respectively.

3.1.3.1.7 Teflon Tape. For capping openings and sealing connections, if necessary, on the sampling train.

3.1.3.2 Sample Recovery. Same as method 5, sections 2.2.1 through 2.2.8 (Nonmetallic Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

3.1.3.2.1 Nonmetallic Probe-Liner and Probe-Nozzle Brushes or Swabs. For quantitative recovery of materials collected in the front half of the sampling train: Description of acceptable all-Teflon component brushes or swabs is to be included in EPA's Emission Measurement Technical Information Center (EMTIC) files.

3.1.3.2.2 Sample Storage Containers. Glass bottles with Teflon-lined caps which are non-reactive to the oxidizing solutions, with a capacity of 1000- and 500-ml, shall be used for $KMnO_4$-containing samples and blanks. Polyethylene bottles may be used for other sample types.

3.1.3.2.3 Graduated Cylinder. Glass or equivalent.

3.1.3.2.4 Funnel. Glass or equivalent.

3.1.3.2.5 Labels. For identification of samples.

3.1.3.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.

3.1.3.3 Sample Preparation and Analysis. For the analysis, the following equipment is needed:

3.1.3.3.1 Volumetric Flasks, 100-ml, 250-ml, and 1000-ml. For preparation of standards and sample dilution.

3.1.3.3.2 Graduated Cylinders. For preparation of reagents.

3.1.3.3.3 Parr Bombs or Microwave Pressure Relief Vessels with Capping Station (GEM Corporation model or equivalent).

3.1.3.3.4 Beakers and Watchglasses. 250-ml beakers for sample digestion with watchglasses to cover the tops.

3.1.3.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

3.1.3.3.6 Filter Funnels. For holding filter paper.

3.1.3.3.7 Whatman 541 Filter Paper (or equivalent). For filtration of digested samples.

3.1.3.3.8 Disposable Pasteur Pipets and Bulbs.

3.1.3.3.9 Volumetric Pipets.

3.1.3.3.10 Analytical Balance. Accurate to within 0.1 mg.

3.1.3.3.11 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures.

3.1.3.3.12 Hot Plates.

3.1.3.3.13 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

3.1.3.3.13.1 Graphite Furnace Attachment. With antimony, arsenic, cadmium, lead,

selenium, thallium hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). (Same as EPA SW-846 methods 7041 (antimony), 7060 (arsenic), 7131 (cadmium), 7421 (lead), 7740 (selenium), and 7841 (thallium).)

3.1.3.3.13.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL. The equipment needed for the cold vapor mercury attachment includes an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp should be capable of raising the ambient temperature at the quartz cell by 10 °C such that no condensation forms on the wall of the quartz cell. (Same as EPA method 7470.)

3.1.3.3.14 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. (Same as EPA method 6010.)

3.1.4 *Reagents*

The complexity of this methodology is such that to obtain reliable results, the testers (including analysts) should be experienced and knowledgeable in source sampling, in handling and preparing (including mixing) reagents as described, and using adequate safety procedures and protective equipment in performing this method, including sampling, mixing reagents, digestions, and analyses. Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

3.1.4.1 Sampling. The reagents used in sampling are as follows:

3.1.4.1.1 Filters. The filters shall contain less than 1.3 $\mu g/in^2$ of each of the metals to be measured. Analytical results provided by filter manufacturers are acceptable. However, if no such results are available, filter blanks must be analyzed for each target metal prior to emission testing. Quartz fiber or glass fiber (which meet the requirement of containing less than 1.3 $\mu g/in^2$ of each metal) filters without organic binders shall be used. The filters should exhibit at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D2986-71 (incorporated by reference). For particulate determination in sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3, as described in EPA method 5. Quartz fiber filters meeting these requirements are recommended for use in this method.

3.1.4.1.2 Water. To conform to ASTM Specification D1193.77, Type II (incorporated by reference). If necessary, analyze the water for all target metals prior to field use. All target metal concentrations should be less than 1 ng/ml.

3.1.4.1.3 Nitric Acid. Concentrated. Baker Instra-analyzed or equivalent.

3.1.4.1.4 Hydrochloric Acid. Concentrated. Baker Instra-analyzed or equivalent.

3.1.4.1.5 Hydrogen Peroxide, 30 Percent (V/V).

3.1.4.1.6 Potassium Permanganate.

3.1.4.1.7 Sulfuric Acid. Concentrated.

3.1.4.1.8 Silica Gel and Crushed Ice. Same as method 5, sections 3.1.2 and 3.1.4, respectively.

3.1.4.2 Pretest Preparation for Sampling Reagents.

3.1.4.2.1 Nitric Acid (HNO_3)/Hydrogen Peroxide (H_2O_2) Absorbing Solution, 5 Percent HNO_3/10 Percent H_2O_2. Carefully with stirring, add 50 ml of concentrated HNO_3 to a 1000-ml volumetric flask containing approximately 500 ml of water, and then, carefully with stirring, add 333 ml of 30 percent H_2O_2. Dilute to volume (1000 ml) with water. Mix well. The reagent shall contain less than 2 ng/ml of each target metal.

3.1.4.2.2 Acidic Potassium Permanganate ($KMnO_4$) Absorbing Solution, 4 Percent $KMnO_4$ (W/V), 10 Percent H_2SO_4 (V/V). Prepare fresh daily. Mix carefully, with stirring, 100 ml of concentrated H_2SO_4 into 800 ml of water, and add water with stirring to make a volume of 1 L: This solution is 10 percent H_2SO_4 (V/V). Dissolve, with stirring, 40 g of $KMnO_4$ into 10 percent H_2SO_4 (V/V) and add 10 percent H_2SO_4 (V/V) with stirring to make a volume of 1 L: this is the acidic potassium permanganate absorbing solution. Prepare and store in glass bottles to prevent degradation. The reagent shall contain less than 2 ng/ml of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottle; these bottles shall not be fully filled and shall be vented both to relieve potential excess pressure and prevent explosion due to pressure buildup. Venting is required, but should not allow contamination of the sample; a No. 70–72 hole drilled in the container cap and Teflon liner has been used.

3.1.4.2.3 Nitric Acid, 0.1 N. With stirring, add 6.3 ml of concentrated HNO_3 (70 percent) to a flask containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of each target metal.

3.1.4.2.4 Hydrochloric Acid (HCl), 8 N. Make the desired volume of 8 N HCl in the following proportions. Carefully with stirring, add 690 ml of concentrated HCl to a flask containing 250 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of Hg.

3.1.4.3 Glassware Cleaning Reagents.

3.1.4.3.1 Nitric Acid, Concentrated. Fisher ACS grade or equivalent.

3.1.4.3.2 Water. To conform to ASTM Specifications D1193-77, Type II.

3.1.4.3.3 Nitric Acid, 10 Percent (V/V). With stirring, add 500 ml of concentrated HNO_3 to a flask containing approximately 4000 ml of water. Dilute to 5000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

3.1.4.4 Sample Digestion and Analysis Reagents.

3.1.4.4.1 Hydrochloric Acid, Concentrated.

3.1.4.4.2 Hydrofluoric Acid, Concentrated.

3.1.4.4.3 Nitric Acid, Concentrated. Baker Instra-analyzed or equivalent.

3.1.4.4.4 Nitric Acid, 50 Percent (V/V). With stirring, add 125 ml of concentrated HNO_3 to 100 ml of water. Dilute to 250 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

3.1.4.4.5 Nitric Acid, 5 Percent (V/V). With stirring, add 50 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

3.1.4.4.6 Water. To conform to ASTM Specifications D1193–77, Type II.

3.1.4.4.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See EPA method 7470 for preparation.

3.1.4.4.8 Stannous Chloride. See method 7470.

3.1.4.4.9 Potassium Permanganate, 5 Percent (W/V). See method 7470.

3.1.4.4.10 Sulfuric Acid, Concentrated.

3.1.4.4.11 Nitric Acid, 50 Percent (V/V).

3.1.4.4.12 Potassium Persulfate, 5 Percent (W/V). See Method 7470.

3.1.4.4.13 Nickel Nitrate, $Ni(NO_3)_2 \cdot 6H_2O$.

3.1.4.4.14 Lanthanum, Oxide, La_2O_3.

3.1.4.4.15 AAS Grade Hg Standard, 1000 μg/ml.

3.1.4.4.16 AAS Grade Pb Standard, 1000 μg/ml.

3.1.4.4.17 AAS Grade As Standard, 1000 μg/ml.

3.1.4.4.18 AAS Grade Cd Standard, 1000 μg/ml.

3.1.4.4.19 AAS Grade Cr Standard, 1000 μg/ml.

3.1.4.4.20 AAS Grade Sb Standard, 1000 μg/ml.

3.1.4.4.21 AAS Grade Ba Standard, 1000 μg/ml.

3.1.4.4.22 AAS Grade Be Standard, 1000 μg/ml.

3.1.4.4.23 AAS Grade Cμ Standard, 1000 μg/ml.

3.1.4.4.24 AAS Grade Mn Standard, 1000 μg/ml.

3.1.4.4.25 AAS Grade Ni Standard, 1000 μg/ml.

3.1.4.4.26 AAS Grade P Standard, 1000 μg/ml.

3.1.4.4.27 AAS Grade Se Standard, 1000 μg/ml.

3.1.4.4.28 AAS Grade Ag Standard, 1000 μg/ml.

3.1.4.4.29 AAS Grade T1 Standard, 1000 μg/ml.

3.1.4.4.30 AAS Grade Zn Standard, 1000 μg/ml.

3.1.4.4.31 AAS Grade Al Standard, 1000 μg/ml.

3.1.4.4.32 AAS Grade Fe Standard, 1000 μg/ml.

3.1.4.4.33 The metals standards may also be made from solid chemicals as described in EPA Method 200.7. EPA SW–846 Method 7470 or Standard Methods for the Analysis of Water and Wastewater, 15th Edition, Method 303F should be referred to for additional information on mercury standards.

3.1.4.4.34 Mercury Standards and Quality Control Samples. Prepare fresh weekly a 10 μg/ml intermediate mercury standard by adding 5 ml of 1000 μg/ml mercury stock solution to a 500-ml volumetric flask; dilute with stirring to 500 ml by first carefully adding 20 ml of 15 percent HNO_3 and then adding water to the 500-ml volume. Mix well.

Prepare a 200 ng/ml working mercury standard solution fresh daily: Add 5 ml of the 10 μg/ml intermediate standard to a 250-ml volumetric flask and dilute to 250 ml with 5 ml of 4 percent $KMnO_4$, 5 ml of 15 percent HNO_3, and then water. Mix well. At least six separate aliquots of the working mercury standard solution should be used to prepare the standard curve. These aliquots should contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng mercury, respectively. Quality control samples should be prepared by making a separate 10 μg/ml standard and diluting until in the range of the calibration.

3.1.4.4.35 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as shown below.

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn.
II	Ba, Cu, Fe.
III	Al, Cr, Ni.
IV	Ag, P, Sb, Tl.

Prepare these standards by combining and diluting the appropriate volumes of the 1000 μg/ml solutions with 5 percent nitric acid. A minimum of one standard and a blank can be used to form each calibration curve. However, a separate quality control sample spiked with known amounts of the target metals in quantities in the midrange of the calibration curve should be prepared. Suggested standard levels are 25 μg/ml for Al, Cr, and Pb, 15 μg/ml for Fe, and 10 μg/ml for the remaining elements. Standards containing less than 1 μg/ml of metal should be prepared daily. Standards containing greater than 1 μg/ml of metal should be stable for a minimum of 1 to 2 weeks.

3.1.4.4.36 Graphite Furnace AAS Standards. Antimony, arsenic, cadmium, lead, selenium, and thallium. Prepare a 10 μg/ml standard by adding 1 ml of 1000 μg/ml standard to a 100-ml volumetric flask. Dilute with stirring to 100 ml with 10 percent nitric acid. For graphite furnace AAS, the standards must be matrix matched. Prepare a 100 ng/ml standard by adding 1 ml of the 10 μg/ml standard to a 110-ml volumetric flask and dilute to 100 ml with the appropriate matrix solution. Other standards should be prepared by dilution of the 100 ng/ml standards. At least five standards should be used to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Quality control samples should be prepared by making a separate 10 μg/ml standard and diluting until it is in the range of the samples. Standards containing less than 1 μg/ml of metal should be prepared daily. Standards containing greater than 1 μg/ml of metal should be stable for a minimum of 1 to 2 weeks.

3.1.4.4.3 Matrix Modifiers.

3.1.4.4.37.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of $Ni(NO_3)_2 \cdot 6H_2O$ in

approximately 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

3.1.4.4.37.2 Nickel Nitrate, 0.1 Percent (V/V). Dilute 10 ml of the 1 percent nickel nitrate solution from section 4.4.37.1 above to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for As.

3.1.4.4.37.3 Lanthanum. Carefully dissolve 0.5864 g of La_2O_3 in 10 ml of concentrated HNO_3 and dilute the solution by adding it with stirring to approximately 50 ml of water, and then dilute to 100 ml with water. Mix well. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for Pb.

3.1.5 Procedure

3.1.5.1 Sampling. The complexity of this method is such that, to obtain reliable results, testers and analysts should be trained and experienced with the test procedures, including source sampling, reagent preparation and handling, sample handling, analytical calculations, reporting, and descriptions specifically at the beginning of and throughout section 3.1.4 and all other sections of this methodology.

3.1.5.1.1 Pretest Preparation. Follow the same general procedure given in method 5, section 4.1.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. All sampling train glassware should first be rinsed with hot tap water and then washed in hot soapy water. Next, glassware should be rinsed three times with tap water, followed by three additional rinses with water. All glassware should then be soaked in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinsed three times with water, rinsed a final time with acetone, and allowed to air dry. All glassware openings where contamination can occur should be covered until the sampling train is assembled for sampling.

3.1.5.1.2 Preliminary Determinations. Same as method 5, section 4.1.2.

3.1.5.1.3 Preparation of Sampling Train. Follow the same general procedures given in method 5, section 4.1.3, except place 100 ml of the nitric acid/hydrogen peroxide solution (section 3.1.4.2.1) in each of the two HNO_3/H_2O_2 impingers as shown in Figure 3.1–1 (normally the second and third impingers), place 100 ml of the acidic potassium permanganate absorbing solution (section 3.1.4.2.2) in each of the two permanganate impingers as shown in Figure A–1, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to train assembly.

Several options are available to the tester based on the sampling requirements and conditions. The use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 ml. If necessary, use as applicable to this methodology the procedure described in section 7.1.1 of EPA method 101A, 40 CFR part 61, appendix B, to maintain the desired color in the last permanganate impinger.

Retain for reagent blanks volumes of the nitric acid/hydrogen peroxide solution per section 3.1.5.2.9 of this method and of the acidic potassium permanganate solution per section 3.1.5.2.10. These reagent blanks should be labeled and analyzed as described in section 3.1.7. Set up the sampling train as shown in Figure 3.1–1, or if mercury analysis is not to be performed in the train, then it should be modified by removing the two permanganate impingers and the impinger preceding the permanganate impingers. If necessary to ensure leak-free sampling train connections and prevent contamination Teflon tape or other non-contaminating material should be used instead of silicone grease.

Precaution: Extreme care should be taken to prevent contamination within the train. Prevent the mercury collection reagent (acidic potassium permanganate) from contacting any glassware of the train which is washed and analyzed for Mn. Prevent hydrogen peroxide from mixing with the acidic potassium permanganate.

Mercury emissions can be measured, alternatively, in a separate train which measures only mercury emissions by using EPA method 101A with the modifications described below (and with the further modification that the permanganate containers shall be processed as described in the precaution in section 3.1.4.2.2 and the note in section 3.1.5.2.5 of this methodology). This alternative method is applicable for measurement of mercury emissions, and it may be of special interest to sources which must measure both mercury and manganese emissions.

Section 7.2.1 of method 101A shall be modified as follows after the 250 to 400-ml $KMnO_4$ rinse:

To remove any precipitated material and any residual brown deposits on the glassware following the permanganate rinse, rinse with approximately 100 ml of deionized distilled water, and add this water rinse carefully assuring transfer of all loose precipitated materials from the three permanganate impingers into the permanganate Container No. 1. If no visible deposits remain after this water rinse, do not rinse with 8 N HCl. However, if deposits do remain on the glassware after this water rinse, wash the impinger surfaces with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled Container No. 1.A. containing 200 ml of water as follows. Place 200 ml of water in a sample container labeled

Container No. 1.A. Wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing *all permanganate impingers combined*. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse, etc. Finally, pour the 25 ml of 8 N HCl rinse carefully with stirring into Container No. 1.A. Analyze the HCl rinse separately by carefully diluting with stirring the contents of Container No. 1.A. to 500 ml with deionized distilled water. Filter (if necessary) through Whatman 40 filter paper, and then analyze for mercury according to section 7.4, except limit the aliquot size to a maximum of 10 ml. Prepare and analyze a water diluted blank 8 N HCl sample by using the same procedure as that used by Container No. 1.A., except add 5 ml of 8 N HCl with stirring to 40 ml of water, and then dilute to 100 ml with water. Then analyze as instructed for the sample from Container No. 1.A. Because the previous separate permanganate solution rinse (section 7.2.1) and water rinse (as modified in these guidelines) have the capability to recover a very high percentage of the mercury from the permanganate impingers, the amount of mercury in the HCl rinse in Container No. 1.A. may be very small, possibly even insignificantly small. However, add the total of any mercury analyzed and calculated for the HCl rinse sample Container No. 1.A. to that calculated from the mercury sample from section 7.3.2 which contains the separate permanganate rinse (and water rinse as modified herein) for calculation of the total sample mercury concentration.

3.1.5.1.4   Leak-Check Procedures. Follow the leak-check procedures given in method 5, section 4.1.4.1 (Pretest Leak-Check), section 4.1.4.2 (Leak-Checks During the Sample Run), and section 4.1.4.3 (Post-Test Leak-Checks).

3.1.5.1.5   Sampling Train Operation. Follow the procedures given in method 5, section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 5–2 of method 5.

3.1.5.1.6   Calculation of Percent Isokinetic. Same as method 5, section 4.1.6.

3.1.5.2   Sample Recovery. Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period.

The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate

matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling. This normally causes a vacuum to form in the filter holder, thus causing the undesired result of drawing liquid from the impingers into the filter.

Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap off the filter holder outlet and impinger inlet. Use noncontaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

Alternatively, the train can be disassembled before the probe and filter holder/oven are completely cooled, if this procedure is followed: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. The sample is recovered and treated as follows (see schematic in Figure 3.1–2). Ensure that all items necessary for recovery of the sample do not contaminate it.

3.1.5.2.1   Container No. 1 (Filter). Carefully remove the filter from the filter holder and place it in its identified petri dish container. Acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water and dried should be used to handle the filters. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metalcontaining materials when recovering this train. Seal the labeled petri dish.

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Figure 3.1-2   Sample recovery scheme.

3.1.5.2.2   Container No. 2 (Acetone Rinse).

Note: Perform section 3.1.5.2.2 only if determination of particulate emissions are desired in addition to metals emissions. If only metals emissions are desired, skip section 3.1.5.2.2 and go to section 3.1.5.2.3. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting (plastic such as Teflon, polypropylene, etc. fittings are recommended to prevent contamination by metal fittings; further, if desired, a single glass piece consisting of a combined probe tip and probe liner may be used, but such a single glass piece is *not* a requirement of this methodology), probe liner, and front half of the filter holder by washing these components with 100 ml of acetone and placing the wash in a glass container.

Note: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis. Perform the acetone rinses as follows: Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nonmetallic brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the sample-exposed, inside parts of the fitting with acetone in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a nonmetallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe three times or more until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

Clean the inside of the front half of the filter holder by rubbing the surfaces with a nonmetallic nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container clearly to identify its contents.

3.1.5.2.3   Container No. 3 (Probe Rinse). Keep the probe assembly clean and free from contamination as described in section 3.1.5.2.2 of this method during the 0.1 N nitric acid rinse described below. Rinse the probe nozzle and fitting probe liner, and front half of the filter holder thoroughly with 100 ml of 0.1 N nitric acid and place the wash into a sample storage container.

Note: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Perform the rinses as applicable and generally as described in method 12, section 5.2.2. Record the volume of the combined rinse. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container and clearly label the contents. Finally, rinse the nozzle, probe liner, and front half of the filter holder with water followed by acetone and discard these rinses.

3.1.5.2.4   Container No. 4 (Impingers 1 through 3, HNO_3/H_2O_2 Impingers and Moisture Knockout Impinger, when used, Contents and Rinses). Due to the potentially large quantity of liquid involved, the tester may place the impinger solutions from impingers 1 through 3 in more than one container. Measure the liquid in the first three impingers volumetrically to within 0.5 ml using a graduated cylinder. Record the volume of liquid present. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N nitric acid using the procedure as applicable and generally as described in method 12, section 5.2.4.

Note: The use of exactly 100 ml of 0.1 N nitric acid rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the volume. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Seal the container and clearly label the contents.

3.1.5.2.5   Container Nos. 5A, 5B, and 5C. 5A (0.1 N HNO_3), 5B ($KMnO_4$/H_2SO_4 absorbing solution), and 5C (8 N HCl rinse and dilution). (As described previously at the end of section 3.1.3.1.5 of this method, if mercury is not being measured in this train, then impingers 4, 5, and 6, as shown in Figure 3.1–2, are not necessary and may be eliminated.) Pour all the liquid, if any, from the impinger which was empty at the start of the run and which immediately precedes the two permanganate impingers (normally impinger No. 4) into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Sample Container No. 5A. Rinse the impinger (No. 4) with 100 ml of 0.1 N HNO_3 and place this into Container No. 5A.

Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place this $KMnO_4$ absorbing solution stack sample from the two permanganate impingers into Container No. 5B. Using 100 ml total of fresh acidified potassium permanganate solution, rinse the two permanganate impingers and connecting glass pieces a minimum of three times and place the rinses into Container No. 5B, carefully ensuring transfer of all loose precipitated materials from the two impingers into Container No. 5B. Using 100 ml total of water, rinse the permanganate impingers and connecting glass pieces a minimum of three times, and place the rinses into Container 5B, carefully ensuring transfer of all loose precipitated material, if any, from the two impingers into Container No. 5B. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and the precaution in paragraph 3.1.4.2.2 and properly prepare the bottle and clearly label the contents.

Note: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottles. These bottles shall not be completely filled and shall be vented to relieve potential excess pressure. Venting is required. A No. 70–72 hole drilled in the container cap and Teflon liner has been used.

If no visible deposits remain after the above described water rinse, do not rinse with 8 N HCl. However, if deposits do remain on the glassware after this water rinse, wash the impinger surfaces with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled Container No. 5C containing 200 ml of water as follows: Place 200 ml of water in a sample container labeled Container No. 5C. Wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing both permananate impingers combined. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully with stirring into Container No. 5C. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport.

3.1.5.2.6   Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger.

The small amount of particles that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

3.1.5.2.7 Container No. 7 (Acetone Blank). If particulate emissions are to be determined, at least once during each field test, place a 100-ml portion of the acetone used in the sample recovery process into a labeled container for use in the front-half field reagent blank. Seal the container.

3.1.5.2.8 Container No. 8A (0.1 N Nitric Acid Blank). At least once during each field test, place 300 ml of the 0.1 N nitric acid solution used in the sample recovery process into a labeled container for use in the front-half and back-half field reagent blanks. Seal the container. Container No. 8B (water blank). At least once during each field test, place 100 ml of the water used in the sample recovery process into a labeled Container No. 8B. Seal the container.

3.1.5.2.9 Container No. 9 (5% Nitric Acid/10% Hydrogen Peroxide Blank). At least once during each field test, place 200 ml of the 5% nitric acid/10% hydrogen peroxide solution used as the nitric acid impinger reagent into a labeled container for use in the back-half field reagent blank. Seal the container.

3.1.5.2.10 Container No. 10 (Acidified Potassium Permanganate Blank). At least once during each field test, place 100 ml of the acidified potassium permanganate

solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back-half field reagent blank for mercury analysis. Prepare the container as described in section 3.1.5.2.5.

Note: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottles. These bottles shall not be completely filled and shall be vented to relieve potential excess pressure. Venting is required. A No. 70-72 hole drilled in the container cap and Teflon liner has been used.

3.1.5.2.11 Container No. 11 (8 N HCl Blank). At least once during each field test, perform *both* of the following: Place 200 ml of water into a sample container. Pour 25 ml of 8N HCl carefully with stirring into the 200 ml of water in the container. Mix well and seal the container.

3.1.5.2.12 Container No. 12 (Filter Blank). Once during each field test, place three unused blank filters from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish. These will be used in the front-half field reagent blank.

3.1.5.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during

shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 3.1-3.

3.1.5.3.1 Container No. 1 (Filter). If particulate emissions are being determined, then desiccate the filter and filter catch without added heat and weigh to a constant weight as described in section 4.3 of method 5. For analysis of metals, divide the filter with its filter catch into portions containing approximately 0.5 g each and place into the analyst's choice of either individual microwave pressure relief vessels or Parr® Bombs. Add 6 ml of concentrated nitric acid and 4 ml of concentrated hydrofluoric acid to each vessel. For microwave heating, microwave the sample vessels for approximately 12-15 minutes in intervals of 1 to 2 minutes at 600 Watts. For conventional heating, heat the Parr Bombs at 140°C (285°F) for 6 hours. Cool the samples to room temperature and combine with the acid digested probe rinse as required in section 3.1.5.3.3, below.

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Figure 3.1-3 Sample preparation and analysis scheme.
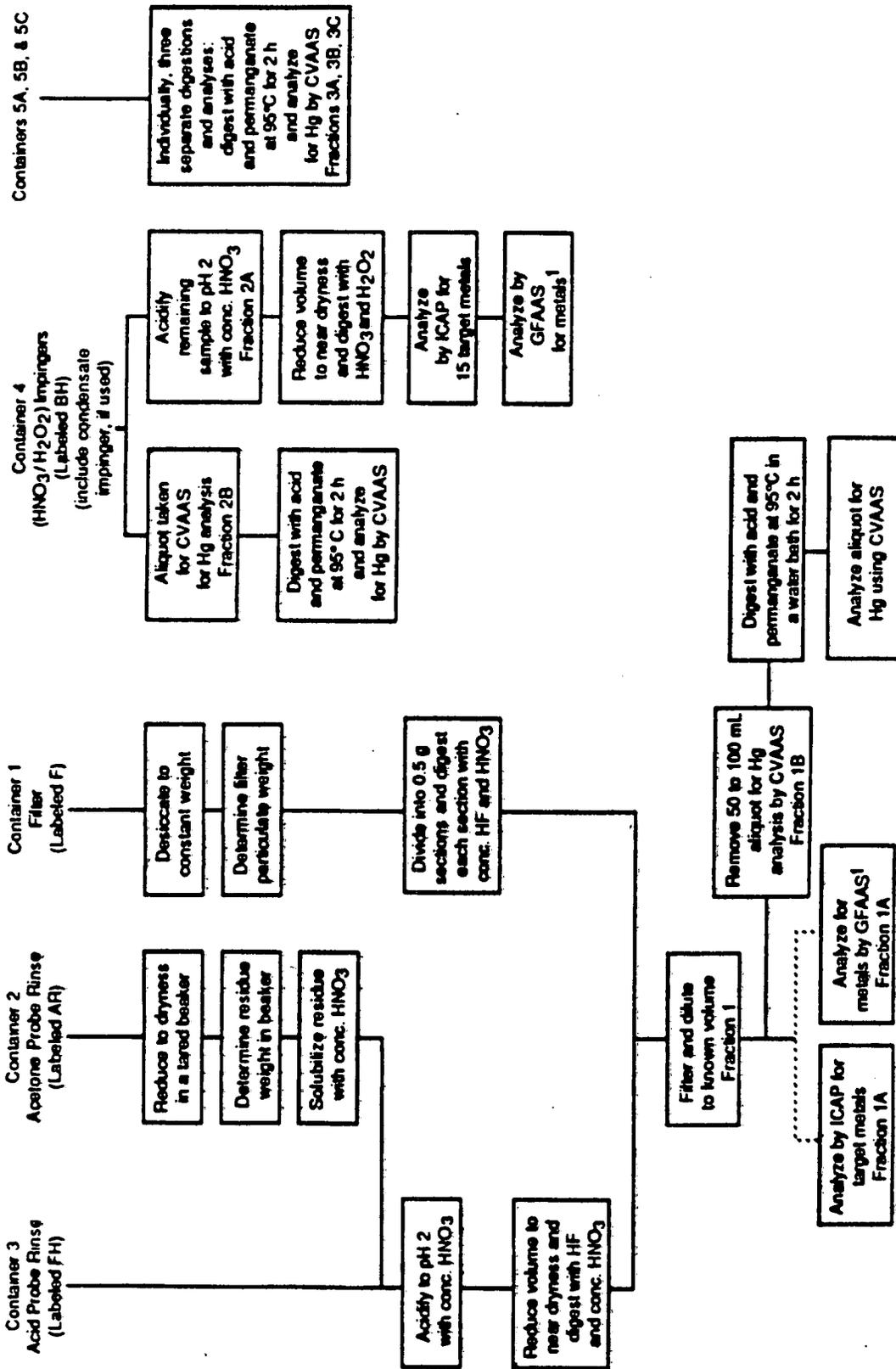
[1] Analysis by AAS for metals found at less than 2 ug/mL in digestate solution, if desired. Or analyze for each metal by AAS, if desired.

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Notes: 1. Suggested microwave heating times are approximate and are dependent upon the number of samples being digested. Twelve to 15 minute heating times have been found to be acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by sorbent reflux within the vessel.

2. If the sampling train uses an optional cyclone, the cyclone catch should be prepared and digested using the same procedures described for the filters and combined with the digested filter samples.

3.1.5.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g. Transfer the contents to an acid-cleaned, tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in section 4.3 of method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated nitric acid and, carefully with stirring, quantitatively combine the resultant sample including all liquid and any particulate matter with Container No. 3 prior to beginning the following section 3.1.5.3.3.

3.1.5.3.3 Container No. 3 (Probe Rinse). The pH of this sample shall be 2 or lower. If the pH is higher, the sample should be acidified to pH 2 by the careful addition with stirring of concentrated nitric acid. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr ® Bombs by quantitatively transferring the sample to the vessel or bomb, by carefully adding the 6 ml of concentrated nitric acid and 4 ml of concentrated hydrofluoric acid and then continuing to follow the procedures described in section 3.1.5.3.1; then combine the resultant sample directly with the acid digested portions of the filter prepared previously in section 3.1.5.3.1. The resultant combined sample is referred to as Fraction 1 precursor. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This dilution is Fraction 1. Measure and record the volume of the Fraction 1 solution to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label as Fraction 1B. Label the remaining 250-ml portion as Fraction 1A. Fraction 1A is used for ICAP or AAS analysis. Fraction 1B is used for the determination of front-half mercury.

3.1.5.3.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample (Fraction 2) to within 0.5 ml. Remove a 75- to 100-ml aliquot for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 4 as aliquot Fraction 2A. Aliquot Fraction 2A defines the volume of 2A *prior* to digestion. All of the aliquot Fraction 2A is digested to produce concentrated Fraction 2A. Concentrated Fraction 2A defines the volume of 2A *after* digestion which is normally 150 ml. Only concentrated Fraction 2A is analyzed for metals (except that it is not analyzed for mercury). The Fraction 2B aliquot should be prepared and analyzed for mercury as described in section 3.1.5.4.3. Aliquot Fraction 2A shall be pH 2 or lower. If necessary, use concentrated nitric acid, by careful addition and stirring, to lower aliquot Fraction 2A to pH 2. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Next follow either the conventional or microwave digestion procedures described in sections 3.1.5.3.4.1 and 3.1.5.3.4.2, below.

3.1.5.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent nitric acid and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent hydrogen peroxide and heat for 20 more minutes. Add 50 ml of hot water and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution is concentrated Fraction 2A. Measure and record the volume of the Fraction 2A solution to within 0.1 ml.

3.1.5.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent nitric acid and heat for 6 minutes in intervals of 1 to 2 minutes at 600 Watts. Allow the sample to cool. Add 10 ml of 3 percent hydrogen peroxide and heat for 2 more minutes. Add 50 ml of hot water and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution is concentrated Fraction 2A. Measure and record the volume of the Fraction 2A solution to within 0.1 ml.

Note: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

3.1.5.3.5 Container Nos. 5A, 5B, and 5C (Impingers 4, 5, and 6). Keep these samples separate from each other and measure and record the volumes of 5A and 5B separately to within 0.5 ml. Dilute sample 5C to 500 ml with water. These samples 5A, 5B, and 5C are referred to respectively as Fractions 3A, 3B, and 3C. Follow the analysis procedures described in section 3.1.5.4.3.

Because the permanganate rinse and water rinse have the capability to recover a high percentage of the mercury from the permanganate impingers, the amount of mercury in the HCl rinse (Fraction 3C) may be very small, possibly even insignificantly small. However, as instructed in this method, add the total of any mercury measured in and calculated for the HCl rinse (Fraction 3C) to that for Fractions 1B, 2B, 3A, and 3B for calculation of the total sample mercury concentration.

3.1.5.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

3.1.5.4 Sample Analysis. For each sampling train, seven individual samples are generated for analysis. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure 3.1-3. The first two samples, labeled Fractions 1A and 1B, consist of the digested samples from the front half of the train. Fraction 1A is for ICAP or AAS analysis as described in sections 3.1.5.4.1 and/or 3.1.5.4.2. Fraction 1B is for determination of front-half mercury as described in section 3.1.5.4.3.

The back half of the train was used to prepare the third through seventh samples. The third and fourth samples, labeled Fractions 2A and 2B, contain the digested samples from the moisture knockout, if used, and HNO_3/H_2O_2 Impingers 1 through 3. Fraction 2A is for ICAP or AAS analysis. Fraction 2B will be analyzed for mercury.

The fifth through seventh samples, labeled Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty and permanganate impingers 4, 5, and 6. These samples are analyzed for mercury as described in section 3.1.5.4.3. The total back-half mercury catch is determined from the sum of Fraction 2B and Fractions 3A, 3B, and 3C.

3.1.5.4.1 ICAP Analysis. Fraction 1A and Fraction 2A are analyzed by ICAP using EPA *SW-846* method 6010 or method 200.7 (40 CFR 136, appendix C). Calibrate the ICAP, and set up an analysis program as described in method 6010 or method 200.7. The quality control procedures described in section 3.1.7.3.1 of this method shall be followed. Recommended wavelengths for use in the analysis are listed below:

Element	Wavelength (nm)
Aluminum	308.215
Antimony	206.833
Arsenic	193.696
Barium	455.403
Beryllium	313.042
Cadmium	226.502
Chromium	267.716
Copper	324.754
Iron	259.940
Lead	220.353
Manganese	257.610
Nickel	231.604
Phosphorus	214.914
Selenium	196.026
Silver	328.068
Thallium	190.864
Zinc	213.856

The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

Initially, analyze all samples for the desired target metals (except mercury) plus iron and aluminum. If iron and aluminum are present in the sample, the sample may have to be diluted so that each of these elements is at a concentration of less than 50 ppm to reduce their spectral interferences on arsenic, cadmium, chromium, and lead.

Note. When analyzing samples in a hydrofluoric acid matrix, an alumina torch should be used; since all front-half samples will contain hydrofluoric acid, use an alumina torch.

3.1.5.4.2   AAS by Direct Aspiration and/or Graphite Furnace. If analysis of metals in Fraction 1A and Fraction 2A using graphite furnace or direct aspiration AAS is desired,

Table 3.1–2 should be used to determine which techniques and methods should be applied for each target metal. Table 3.1–2 should also be consulted to determine possible interferences and techniques to be followed for their minimization. Calibrate the instrument according to section 3.1.6.3 and follow the quality control procedures specified in section 3.1.7.3.2.

TABLE 3.1–2—APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTERFERENCE FOR AAS ANALYSIS

Metal	Technique	SW–846 Method No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Sb..........	Aspiration	7040	217.6	1000 mg/mL Pb Ni, Cu, or acid...........................	Use secondary wavelength of 231.1 nm; match sample & standards' acid concentration or use nitrous oxide/acetylene flame.
Sb..........	Furnace	7041	217.6	High Pb...	Secondary wavelength or Zeeman correction.
As..........	Furnace	7060	193.7	Arsenic volatization...	Spiked samples and add nickel nitrate solution to digestates prior to analysis.
				Aluminum	Use Zeeman background correction.
Ba..........	Aspiration	7080	553.6	Calcium..	High hollow cathode current and narrow band set.
				Barium ionization...	2 mL of KC1 per 100 mL of sample.
Be..........	Aspiration	7090	234.9	500 ppm A1...	Add 0.1% fluoride.
				High Mg and Si	Use method of standard additions.
Be..........	Furnace	7091	234.9	Be in optical path..	Optimize parameters to minimize effects.
Cd..........	Aspiration.......	7130	228.8	Absorption and light scattering	Background correction is required.
Cd..........	Furnace	7131	228.8	As above...	As above.
				Excess chloride...	Ammonium phosphate used as a matrix modifier.
				Pipet tips..	Use cadmium-free tips.
Cr..........	Aspiration	7190	357.9	Alkali metal...	KC1 ionization suppressant in samples and standards.
				Absorption and scatter...	Consult manufacturer's literature.
Cr..........	Furnace	7191	357.9	200 mg/L Ca and P..	All calcium nitrate for a known constant effect and to eliminate effect of phosphate.
Cu..........	Aspiration	7210	324.7	Absorption and scatter...	Consult manufacturer's manual.
Fe..........	Aspiration	7380	248.3	Contamination	Great care taken to avoid contamination.
Pb..........	Aspiration	7420	283.3	217.0 nm alternate..	Background correction required.
Pb..........	Furnace	7421	283.3	Poor recoveries...	Matrix modifier, add 10 uL of phosphorus acid to 1 mL of prepared sample in sampler cup.
Mn.........	Aspiration	7460	279.5	403.1 nm alternate..	Background correction required.
Ni...........	Aspiration	7520	232.0	352.4 nm alternate..	Background correction required.
				Fe, Co, and Cr..	Matrix matching or nitrous-oxide/acetylene flame.
				Nonlinear response	Sample dilution or use 352.3 nm line.
Se..........	Furnace	7740	196.0	Volatility..	Spike samples and reference materials and add nickel nitrate to minimize volatilization.
				Adsorption & scatter..	Background correction is required and Zeeman background correction can be useful.
Ag..........	Aspiration	7760	328.1	Adsorption & scatter..	Background correction is required.
				AgC1 insolube..	Avoid hydrochloric acid unless silver is in solution as a chloride complex.
				Viscosity...	Sample and standards monitored for aspiration rate.
Tl...........	Aspiration	7840	276.8		Background correction is required. Hydrochloric acid should not be used.
Tl...........	Furnace	7841	276.8	Hydrochloric acid or chloride................................	Background correction is required. Verify that losses are not occurring for volatization by spiked samples or standard addition; Palladium is a suitable matrix modifier.
Zn..........	Aspiration	7950	213.9	High Si, Cu, & P..	Strontium removes Cu and phosphate.
				Contamination	Great care taken to avoid contamination.

3.1.5.4.3 Cold Vapor AAS Mercury Analysis. Fraction 1B, Fraction 2B, and Fractions 3A, 3B, and 3C should be analyzed separately for mercury using cold vapor atomic absorption spectroscopy following the method outlined in EPA SW–846 method 7470 or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 303F. Set up the calibration curve (zero to 1000 ng) as described in SW–846 method 7470 or similar to method 303F, using 300-ml BOD bottles instead of Erlenmeyers. Dilute separately, as described below, a 1 ml to 10 ml aliquot of each original sample to 100 ml with water. Record the amount of the aliquot used for dilution to 100 ml. If no prior knowledge exists of the expected amount of

mercury in the sample, a 5-ml aliquot is suggested for the first dilution to 100 ml and analysis. To determine the stack emission value for mercury, the amount of the aliquot of the sample used for dilution and analysis is dependent on the amount of mercury in the aliquot: The total amount of mercury in the aliquot used for analysis shall be less than 1 µg, and within the range (zero to 1000 ng) of the calibration curve. Place each sample aliquot into a separate 300-ml BOD bottle and add enough Type II water to make a total volume of 100 ml. Then analyze the 100 ml for mercury by adding to it sequentially the sample preparation solutions and performing the sample preparation and analysis as described in the procedures of SW–846

method 7470 or method 303F. If, during the described analysis, the reading maximum(s) are off-scale (because the aliquot of the original sample analyzed contained more mercury than the maximum of the calibration range) including the analysis of the 100-ml dilution of the 1-ml aliquot of the original sample causing a reading maximum which is off-scale, then perform the following: Dilute the original sample (or a portion of it) with 0.15% HNO₃ in water (1.5 ml concentrated HNO₃ per liter aqueous solution) so that when a 1-ml to 10-ml aliquot of the dilution of the original sample is then further diluted to 100 ml in the BOD bottle, and analyzed by the procedures described above, it will yield an

analysis within the range of the calibration curve.

3.1.6 *Calibration*

Maintain a laboratory log of all calibrations.

3.1.6.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of method 5: Probe Nozzle (section 5.1); Pitot Tube (section 5.2); Metering System (section 5.3); Probe Heater (section 5.4); Temperature Gauges (section 5.5); Leak-Check of the Metering System (section 5.6); and Barometer (section 5.7).

3.1.6.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in section 3.1.4.4. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures using the above standards. The instrument calibration should be checked once per hour. If the instrument does not reproduce the concentrations of the standard within 10 percent, the complete calibration procedures should be performed.

3.1.6.3 Atomic Absorption Spectrometer—Direct Aspiration, Graphite Furnace and Cold Vapor Mercury Analyses. Prepare the standards as outlined in section 3.1.4.4. Calibrate the spectrometer using these prepared standards. Calibration procedures are also outlined in the EPA methods referred to in Table 3.1–2 and in SW–846 Method 7470 or Standard Methods for Water and Wastewater, 15th Edition, method 303F (for mercury). Each standard curve should be run in duplicate and the mean values used to calculate the calibration line. The instrument should be recalibrated approximately once every 10 to 12 samples.

3.1.7 *Quality Control*

3.1.7.1 Sampling. Field Reagent Blanks. When analyzed, the blank samples in Container Numbers 7 through 12 produced previously in sections 3.1.5.2.7 through 3.1.5.2.12, respectively, shall be processed, digested, and analyzed as follows: Digest and process one of the filters from Container No. 12 per section 3.1.5.3.1, 100 ml from Container No. 7 per section 3.1.5.3.2, and 100 ml from Container No. 8A per section 3.1.5.3.3. This produces Fraction Blank 1A and Fraction Blank 1B from Fraction Blank 1. (If desired, the other two filters may be digested separately according to section 3.1.5.3.1, diluted separately to 300 ml each, and analyzed separately to produce a blank value for each of the two additional filters. If these analyses are performed, they will produce two additional values for each of Fraction Blank 1A and Fraction Blank 1B. The three Fraction Blank 1A values will be calculated as three values of M_{fnb} in Equation 3 of section 3.1.8.4.3, and then the three values shall be totalled and divided by 3 to become the value M_{fnb} to be used in the computation of M_t by Equation 3. Similarly, the three Fraction Blank 1B values will be calculated separately as three values, totalled, averaged, and used as the value for Hg_{fnb} in Equation 8 of section 3.1.8.5.3. The analyses of the two extra filters are optional and are *not* a requirement of this method, but if the analyses are performed, the results must be considered as described above.) Combine 100

ml of Container No. 8A with 200 ml of the contents of Container No. 9 and digest and process the resultant volume per section 3.1.5.3.4. This produces concentrated Fraction Blank 2A and Fraction Blank 2B from Fraction Blank 2. A 100-ml portion of Container No. 8A is Fraction Blank 3A. Combine 100 ml of the contents of Container No. 10 with 33 ml of the contents of Container No. 8B. This produces Fraction Blank 3B (use 400 ml as the volume of Fraction Blank 3B when calculating the blank value. Use the actual volumes when calculating all the other blank values). Dilute 225 ml of the contents of Container No. 11 to 500 ml with water. This produces Fraction Blank 3C. Analyze Fraction Blank 1A and Fraction Blank 2A per section 3.1.5.4.1 and/or 3.1.5.4.2. Analyze Fraction Blank 1B, Fraction Blank 2B, and Fraction Blanks 3A, 3B, and 3C per section 3.1.5.4.3. The analysis of Fraction Blank 1A produces the front-half reagent blank correction values for the metals except mercury; the analysis of Fraction Blank 1B produces the front-half reagent blank correction value for mercury. The analysis of concentrated Fraction Blank 2A produces the back-half reagent blank correction values for the metals except mercury, while separate analysis of Fraction Blanks 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for mercury.

3.1.7.2 An attempt may be made to determine if the laboratory reagents used in section 3.1.5.3 caused contamination. They should be analyzed by the procedures in section 3.1.5.4. The Administrator will determine whether the laboratory blank reagent values can be used in the calculation of the stationary source test results.

3.1.7.3 Quality Control Samples. The following quality control samples should be analyzed.

3.1.7.3.1 ICAP Analysis. Follow the quality control shown in section 8 of method 6010. For the purposes of a three-run test series, these requirements have been modified to include the following: Two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (must be within 25% or analyze by the method of standard additions), one quality control sample to check the accuracy of the calibration standards (must be within 25% of calibration), and one duplicate analysis (must be within 10% of average or repeat all analyses).

3.1.7.3.2 Direct Aspiration and/or Graphite Furnace AAS Analysis for antimony, arsenic, barium, beryllium, cadmium, copper, chromium, lead, nickel, manganese, mercury, phosphorus, selenium, silver, thallium, and zinc. All samples should be analyzed in duplicate. Perform a matrix spike on at least one front-half sample and one back-half sample or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the method of standard additions. A quality control sample should be analyzed to check the accuracy of the calibration standards. The results must be within 10% or the calibration repeated.

3.1.7.3.3 Cold Vapor AAS Analysis for Mercury. All samples should be analyzed in

duplicate. A quality control sample should be analyzed to check the accuracy of the calibration standards (within 15% or repeat calibration). Perform a matrix spike on one sample from the nitric impinger portion (must be within 25% or samples must be analyzed by the method of standard additions). Additional information on quality control can be obtained from EPA SW–846 method 7470 or in Standard Methods for the Examination of Water and Wastewater, 15th Edition, method 303F.

3.1.8 *Calculations*

3.1.8.1 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method 5.

3.1.8.2 Volume of Water Vapor and Moisture Content. Using the data obtained from this test, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5–2 and 5–3 of Method 5.

3.1.8.3 Stack Gas Velocity. Using the data from this test and Equation 2–9 of Method 2, calculate the average stack gas velocity.

3.1.8.4 Metals (Except Mercury) in Source Sample.

3.1.8.4.1 Fraction 1A, Front Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 1 of the sampling train using the following equation:

$$M_{fn} = C_{a1} \, F_d \, V_{soln,1} \qquad \text{Eq. 1 *}$$

where:

M_{fn} = total mass of each metal (except Hg) collected in the front half of the sampling train (Fraction 1), μg.

C_{a1} = concentration of metal in sample Fraction 1A as read from the standard curve (μg/ml).

F_d = dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1}. For example, when 2 ml of Fraction 1A are diluted to 10 ml, F_d = 5).

$V_{soln,1}$ = total volume of digested sample solution (Fraction 1), ml.

3.1.8.4.2 Fraction 2A, Back Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 2 of the sampling train using the following equation:

$$M_{bh} = C_{a2} F_a V_a \qquad \text{Eq. 2*}$$

where:

M_{bh} = total mass of each metal (except Hg) collected in the back half of the sampling train (Fraction 2), μg.

C_{a2} = concentration of metal in sample concentrated Fraction 2A, as read from the standard curve (μg/ml).

F_a = aliquot factor, volume of Fraction 2 divided by volume of aliquot Fraction 2A (see section 3.1.5.3.4).

V_a = total volume of digested sample solution (concentrated Fraction 2A), ml (see section 3.1.5.3.4.1 or 3.1.5.3.4.2, as applicable).

3.1.8.4.3 Total Train, Metals (except Hg). Calculate the total amount of each of the

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* If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 1–3 to reflect this approach.

quantified metals collected in the sampling train as follows:

$$M_t = (M_{fh} - M_{fhb}) + (M_{bh} - M_{bhb}) \qquad \text{Eq. 3*}$$

where:

M_t = total mass of each metal (separately stated for each metal) collected in the sampling train, μg.

M_{fhb} = blank correction value for mass of metal detected in front-half field reagent blank, μg.

M_{bhb} = blank correction value for mass of metal detected in back-half field reagent blank, μg.

Note: If the measured blank value for the front half (m_{fhb}) is in the range 0.0 to A μg (where A μg equals the value determined by multiplying 1.4 μg per square inch (1.4 μg/in²) times the actual area in square inches (in²) of the filter used in the emission sample) m_{fhb} may be used to correct the emission sample value (m_{fh}); if m_{fhb} exceeds A μg, the greater of the two following values (either I. or II.) may be used:

I. A μg, or

II. the lesser of (a) m_{fhb}, or (b) 5 percent of m_{fh}.

If the measured blank value for the back half (m_{bhb}) is in the range of 0.0 to 1 μg, m_{bhb} may be used to correct the emission sample value (m_{bh}); if m_{bhb} exceeds 1 μg, the greater of the two following values may be used: 1 μg or 5 percent of m_{bh}.

3.1.8.5 Mercury in Source Sample.

3.1.8.5.1 Fraction 1B, Front Half, Hg. Calculate the amount of mercury collected in the front half, Fraction 1, of the sampling train using the following equation:

$$Hg_{fh} = \frac{Q_{fh}}{V_{f1B}} \times V_{soln.1} \qquad \text{Eq. 4}$$

where:

Hg_{fh} = total mass of mercury collected in the front half of the sampling train (Fraction 1), μg.

Q_{fh} = quantity of mercury in analyzed sample, μg.

$V_{soln.1}$ = total volume of digested sample solution (Fraction 1), ml.

V_{f1B} = volume of Fraction 1B analyzed, ml. See the following notice.

Note: V_{f1B} is the actual amount of Fraction 1B analyzed. For example, if 1 ml of Fraction lB were diluted to 100 ml to bring it into the proper analytical range, and 1 ml of the 100-ml dilution were analyzed, V_{f1B} would be 0.01 ml.

3.1.8.5.2 Fraction 2B and Fractions 3A, 3B, and 3C, Back Half, Hg. Calculate the amount of mercury collected in Fractions 2 using Equation 5 and in Fractions 3A, 3B, and 3C using Equation 6. Calculate the total amount of mercury collected in the back half of the sampling train using Equation 7.

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f2B}} \times V_{soln.2} \qquad \text{Eq. 5}$$

where:

Hg_{bh2} = total mass of mercury collected in Fraction 2, μg.

Q_{bh2} = quantity of mercury in analyzed sample, μg.

$V_{soln.2}$ = total volume of Fraction 2, ml.

V_{f2B} = volume of Fraction 2B analyzed, ml (see the following note).

Note: V_{f2B} is the actual amount of Fraction 2B analyzed. For example, if 1 ml of Fraction 2B were diluted to 10 ml to bring it into the proper analytical range, and 5 ml of the 10-ml dilution was analyzed, V_{f2B} would be 0.5.

Use Equation 6 to calculate separately the back-half mercury for Fractions 3A, then 3B, then 3C.

$$Hg_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}} \times V_{soln.3(A,B,C)} \qquad \text{Eq. 6}$$

where:

$Hg_{bh3(A,B,C)}$ = total mass of mercury collected separately in Fraction 3A, 3B, or 3C, μg.

$Q_{bh3(A,B,C)}$ = quantity of mercury in separately analyzed samples, μg.

$V_{f3(A,B,C)}$ = volume of Fraction 3A, 3B, or 3C analyzed, ml (see Note in sections 3.1.8.5.1 and 3.1.8.5.2, and calculate similarly).

$V_{soln.3(A,B,C)}$ = total volume of Fraction 3A, 3B, or 3C, ml.

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3A} + Hg_{bh3B} + Hg_{bh3C} \qquad \text{Eq. 7}$$

where:

Hg_{bh} = total mass of mercury collected in the back half of the sampling train, μg.

3.1.8.5.3 Total Train Mercury Catch. Calculate the total amount of mercury collected in the sampling train using Equation 8.

$$Hg_t = (Hg_{fh} - Hg_{fhb}) + (Hg_{bh} - Hg_{bhb}) \qquad \text{Eq. 8}$$

where:

Hg_t = total mass of mercury collected in the sampling train, μg.

Hg_{fhb} = blank correction value for mass of mercury detected in front-half field reagent blank, μg.

Hg_{bhb} = blank correction value for mass of mercury detected in back-half field reagent blanks, μg.

Note: If the total of the measured blank values ($Hg_{fhb} + Hg_{bhb}$) is in the range of 0 to 6 μg, then the total may be used to correct the emission sample value ($Hg_{fh} + Hg_{bh}$); if it exceeds 6 μg, the greater of the following two values may be used: 6 μg or 5 percent of the emission sample value ($Hg_{fh} + Hg_{bh}$).

3.1.8.6 Metal Concentration of Stack Gas. Calculate each metal separately for the cadmium, total chromium, arsenic, nickel, manganese, beryllium, copper, lead, phosphorus, thallium, silver, barium, zinc, selenium, antimony, and mercury concentrations in the stack gas (dry basis, adjusted to standard conditions) as follows:

$$C_s = K_4(M_t/V_{m(std)}) \qquad \text{Eq. 9}$$

where:

C_s = concentration of each metal in the stack gas, mg/dscm.

$K_4 = 10^{-3}$mg/μg.

M_t = total mass of each metal collected in the sampling train, μg; (substitute Hg_t for M_t for the mercury calculation).

$V_{m(std)}$ = volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

3.1.8.7 Isokinetic Variation and Acceptable Results. Same as method 5, sections 6.11 and 6.12, respectively.

3.1.9 *Bibliography*

3.1.9.1 Method 303F in Standard Methods for the Examination of Water and Wastewater, 15th Edition, 1980. Available from the American Public Health Association. 1015 18th Street NW., Washington, DC 20036.

3.1.9.2 EPA Methods 6010, 7000, 7041, 7060, 7131, 7421. 7470, 7740. and 7841. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods SW-846, Third Edition. September 1986. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC 20460.

3.1.9.3 EPA Method 200.7, Code of Federal Regulations, title 40, part 136, appendix C. July 1, 1987.

3.1.9.4 EPA Methods 1 through 5, and 12 Code of Federal Regulations, title 40, part 60, appendix A, July 1, 1987.

3.2 *Determination of Hexavalent Chromium Emissions from Stationary Sources (Method Cr+6)*

3.2.1 *Applicability and Principle*

3.2.1.1 Applicability. This method applies to the determination of hexavalent chromium (Cr+6) emissions from hazardous waste incinerators. municipal waste combustors, sewage sludge incinerators, and boilers and industrial furnaces. With the approval of the Administrator, this method may also be used to measure total chromium. The sampling train, constructed of Teflon components, has only been evaluated at temperatures less than 300 °F. Trains constructed of other materials, for testing at higher temperatures, are currently being evaluated.

3.2.1.2 Principle. For incinerators and combustors, the Cr+6 emissions are collected

isokinetically from the source. To eliminate the possibility of Cr^{+6} reduction between the nozzle and impinger, the emission samples are collected with a recirculatory train where the impinger reagent is continuously recirculated to the nozzle. Recovery procedures include a post-sampling purge and filtration. The impinger train samples are analyzed for Cr^{+6} by an ion chromatograph equipped with a post-column reactor and a visible wavelength detector. The IC/PCR separates the Cr^{+6} as chromate (CrO^{4+6-}) from other components in the sample matrices that may interfere with the Cr^{+6}-specific diphenylcarbazide reaction that occurs in the post-column reactor. To increase sensitivity for trace levels of chromium, a preconcentration system is also used in conjunction with the IC/PCR.

3.2.2 *Range, Sensitivity, Precision, and Interference*

3.2.2.1 Range. Employing a preconcentration procedure, the lower limit of the detection range can be extended to 16 nanograms per dry standard cubic meter (ng/dscm) with a 3 dscm gas sample (0.1 ppb in

solution). With sample dilution, there is no upper limit.

3.2.2.2 Sensitivity. A minimum detection limit of 8 ng/dscm with a 3 dscm gas sample can be achieved by preconcentration (0.05 ppb in solution).

3.2.2.3 Precision. The precision of the IC/PCR with sample preconcentration is 5 to 10 percent. The overall precision for sewage sludge incinerators emitting 120 ng/dscm of Cr^{+6} and 3.5 μg/dscm of total chromium is 25% and 9% for Cr^{+6} and total chromium, respectively; for hazardous waste incinerators emitting 300 ng/dscm of Cr^{+6} it is 20 percent.

3.2.2.4 Interference. Components in the sample matrix may cause Cr^{+6} to convert to trivalent chromium (Cr^{+3}) or cause Cr^{+3} to convert to Cr^{+6}. A post-sampling nitrogen purge and sample filtration are included to eliminate many of these interferences. The chromatographic separation of Cr^{+6} using ion chromatography reduces the potential for other metals to interfere with the post-column reaction. For the IC/PCR analysis, only compounds that coelute with Cr^{+6} and affect the diphenylcarbazide reaction will cause

interference. Periodic analysis of deionized (DI) water blanks is used to demonstrate that the analytical system is essentially free from contamination. Sample cross-contamination that can occur when high-level and low-level samples or standards are analyzed alternately is eliminated by thorough purging of the sample loop. Purging can easily be achieved by increasing the injection volume of the samples to ten times the size of the sample loop.

3.2.3 *Apparatus*

3.2.3.1 Sampling Train. Schematics of the recirculating sampling trains employed in this method are shown in Figures 3.2-1 and 3.2-2. The recirculatory train is readily assembled from commercially available components. All portions of the train in contact with the sample are either glass, quartz, Tygon, or Teflon, and are to be cleaned as per subsection 3.2.5.1.1.

The metering system is identical to that specified by Method 5 (see section 3.8.1); the sampling train consists of the following components:
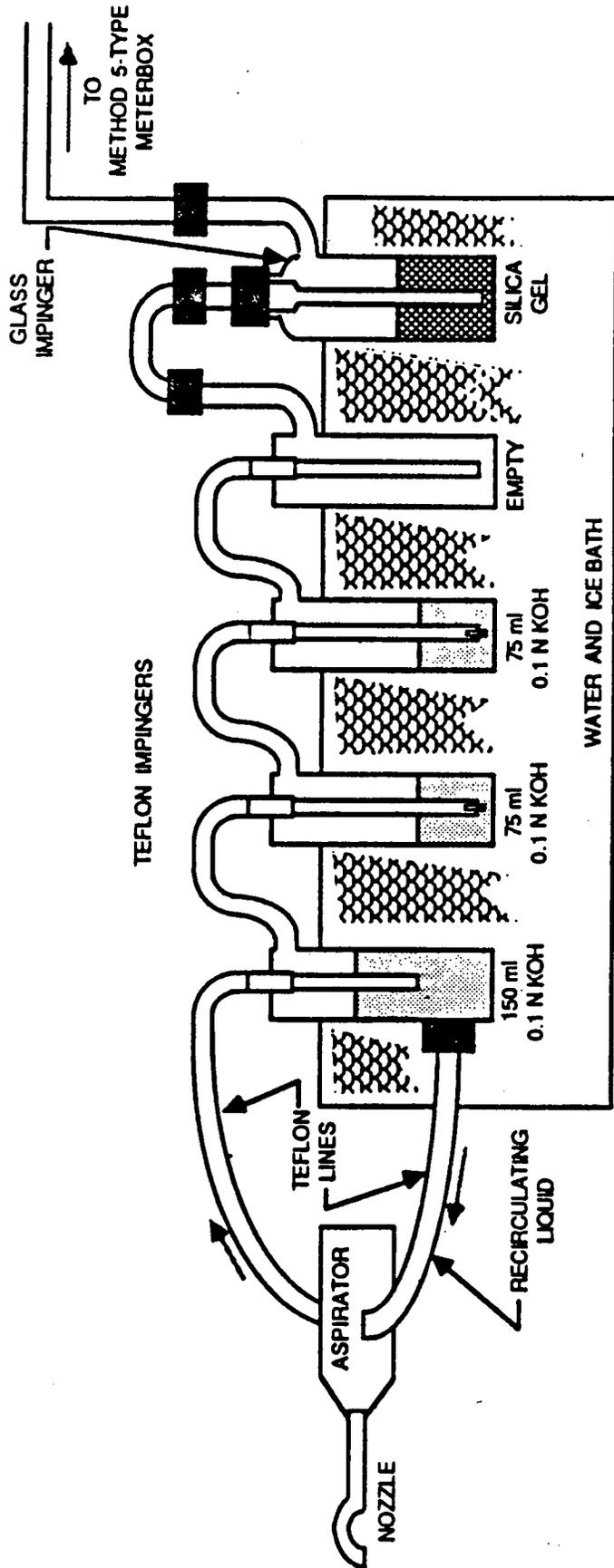
BILLING CODE 6560-50-M

Figure 3.2-1 Schematic of recirculatory impinger train with aspirator assembly.
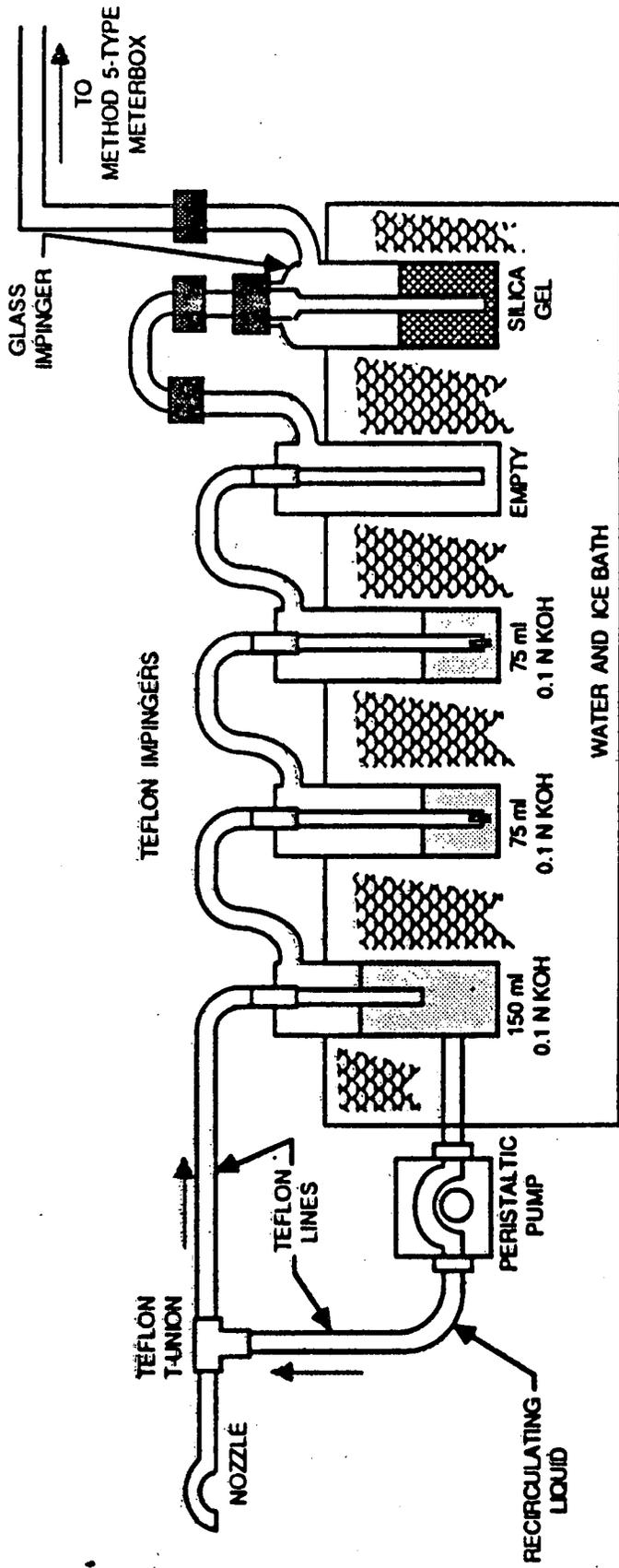
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Figure 3.2-2. Schematic of recirculatory impinger train with pump/sprayer assembly.

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3.2.3.1.1 Probe Nozzle. Glass or Teflon with a sharp, tapered leading edge. The angle of taper shall be $\leq 30°$ and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (⅛ to ½ in) (or larger if higher volume sample trains are used) inside diameter (ID) nozzles in increments of 0.16 cm (¹⁄₁₆ in). Each nozzle shall be calibrated according to the procedures outlined in section 3.2.6.

3.2.3.1.2 Teflon Aspirator or Pump/ Sprayer Assembly. Teflon aspirator capable of recirculating absorbing reagent at 50 ml/ min while operating at 0.75 cfm. Alternatively, a pump/sprayer assembly may be used instead of the Teflon aspirator. A Teflon union-T is connected behind the nozzle to provide the absorbing reagent/ sample gas mix; a peristaltic pump is used to recirculate the absorbing reagent at a flow rate of at least 50 ml/min. Teflon fittings, Teflon ferrules, and Teflon nuts are used to connect a glass or Teflon nozzle. recirculating line. and sample line to the Teflon aspirator

or union-T. Tygon, C-flex** or other suitable inert tubing for use with peristaltic pump.

3.2.3.1.3 Teflon Sample Line. Teflon, ⅜″ outside diameter (OD) and ¼″ inside diameter (ID), or ½″ OD x ⅜″ ID, of suitable length to connect aspirator (or T-union) to first Teflon impinger.

3.2.3.1.4 Teflon Recirculation Line. Teflon, ¼″ O.D. and ⅛″ I.D., of suitable length to connect first impinger to aspirator (or T-union).

3.2.3.1.5 Teflon Impingers. Four Teflon Impingers; Teflon tubes and fittings, such as made by Savillex** can be used to construct impingers 2″ diameter by 12″ long, with vacuum-tight ⅜″ O.D. Teflon compression fittings. Alternatively, standard glass impingers that have been Teflon-lined, with Teflon stems and U-tubes, may be used. Inlet fittings on impinger top to be bored through to accept ⅜″ O.D. tubing as impinger stem. The second and third ⅜″ OD Teflon stem has a ¼″ OD Teflon tube, 2″ long. inserted at its end to duplicate the effects of the Greenburg-Smith impinger stem. The first impinger stem should extend 2″ from impinger bottom, high enough in the impinger reagent to prevent air

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*Note: Mention of trade names or specific product does not constitute endorsement by the Environmental Protection Agency.

from entering recirculating line; the second and third impinger stems should extent to ½″ from impinger bottom. The first impinger should include a ¼″ O.D. Teflon compression fitting for recirculation line. The fourth impinger serves as a knockout impinger.

3.2.3.1.6 Glass Impinger. Silica gel impinger. Vacuum-tight impingers, capable of containing 400 g of silica gel, with compatible fittings. The silica gel impinger will have a modified stem (½″ ID at tip of stem).

3.2.3.1.7 Thermometer, (identical to that specified by Method 5) at the outlet of the silica gel impinger, to monitor the exit temperature of the gas.

3.2.3.1.8 Metering System, Barometer, and Gas Density Determinations Equipment. Same as method 5, sections 2.1.8 through 2.1.10, respectively.

3.2.3.2 Sample Recovery. Clean all items for sample handling or storage with 10% nitric acid solution by soaking, where possible, and rinse thoroughly with DI water before use.

3.2.3.2.1 Nitrogen Purge Line. Inert tubing and fittings capable of delivering 0 to 1 scf/ min (continuously adjustable) of nitrogen gas to the impinger train from a standard gas cylinder (see Figure 3.2.3). Standard ⅜-inch Teflon tubing and compression fittings in conjunction with an adjustable pressure regulator and needle valve may be used.
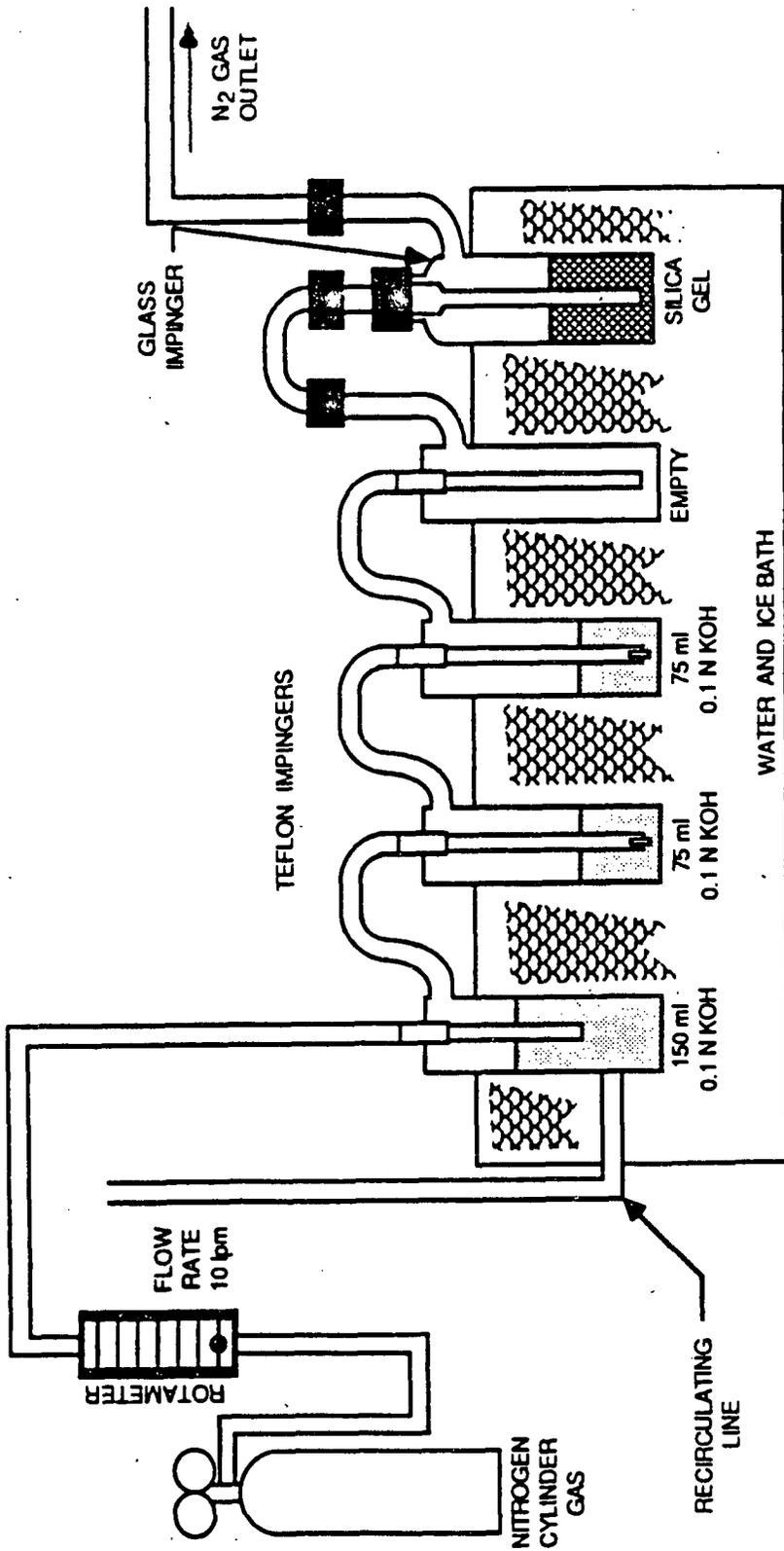
BILLING CODE 6560-50-M

Figure 3.2-3 Schematic of post test nitrogen purge system.

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BILLING CODE 6560-50-C

3.2.3.2.2 Wash bottles. Two polyethylene wash bottles, for DI water and nitric rinse solution.

3.2.3.2.3 Sample Storage Containers. Polyethylene, with leak-free screw cap, 500-ml or 1000-ml.

3.2.3.2.4 1000-ml Graduated Cylinder.

3.2.3.2.5 Plastic Storage Containers. Air tight containers to store silica gel.

3.2.3.2.6 Funnel and Rubber Policeman. To aid in transfer of silica gel from impinger to storage container; not necessary if silica gel is weighed directly in the impinger.

3.2.3.2.7 Balance.

3.2.3.3 Sample Preparation for Analysis. Sample preparation prior to analysis includes purging the sample train immediately following the sample run. and filtering the recovered sample to remove particulate matter immediately following recovery.

3.2.3.3.1 Beakers, Funnels, Volumetric Flasks, Volumetric Pipets, and Graduated Cylinders. Assorted sizes, Teflon or glass, for preparation of samples, sample dilution, and preparation of calibration standards. Prepare initially following procedure described in section 3.2.5.1.3 and rinse between use with 0.1 N HNO_3 and DI water.

3.2.3.3.2 Filtration Apparatus. Teflon, or equivalent, for filtering samples, and Teflon filter holder. Teflon impinger components have been found to be satisfactory as a sample reservoir for pressure filtration using nitrogen.

3.2.3.4 Analysis.

3.2.3.4.1 IC/PCR System. High performance liquid chromatograph pump, sample injection valve, post-column reagent delivery and mixing system, and a visible detector, capable of operating at 520 nm, all with a non-metallic (or inert) flow path. An electronic recording integrator operating in the peak area mode is recommended, but other recording devices and integration techniques are acceptable provided the repeatability criteria and the linearity criteria for the calibration curve described in section 3.2.5.5 can be satisfied. A sample loading system will be required if preconcentration is employed.

3.2.3.4.2 Analytical Column. A high performance ion chromatograph (HPIC) non-metallic column with anion separation characteristics and a high loading capacity designed for separation of metal chelating compounds to prevent metal interference. Resolution described in section 3.2.5.4 must be obtained. A non-metallic guard column with the same ion-exchange material is recommended.

3.2.3.4.3 Preconcentration Column. An HPIC non-metallic column with acceptable anion retention characteristics and sample loading rates as described in section 3.2.5.5.

3.2.3.4.4 0.45 um filter cartridge. For the removal of insoluble material. To be used just prior to sample injection/analysis.

3.2.4 *Reagents*

All reagents should, at a minimum, conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. All prepared reagents should be checked by IC/PCR analysis for Cr^{+6} to ensure that contamination is below the analytical

detection limit for direct injection or, if selected, preconcentration. If total chromium is also to be determined, the reagents should also be checked by the analytical technique selected to ensure that contamination is below the analytical detection limit.

3.2.4.1 Sampling.

3.2.4.1.1 Water. Deionized water. It is recommended that water blanks be checked prior to preparing sampling reagents to ensure that the Cr^{+6} content is less than the analytical detection limit.

3.2.4.1.2 Potassium Hydroxide, 0.1 N. Add 5.6 gm of KOH(s) to approximately 900 ml of DI water and let dissolve. Dilute to 1000 ml with DI water.

Note: At sources with high concentrations of acids and/or SO_2, the concentration of KOH should be increased to 0.5 N to ensure that the pH of the solution is above 8.5 after sampling.

3.2.4.1.3 Silica Gel and Crushed Ice. Same as Method 5, sections 3.1.2 and 3.1.4, respectively.

3.2.4.2 Sample Recovery. The reagents used in sample recovery are as follows:

3.2.4.2.1 Water. Same as subsection 3.2.4.1.1.

3.2.4.2.2 Nitric Acid, 0.1 N. Add 6.3 ml of concentrated HNO_3 (70 percent) to a graduated cylinder containing approximately 900 ml of DI water. Dilute to 1000 ml with DI water, and mix well.

3.2.4.2.3 pH Indicator Strip. pH indicator capable of determining pH of solution between the pH range of 7 and 12, at 0.5 pH intervals.

3.2.4.3 Sample Preparation

3.2.4.3.1 Water. Same as subsection 3.2.4.1.1.

3.2.4.3.2 Nitric Acid, 0.1 N. Same as subsection 3.2.4.2.2.

3.2.4.3.3 Filters. Acetate membrane, or equivalent, filters with 0.45 micrometer or smaller pore size to remove insoluble material.

3.2.4.4 Analysis.

3.2.4.4.1 Chromatographic Eluent. The eluent used in the analytical system is ammonium sulfate based. It is prepared by adding 6.5 ml of 29 percent ammonium hydroxide (NH_4OH) and 33 grams of ammonium sulfate (($NH_4)_2SO_4$) to 500 ml of DI water. The mixture should then be diluted to 1 liter with DI water and mixed well. Other combinations of eluents and/or columns may be employed provided peak resolution, as described in section 3.2.5.4, repeatability and linearity, as described in section 3.2.6.2, and analytical sensitivity are acceptable.

3.2.4.4.2 Post-Column Reagent. An effective post-column reagent for use with the chromatographic eluent described in section 3.2.4.4.1 is a diphenylcarbazide (DPC) based system. Dissolve 0.5 g of 1.5-diphenylcarbazide (DPC) in 100 ml of ACS grade methanol. Add to 500 ml of degassed DI water containing 50 ml of 96 percent spectrophotometric grade sulfuric acid. Dilute to 1 liter with degassed DI water.

3.2.4.4.3 Cr^{+6} Calibration Standard. Prepare Cr^{+6} standards from potassium dichromate ($K_2Cr_2O_7$, FW 294.19). To prepare a 1000 μg/ml Cr^{+6} stock solution, dissolve 2.829 g of dry $K_2Cr_2O_7$ in 1 liter of DI water. To prepare working standards, dilute the

stock solution to the chosen standard concentrations for instrument calibration with 0.05 N KOH to achieve a matrix similar to the actual field samples.

3.2.4.4.4 Performance Audit Sample. A performance audit sample shall be obtained from the Quality Assurance Division of EPA and analyzed with the field samples. The mailing address to request audit samples is: U.S. Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory, Quality Assurance Division, Source Branch. Mail Drop 77–A, Research Triangle Park, North Carolina 27711.

The audit sample should be prepared in a suitable sample matrix at a concentration similar to the actual field samples.

3.2.5 *Procedure*

Safety First—Wear Safety Glasses at All Times During This Test Method

3.2.5.1 Sampling. The complexity of this method is such that to obtain reliable results, testers should be trained and experienced with test procedures.

3.2.5.1.1 Pretest Preparation. All components shall be maintained and calibrated according to the procedures described in APTD–0576, unless otherwise specified herein.

Rinse all sample train components from the glass nozzle up to the silica gel impinger and sample containers with hot tap water followed by washing with hot soapy water. Next, rinse the train components and sample containers three times with tap water followed by three rinses with DI water. All the components and containers should then be soaked overnight, or a minimum of 4 hours, in a 10 percent (v/v) nitric acid solution, then rinsed three times with DI water. Allow the components to air dry prior to covering all openings with Parafilm, or equivalent.

3.2.5.1.2 Preliminary Determinations. Same as method 5, section 4.1.2.

3.2.5.1.3 Preparation of Sampling Train. Measure 300 ml of 0.1 N KOH into a graduated cylinder (or tare-weighed precleaned polyethylene container). Place approximately 150 ml of the 0.1 N KOH reagent in the first Teflon impinger. Split the rest of the 0.1 N KOH between the second and third Teflon impingers. The next Teflon impinger is left dry. Place a preweighed 200- to 400-g portion of indicating silica gel in the final glass impinger. (For sampling periods in excess of two hours, or for high moisture sites. 400-g of silica gel is recommended.)

Retain reagent blanks of the 0.1 N KOH equal to the volumes used with the field samples.

3.2.5.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).

3.2.5.1.5 Sampling Train Operation. Follow the procedures given in method 5, section 4.1.5. The sampling train should be iced down with water and ice to ensure heat transfer with the Teflon impingers.

Note: If the gas to be sampled is above 200 °F, it may be necessary to wrap three or

four feet of the Teflon sample and recirculating lines inside the ice bath to keep the recirculated reagent cool enough so it does not turn to steam.

For each run, record the data required on a data sheet such as the one shown in Figure 5.2 of method 5.

At the end of the sampling run, determine the pH of the reagent in the first impinger using a pH indicator strip. The pH of the solution shall be greater than 8.5.

3.2.5.1.6 Calculation of Percent Isokinetic. Same as method 5, section 4.1.6.

3.2.5.2 Post-Test Nitrogen Purge. The nitrogen purge is used as a safeguard against the conversion of hexavalent chromium to the trivalent oxidation state. The purge is effective in the removal of SO_2 from the impinger contents.

Attach the nitrogen purge line to the input of the impinger train. Check to ensure the output of the impinger train is open, and that the recirculating line is capped off. Open the nitrogen gas flow slowly and adjust the delivery rate to 10 L/min. Check the recirculating line to ensure that the pressure is not forcing the impinger reagent out through this line. Continue the purge under these conditions for one-half hour, periodically checking the flow rate.

3.2.5.3 Sample Recovery. Begin cleanup procedures as soon as the train assembly has been purged at the end of the sampling run. The probe assembly may be disconnected from the sample train prior to sample purging.

The probe assembly should be allowed to cool prior to sample recovery. Disconnect the umbilical cord from the sample train. When the probe assembly can be safely handled, wipe off all external particulate matter near the tip of the nozzle, and cap the nozzle prior to transporting the sample train to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions.

3.2.5.3.1 Container No. 1 (Impingers 1 through 3). Disconnect the first impinger from the second impinger and disconnect the recirculation line from the aspirator or peristaltic pump. Drain the Teflon impingers into a precleaned graduated cylinder or tare-weighed precleaned polyethylene sample

container and measure the volume of the liquid to within 1 ml or 1 g. Record the volume of liquid present as this information is required to calculate the moisture content of the flue gas sample. If necessary, transfer the sample from the graduated cylinder to a precleaned polyethylene sample container. With DI water, rinse four times the insides of the glass nozzle, the aspirator, the sample and recirculation lines, the impingers, and the connecting tubing, and combine the rinses with the impinger solution in the sample container.

3.2.5.3.2 Container No. 2 (HNO_3 rinse optional for total chromium). With 0.1 N HNO_3, rinse three times the entire train assembly, from the nozzle to the fourth impinger and combine the rinses into a separate precleaned polyethylene sample container for possible total chromium analysis. Repeat the rinse procedure a final time with DI water, and discard the water rinses. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

3.2.5.3.3 Container No. 3 (Silica Gel). Note the color of the indicating silica gel to determine if it has been completely spent. Quantitatively transfer the silica gel from its impinger to the original container, and seal the container. A funnel and a rubber policeman may be used to aid in the transfer. The small amount of particulate that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or the silica gel plus impinger) to the nearest 0.5 g.

3.2.5.3.4 Container No. 4 (0.1 N KOH Blank). Once during each field test, place a volume of reagent equal to the volume placed in the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

3.2.5.3.5 Container No. 5 (DI Water Blank). Once during each field test, place a

volume of DI water equal to the volume employed to rinse the sample train into a precleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

3.2.5.3.6 Container No. 6 (0.1 N HNO_3 Blank). Once during each field test if total chromium is to be determined, place a volume of 0.1 N HNO_3 reagent equal to the volume employed to rinse the sample train into a pre-cleaned polyethylene sample container, and seal the container. Mark the height of the fluid level on the container or, alternatively if a balance is available, weigh the container and record the weight to permit determination of any leakage during transport. Label the container clearly to identify its contents.

3.2.5.4 Sample Preparation. For determination of Cr^{+6}, the sample should be filtered *immediately following recovery* to remove any insoluble matter. Nitrogen gas may be used as a pressure assist to the filtration process (see Figure Cr^{+6}—4).

Filter the entire impinger sample through a 0.45-micrometer acetate filter (or equivalent), and collect the filtrate in a 1000-ml graduated cylinder. Rinse the sample container with DI water three separate times, pass these rinses through the filter, and add the rinses to the sample filtrate. Rinse the Teflon reservoir with DI water three separate times, pass these rinses through the filter, and add the rinses to the sample. Determine the final volume of the filtrate and rinses and return them to the rinsed polyethylene sample container. Label the container clearly to identify its contents. Rinse the Teflon reservoir once with 0.1 N HNO_3 and once with DI water and discard these rinses.

If total chromium is to be determined, quantitatively recover the filter and residue and place them in a vial. (The acetate filter may be digested with 5 ml of 70 percent nitric acid; this digestion solution may then be diluted with DI water for total chromium analysis.)
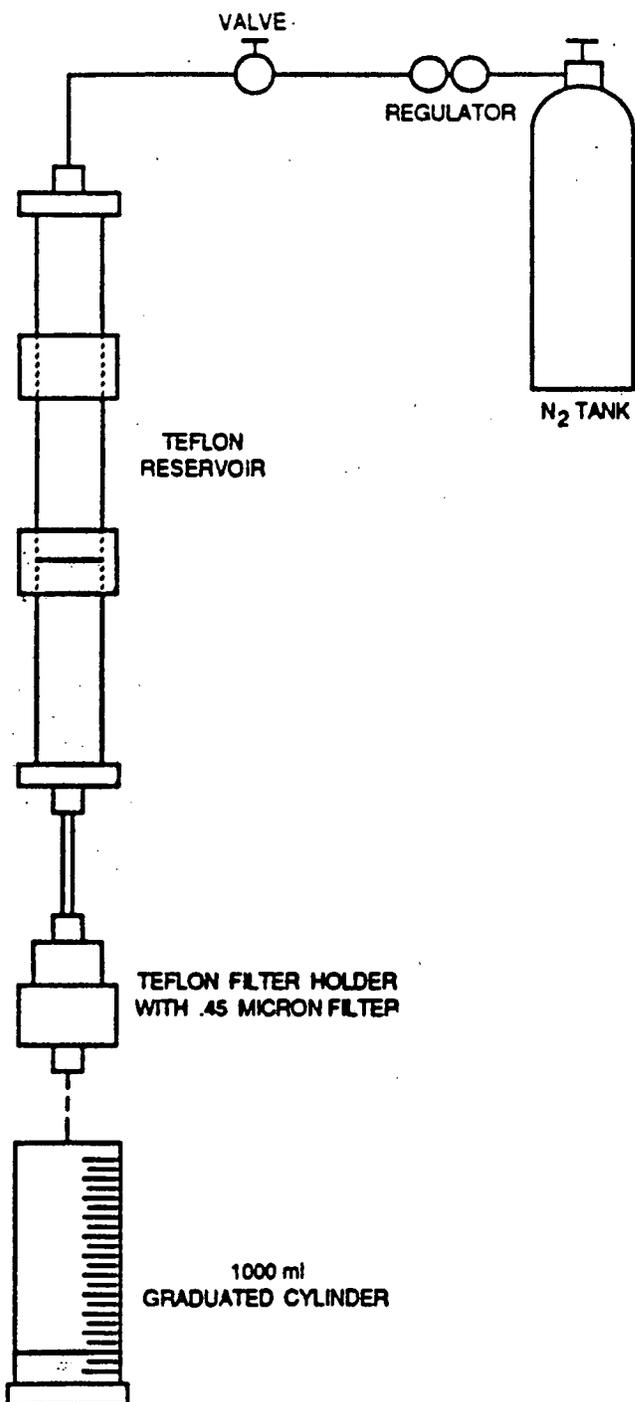
BILLING CODE 6560-50-M

VALVE

REGULATOR

N₂ TANK

TEFLON
RESERVOIR

TEFLON FILTER HOLDER
WITH .45 MICRON FILTER

1000 ml
GRADUATED CYLINDER

Figure 3.2-4   Schematic of sample filter system.

4196 2/90

Note: If the source has a large amount of particulate in the effluent stream, testing teams may wish to filter the sample twice, once through a 2 to 5-micrometer filter, and then through the 0.45-micrometer filter.

3.2.5 4.1 Container 2 (HNO$_3$ rinse, optional for total chromium). This sample shall be analyzed in accordance with the selected procedure for total chromium analysis. At a minimum, the sample should be subjected to a digestion procedure sufficient to solubilize all chromium present.

3.2.5.4.2 Container 3 (Silica Gel). Weigh the spent silica gel to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

3.2.5.5 Sample analysis. The Cr^{+6} content of the sample filtrate is determined by ion chromatography coupled with a post-column reactor (IC/PCR). To increase sensitivity for trace levels of chromium, a preconcentration system is also used in conjunction with the IC/PCR.

Prior to preconcentration and/or analysis, all field samples will be filtered through a 0.45-μ filter. This filtration should be conducted just prior to sample injection/analysis.

The preconcentration is accomplished by selectively retaining the analyte on a solid absorbent (as described in 3.2.3.4.3), followed by removal of the analyte from the absorbent. The sample is injected into a sample loop of the desired size (repeated loadings or larger size loop for greater sensitivity) and the Cr^{+6} is collected on the resin bed of the column. When the injection valve is switched, the eluent displaces the concentrated Cr^{+6} sample moving it off the preconcentration column and onto the IC anion separation column. After separation from other sample components, Cr^{+6} forms a specific complex in the post column reactor with a diphenylcarbazide reaction solution, and the complex is then detected by visible absorbance at a wavelength of 520 nm. The amount of absorbance measured is proportional to the concentration of the Cr^{+6} complex formed. The IC retention time and absorbance of the Cr^{+6} complex is compared with known Cr^{+6} standards analyzed under identical conditions to provide both qualitative and quantitative analyses.

Prior to sample analysis, establish a stable baseline with the detector set at the required attenuation by setting the eluent flowrate at approximately 1 ml/min and post-column reagent flowrate at approximately 0.5 ml/min.

Note: As long as the ratio of eluent flowrate to PCR flowrate remains constant, the standard curve should remain linear. Inject a sample of DI water to ensure that no Cr^{+6} appears in the water blank.

First, inject the calibration standards prepared, as described in section 3.2.4.4.4, to cover the appropriate concentration range, starting with the lowest standard first. Next, inject, in duplicate, the performance audit sample, followed by the 0.1 N KOH field blank and the field samples. Finally, repeat the injection of the calibration standards to allow for compensation of instrument drift. Measure areas or heights of the Cr^{+6}/DPC complex chromatogram peak. The response for replicate, consecutive injections of

samples must be within 5 percent of the average response, or the injection should be repeated until the 5 percent criterion can be met. Use the average response (peak areas or heights) from the duplicate injections of calibration standards to generate a linear calibration curve. From the calibration curve, determine the concentration of the field samples employing the average response from the duplicate injections.

The results for the analysis of the performance audit sample must be within 10 percent of the reference value for the field sample analysis to be valid.

3.2.6 *Calibration*. Maintain a written log of all calibration activities.

3.2.6.1 Sample Train Calibration. Calibrate the sample train components according to the indicated sections of method 5: Probe Nozzle (section 5.1); Pitot Tube (section 5.2); Metering System (section 5.3); Temperature Gauges (section 5.5); Leak-Check of the Metering System (section 5.6); and Barometer (section 5.7).

3.2.6.2 Calibration Curve for the IC/PCR. Prepare working standards from the stock solution described in section 3.2.4.4.4 by dilution with a DI water solution to approximate the field sample matrix. Prepare at least four standards to cover one order of magnitude that bracket the field sample concentrations. Run the standards with the field samples as described in section 3.2.5.5. For each standard, determine the peak areas (recommended) or the peak heights, calculate the average response from the duplicate injections, and plot the average response against the Cr^{+6} concentration in μg/L. The individual responses for each calibration standard determined before and after field sample analysis must be within 5 percent of the average response for the analysis to be valid. If the 5 percent criteria is exceeded, excessive drift and/or instrument degradation may have occurred, and must be corrected before further analyses are performed.

Employing linear regression, calculate a predicted value for each calibration standard with the average response for the duplicate injections. Each predicted value must be within 7 percent of the actual value for the calibration curve to be considered acceptable. If not acceptable, remake and/or rerun the calibration standards. If the calibration curve is still unacceptable, reduce the range of the curve.

3.2.7 *Calculations*

3.2.7.1 Dry Gas Volume. Using the data from the test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method 5.

3.2.7.2 Volume of Water Vapor and Moisture Content. Using the data from the test, calculate $V_{w(std)}$ and B_{ws}, the volume of water vapor and the moisture content of the stack gas, respectively, using Equations 5-2 and 5-3 of Method 5.

3.2.7.3 Stack Gas Velocity. Using the data from the test and Equation 2-9 of Method 2, calculate the average stack gas velocity.

3.2.7.4 Total μg Cr^{+6} per Sample. Calculate as described below:

$$m = (S-B) \times V_{1s} \times d$$

where:
m = Mass of Cr^{+6} in the sample, μg.

S = Concentration of sample, μg Cr^{+6}/ml.
B = Concentration of blank, μg Cr^{+6}/ml.
V_{1s} = Volume of sample after filtration, ml.
d = Dilution factor (1 if not diluted).

3.3 *Measurement of HCl and Cl$_2$*

3.3.1 *Isokinetic HCl/Cl$_2$ Emission Sampling Train (Method 0050)*

3.3.1.1 Scope and Application.

3.3.1.1.1 This method describes the collection of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chlorine (Cl$_2$, CAS Registry Number 7782-50-5) in stack gas emission samples from hazardous waste incinerators' municipal waste combustors, and boilers and industrial furnaces. The collected samples are analyzed using Method 9057. This method collects the emission sample isokinetically and is therefore particularly suited for sampling at sources, such as those controlled by wet scrubbers, emitting acid particulate matter (e.g., HCl dissolved in water droplets). A midget impinger train sampling method designed for sampling sources of HCl/Cl$_2$ emissions not in particulate form is presented in method 0051.

3.3.1.1.2 This method is not acceptable for demonstrating compliance with HCl emission standards less than 20 ppm.

3.3.1.1.3 This method may also be used to collect samples for subsequent determination of particulate emissions (by EPA method 5, reference 1) following the additional sampling procedures described.

3.3.1.2 Summary of Method.

3.3.1.2.1 Gaseous and particulate pollutants are withdrawn from an emission source and are collected in an optional cyclone, on a filter, and in absorbing solutions. The cyclone collects any liquid droplets and is not necessary if the source emissions do not contain liquid droplets. The Teflon mat or quartz-fiber filter collects other particulate matter including chloride salts. Acidic and alkaline absorbing solutions collect gaseous HCl and Cl$_2$, respectively. Following sampling of emissions containing liquid droplets, any HCl/Cl$_2$ dissolved in the liquid in the cyclone and/or on the filter is vaporized and ultimately collected in the impingers by pulling Ascarite II^R conditioned ambient air through the sampling train. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride (Cl$^-$) ions. The Cl$_2$ gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H$^+$), Cl$^-$, and hypochlorous acid (HClO). The Cl$^-$ ions in the separate solutions are measured by ion chromatography (method 9057). If desired, the particulate matter recovered from the filter and the probe is analyzed following the procedures in EPA Method 5 (reference 1).

3.3.1.3 Interferences.

3.3.1.3.1 Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferant for HCl is diatomic chlorine (Cl$_2$) gas which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water. Cl$_2$ gas exhibits a low solubility in water,

however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present.

3.3.1.4   Apparatus and Materials.

3.3.1.4.1   Sampling Train.

3.3.1.4.1.1   A schematic of the sampling train used in this method is shown in Figure 3.3–1. This sampling train configuration is adapted from EPA method 5 procedures, and, as such, the majority of the required equipment is identical to that used in EPA Method 5 determinations. The new components required are a glass nozzle and probe, a Teflon union, a quartz-fiber or Teflon mat filter (see section 3.3.1.5.5), a Teflon frit, and acidic and alkaline absorbing solutions.

3.3.1.4.1.2   Construction details for the basic train components are provided in section 3.4 of EPA's Quality Assurance Handbook, Volume III (reference 2); commercial models of this equipment are also available.
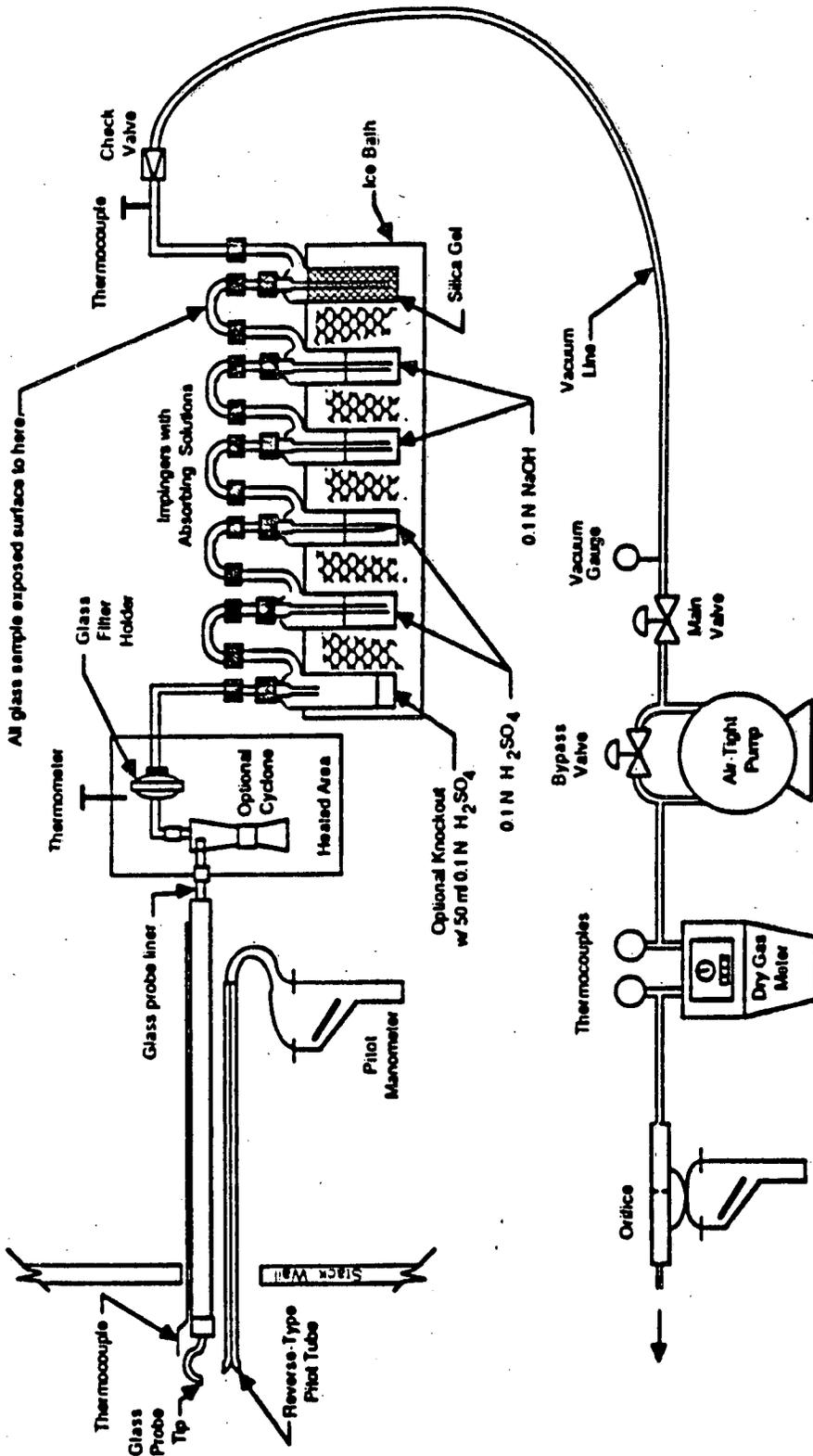
BILLING CODE 6560-50-M

Figure 3.3-1 Isokinetic HCl/Cl₂ Sampling Train

BILLING CODE 6560-50-C

Additionally, the following subsections identify allowable train configuration modifications.

3.3.1.4.1.3 Basic operating and maintenance procedures for the sampling train are also described in Reference 2. As correct usage is important in obtaining valid results, all users should refer to Reference 2 and adopt the operating and maintenance procedures outlined therein unless otherwise specified. The sampling train consists of the components detailed below.

3.3.1.4.1.3.1 Probe nozzle. Glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant I.D. The nozzle shall be buttonhook or elbow design. The nozzle should be coupled to the probe liner using a Teflon union. It is recommended that a stainless steel nut be used on this union. In cases where the stack temperature exceeds 210 °C (410 °F), a one-piece glass nozzle/liner assembly must be used. A range of nozzle sizes suitable for isokinetic sampling should be available. Each nozzle shall be calibrated according to the procedures outlined in EPA Method 5 (see References 1 and 2).

3.3.1.4.1.3.2 Probe liner. Borosilicate or quartz-glass tubing with a heated system capable of maintaining a gas temperature of 120 ± 14 °C (248 ± 25 °F) at the exit end during sampling. Because the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed and calibrated according to the procedure in Reference 2 are considered acceptable. Either borosilicate or quartz-glass probe liners may be used for stack temperatures up to about 480 °C (900 °F). Quartz liners shall be used for temperatures between 480 and 900 °C (900 and 1650 °F). (The softening temperature for borosilicate is 820 °C (1508 °F), and for quartz is 1500 °C (2732 °F).) Water-cooling of the stainless steel sheath will be necessary at temperatures approaching and exceeding 500 °C.

3.3.1.4.1.3.3 Pitot tube. Type S, as described in section 2.1 of EPA Method 2 (Reference 1). The pitot tube shall be attached to the probe to allow constant monitoring of the stack-gas velocity. The impact (high-pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see section 3.1.1 of Reference 2) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in section 3.1.1 of Reference 2.

3.3.1.4.1.3.4 Differential pressure gauge. Inclined manometer or equivalent device as described in section 2.2 of EPA method 2 (Reference 1). One manometer shall be used for velocity-head (delta P) readings and the other for orifice differential pressure (delta H) readings.

3.3.1.4.1.3.5 Cyclone (optional). Glass.

3.3.1.4.1.3.6 Filter holder. Borosilicate glass, with a Teflon frit filter support and a sealing gasket. The sealing gasket shall be constructed of Teflon or equivalent materials. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone.

3.3.1.4.1.3.7 Filter heating system. Any heating system capable of maintaining a temperature of 120±14 °C (248±25 °F) around the filter and cyclone during sampling. A temperature gauge capable of measuring temperature to within 3 °C (5.4 °F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.

3.3.1.4.1.3.8 Impinger train. The following system shall be used to determine the stack gas moisture content and to collect HCl and Cl₂: five or six impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first impinger shown in Figure 1 (knockout or condensate impinger) is optional and is recommended as a water knockout trap for use under test conditions which require such a trap. If used, this impinger should be constructed as described below for the alkaline impingers, but with a shortened stem, and should contain 50 ml of 0.1 N H_2SO_4. The following two impingers (acid impingers which each contain 100 ml of 0.1 N H_2SO_4) shall be of the Greenburg-Smith design with the standard tip (see method 5, paragraph 2.1.7). The next two impingers (alkaline impingers which each contain 100 ml of 0.1 N NaOH) and the last impinger (containing silica gel) shall be of the Greenburg-Smith design modified by replacing the tip with a 1.3-cm (½-in) I.D. glass tube extending about 1.3 cm (½ in) from the bottom of the impinger (see method 5, paragraph 2.1.7). The condensate, acid, and alkaline impingers shall contain known quantities of the appropriate absorbing reagents. The last impinger shall contain a known weight of silica gel or equivalent desiccant.

3.3.1.4.1.3.9 Metering system. The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3 °C (5.4 °F). dry-gas meter capable of measuring volume to within 1 percent, an orifice meter, (rate meter). and related equipment, as shown in Figure 1. At a minimum, the pump should be capable of 4 cfm free flow, and the dry-gas meter should have a recording capacity of 0–999.9 cu ft with a resolution of 0.005 cu ft. Other metering systems capable of maintaining sampling rates within 10 percent of isokineticity and of determining sample volumes to within 2 percent may be used. The metering system should be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.

3.3.1.4.1.3.10 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 300-m (100 ft) elevation increase (vice versa for elevation decrease).

3.3.1.4.1.3.11 Gas density determination equipment. Temperature sensor and pressure gauge (as described in sections 2.3 and 2.4 of EPA method 2), and gas analyzer, if necessary (as described in EPA method 3, Reference 1). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see EPA method 2, Figure 2–7). As a second alternative, if the stack gas is saturated, the stack temperature may be measured at a single point near the center of the stack.

3.3.1.4.1.3.12 Ascarite tube for conditioning ambient air. Tube tightly packed with approximately 150 g of fresh 8 to 20 mesh Ascarite II® sodium hydroxide coated silica, or equivalent, to dry and remove acid gases from the ambient air used to remove moisture from the filter and optional cyclone. The inlet and outlet ends of the tube should be packed with at least 1 cm thickness of glass wool or filter material suitable to prevent escape of Ascarite II fines. Fit one end with flexible tubing. etc. to allow connection to probe nozzle.

3.3.1.4.2 Sample Recovery.

3.3.1.4.2.1 Probe liner. Probe and nozzle brushes; nylon bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner and the probe nozzle.

3.3.1.4.2.2 Wash bottles. Two. Polyethylene or glass, 500 ml or larger.

3.3.1.4.2.3 Glass sample storage containers. Glass, 500- or 1000-mL Screw-cap liners shall be Teflon and constructed so as to be leak-free. Narrow-mouth glass bottles have been found to exhibit less tendency toward leakage.

3.3.1.4.2.4 Petri dishes. Glass or plastic, sealed around the circumference with Teflon tape, for storage and transport of filter samples.

3.3.1.4.2.5 Graduated cylinder and/or balances. To measure condensed water to the nearest 1 ml or 1 g. Graduated cylinders shall have subdivisions not >2 mL Laboratory triple-beam balances capable of weighing to ± 0.5 g or better are required.

3.3.1.4.2.6 Plastic storage containers. Screw-cap polypropylene or polyethylene containers to store silica gel.

3.3.1.4.2.7 Funnel and rubber policeman. To aid in transfer of silica gel to container (not necessary if silica gel is weighed in field).

3.3.1.4.2.8 Funnels. Glass, to aid in sample recovery.

3.3.1.5 Reagents

3.3.1.5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently higher purity to

permit its use without lessening the accuracy of the determination.

3.3.1.5.2 ASTM Type II water (ASTM D1193–77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified. It is advisable to analyze a blank sample of this reagent *prior* to sampling, since the reagent blank values obtained during the field sample analysis must be less than 10 percent of the sample values (see method 9057).

3.3.1.5.3 Sulfuric acid (0.1 N), H_2SO_4. Used as the HCl absorbing reagent in the impinger train. To prepare 1 L, slowly add 2.80 ml of concentrated H_2SO_4 to about 900 ml of water while stirring, and adjust the final volume to 1 L using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent *prior* to sampling, since the reagent blank values obtained during the field sample analysis must be less than 10 percent of the sample values (see method 9057).

3.3.1.5.4 Sodium hydroxide (0.1 N). NaOH. Used as the Cl_2 absorbing reagent in the impinger train. To prepare 1 L, dissolve 4.00 g of solid NaOH in about 900 ml of water and adjust the final volume of 1 L using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent *prior* to sampling, since the reagent blank values obtained during the field sample analysis must be less than 10 percent of the sample values (see Method 9057).

3.3.1.5.5 Filter. Quartz-fiber or Teflon mat (e.g., Pallflex® TX40HI45) filter.

3.3.1.5.6 Silica gel. Indicating type, 6–16 mesh. If previously used, dry at 175 °C (350°F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.3.1.5.7 Acetone. When using this train for determination of particulate emissions, reagent grade acetone, <0.001 percent residue, in glass bottles is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (<0.001 percent) shall be used. In no case shall a blank value greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

3.3.1.5.8 Crushed ice. Quantities ranging from 10–50 lbs may be necessary during a sampling run, depending on ambient air temperature.

3.3.1.5.9 Stopcock grease. Acetone-insoluble, heat-stable silicone grease may be used, if needed. Silicone grease usage is not .necessary if screw-on connectors or Teflon sleeves on ground-glass joints are used.

3.3.1.6 Sample Collection, Preservation, and Handling.

3.3.1.6.1 Sample collection is described in this method. The analytical procedures for HCl and Cl_2 are described in method 9057 and for particulate matter in EPA method 5 (Reference 1).

3.3.1.6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

3.3.1.7 Procedure.

3.3.1.7.1 Preparation for Field Test.

3.3.1.7.1.1 All sampling equipment shall be maintained and calibrated according to the procedures described in section 3.4.2 of EPA's Quality Assurance Handbook, Volume III (Reference 2).

3.3.1.7.1.2 Weigh several 200- to 300-g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may instead be weighed directly in the impinger just prior to train assembly.

3.3.1.7.1.3 Check filters visually against light for irregularities and flaws or pinhole leaks. Label the shipping containers (glass or plastic Petri dishes) and keep the filters in these containers at all times except during sampling (and weighing for particulate analysis).

3.3.1.7.1.4 If a particulate determination will be conducted, desiccate the filters at $20\pm5.6°C$ ($68\pm10°F$) and ambient pressure for at least 24 hours, and weigh at intervals of at least 6 hours to a constant weight (i.e., <0.5-mg change from previous weighing), recording results to the nearest 0.1 mg. During each weighing, the filter must not be exposed for more than a 2-min period to the laboratory atmosphere and relative humidity above 50 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven-dried at 105°C (220°F) for 2–3 hours, desiccated for 2 hours, and weighed.

3.3.1.7.2 Preliminary Field Determinations.

3.3.1.7.2.1 Select the sampling site and the minimum number of sampling points according to EPA method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and range of velocity heads using EPA method 2. It is recommended that a leak-check of the pitot lines (see EPA method 2, section 3.1) be performed. Determine the stack-gas moisture content using EPA method 4 or its alternatives to establish estimates of isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in EPA method 2, section 3.6. if integrated EPA method 3 (Reference 1) sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as the sample run.

3.3.1.7.2.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size to maintain isokinetic sampling rates. During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see section 2.2 of EPA method 2).

3.3.1.7.2.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

3.3.1.7.2.4 The total sampling time should be two hours. Allocate the same time to all traverse points defined by EPA method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus one-half min. Size the condensate impinger for the expected moisture catch or be prepared to empty it during the run.

3.3.1.7.3 Preparation of Sampling Train.

3.3.1.7.3.1 Add 50 ml of 0.1 N H_2SO_4 to the condensate impinger, if used. Place 100 ml of 0.1 N H_2SO_4 in each of the next two impingers. Place 100 ml of 0.1 N NaOH in each of the following two impingers.. Finally,transfer approximately 200–300 g of preweighed silica gel from its container to the last impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

3.3.1.7.3.2 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) filter (weighed, if particulate matter to be determined) in the filter holder. Be sure that the filter is properly centered and the gasket properly placed to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

3.3.1.7.3.3 To use glass liners, install the selected nozzle using a Viton-A O-ring when stack temperatures are <260°C (500°F) and a woven glass-fiber gasket when temperatures are higher. Other connecting systems utilizing either 316 stainless steel or Teflon ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

3.3.1.7.3.4 Set up the train as in Figure 3.3–1. A minimal amount of silicone grease may be used on ground glass joints. Connect temperature sensors to the appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

3.3.1.7.3.5 Place crushed ice around the impingers.

3.3.1.7.3.6 Turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize.

3.3.1.7.4 Leak-Check Procedures.

3.3.1.7.4.1 Pretest leak-check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

3.3.1.7.4.1.1 If a Viton-A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380-mm Hg (15-in. Hg) vacuum.

Note: A lower vacuum may be used, provided that it is not exceeded during the test.

3.3.1.7.4.1.2 If a woven glass-fiber gasket is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the cyclone, if used, or the filter holder and pulling a 380-mm Hg (15-in. Hg) vacuum (see Note above). Then, connect the probe to the train and leak-

check at about 25-mm Hg (1-in. Hg) vacuum; alternatively, leak-check the probe with the rest of the sampling train in one step at 380-mm Hg (15-in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

3.3.1.7.4.1.3 The following leak-check instructions for the sampling train may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of the bypass valve; this will cause water to back up into the filter holder. If the desired volume is exceeded, either leak-check at this higher vacuum or end the leak-check, as shown below, and start over.

3.3.1.7.4.1.4 When the leak-check is completed, first slowly remove the plug from the inlet to the probe, cyclone, or filter holder and immediately turn off the vacuum pump. This prevents the liquid in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the fifth impinger.

3.3.1.7.4.2 Leak-checks during sample run. If during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary or a port change is conducted, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be conducted according to the procedure outlined in Section 3.3.1.7.4.1, except that it shall be conducted at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average

sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester shall void the sampling run. Immediately after a component change or port change, and before sampling is reinitiated, another leak-check similar to a pre-test leak-check is recommended.

3.3.1.7.4.3 Post-test leak-check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done using the same procedures as those with the pre-test leak-check, except that it shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester shall void the sampling run.

3.3.1.7.5 Train Operation.

3.3.1.7.5.1 During the sampling run, maintain an isokinetic sampling rate to within 10 percent of true isokinetic, unless otherwise specified by the Administrator. Maintain a temperature around the filter (and cyclone, if used) of 120±14°C (248±25°F).

3.3.1.7.5.2 For each run, record the data required on a data sheet such as the one shown in Figure 3.3-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made before and after each leak-check, and when sampling is halted. Take other readings required by Figure 3.3-2 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head

readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

3.3.1.7.5.3 Clean the stack access ports prior to the test run to eliminate the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are at the specified temperature, and verify that the pitot tube and probe are positioned properly. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions using a calculator or a nomograph. Nomographs are designed for use when the Type S pitot tube coefficient is 0.84±0.02 and the stack gas equivalent density (dry molecular weight) is equal to 29±4. If the stack gas molecular weight and the pitot tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps are taken to compensate for the deviations (see Reference 3).

3.3.1.7.5.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack, to prevent water from backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

3.3.1.7.5.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

BILLING CODE 6560-50-M

Plant _____
Location _____
Operator _____
Date _____
Run No. _____
Sample Box No. _____
Meter Box No. _____
Meter H@ _____
C Factor _____
Pitot Tube Coefficient C_p _____

Schematic of Stack Cross Section

Ambient Temperature _____
Barometric Pressure _____
Assumed Moisture % _____
Probe Length, m (ft) _____
Nozzle Identification No. _____
Average Calibrated Nozzle Diameter, cm (in) _____
Probe Heater Setting _____
Leak Rate, m^3/min. (cfm) _____
Probe Liner Material _____
Static Pressure, mm Hg (in Hg) _____
Filter No. _____

Traverse Point Number	Sampling Line (θ) min	Vacuum mm Hg (in. Hg)	Stack Temperature (T_s) °C(f)	Velocity Head (P_s) mm (in) H_2O	Pressure Differential Across Orifice Meter mm (H_2O) (in H_2O)	Gas Sample Volume m^3 (ft_3)	Gas Sample Temp at Dry Gas Meter — Inlet °C(°F)	Gas Sample Temp at Dry Gas Meter — Outlet °C(°F)	Filter Holder Temperature °C(F°)	Temperature of Gas Leaving Condenser or Last Impinger
Total										
Average							Avg.	Avg.		

Figure 3.3-2 Field Data Form

3.3.1.7.5.6 Traverse the stack cross section, as required by EPA Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.

3.3.1.7.5.7 During the test run, make periodic adjustments to keep the temperature around the filter holder (and cyclone, if used) at the proper level. Add more ice, and, if necessary, salt to maintain a temperature of <20 °C (68 °F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

3 3.1.7.5.8 If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, it may be replaced in the midst of a sample run. Using another complete filter holder assembly is recommended, rather than attempting to change the filter itself. After a new filter assembly is installed, conduct a leak-check. If determined, the total particulate weight shall include the summation of all filter assembly catches.

3.3.1.7.5.9 If the condensate impinger becomes too full, it may be emptied, recharged with 50 ml of 0.1 N H_2SO_4, and replaced during the sample run. The condensate emptied must be saved and included in the measurement of the volume of moisture collected and included in the sample for analysis. The additional 50 ml of absorbing reagent must also be considered in calculating the moisture. After the impinger is reinstalled in the train, conduct a leak check.

3.3.1.7.5.10 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

3.3.1.7.5.11 Note that when two or more trains are used, separate analyses of the particulate catch (if applicable) and the HCl and Cl_2 impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains. In that case, the particulate catch and the HCl and Cl_2 impinger catches from the individual trains may be combined, and a single particulate analysis and single HCl and Cl_2 analyses of the impinger contents may be performed.

3.3.1.7.5.12 At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, and record the final dry gas meter reading.

3.3.1.7.5.13 If there is any possibility that liquid has collected in the glass cyclone and/or on the filter, connect the Ascarite tube at the probe inlet and operate the train with the filter heating system at 120± 14 °C (248± 25 °F) at a low flow rate (e.g., H=1) sufficient to vaporize the liquid and any HCl in the cyclone or on the filter and pull it through the train into the impingers. After 30 minutes, turn off the flow, remove the Ascarite tube, and examine the cyclone and filter for any visible moisture. If moisture is visible, repeat this step for 15 minutes.

3.3.1.7.5.14 Conduct a post-test leak check. Also, leak-check the pitot lines as described in EPA method 2. The lines must pass this leak-check in order to validate the velocity-head data.

3.3.1.7.5.15 If the moisture value is available, calculate percent isokineticity (see section 3.3.1.7.7.10) to determine whether the run was valid or another test run should be conducted.

3.3.1.7.6 Sample Recovery.

3.3.1.7.6.1 Allow the probe to cool. When the probe can be handled safely, wipe off all the external surfaces of the tip of the probe nozzle and place a cap over the tip. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the holder.

3.3.1.7.6.2 Before moving the sampling train to the cleanup site, remove the probe, wipe off any silicone grease, and cap the open outlet, being careful not to lose any condensate that might be present. Wipe off any silicone grease and cap the filter or cyclone inlet. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger and the filter holder, disconnect it at the filter holder and let any condensed water drain into the first impinger. Wipe off any silicone grease and cap the filter holder outlet and the impinger inlet. Ground glass stoppers, plastic caps, serum caps, Teflon tape, Parafilm®, or aluminum foil may be used to close these openings.

3.3.1.7.6.3 Transfer the probe and filter/impinger assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss.

3.3.1.7.6.4 Save portions of all washing solutions used for cleanup (acetone and Type II water) and the absorbing reagents (0.1 N H_2SO_4 and 0.1 N NaOH) as blanks. Transfer 200 ml of each solution directly from the wash bottle being used (rinse solutions) or the supply container (absorbing reagents) and place each in a separate, prelabeled glass sample container.

3.3.1.7.6.5 Inspect the train prior to and during disassembly and note any abnormal conditions.

3.3.1.7.6.6 Container No. 1 (filter catch for particulate determination). Carefully remove the filter from the filter holder and place it in its identified Petri dish container. Use one or more pair of tweezers to handle the filter. If it is necessary to fold the filter, ensure that the particulate cake is inside the fold. Carefully transfer to the Petri dish any particulate matter or filter fibers that adhere to the filter holder gasket, using a dry nylon bristle brush or sharp-edged blade, or both. Label the container and seal with Teflon tape around the circumference of the lid.

3.3.1.7.6.7 Container No. 2 (front-half rinse for particulate determination). Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone into a glass container. Retain an acetone blank and analyze with the samples.

3.3.1.7.6.8 Perform rinses as follows: Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nylon bristle brush. Brush until the rinse shows no visible particles; then make a final rinse of the inside surface with the acetone. Brush and rinse the inside parts of the Swagelok fitting with the acetone in a similar way until no visible particles remain.

3.3.1.7.6.9 Have two people rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with solvent. Let the acetone drain from the lower end into the sample container. A glass funnel may be used to aid in transferring liquid washed to the container.

3.3.1.7.6.10 Follow the acetone rinse with a probe brush. Hold the probe in an inclined position and squirt acetone into the upper end while pushing the probe brush through the probe with a twisting action; place a sample container underneath the lower end of the probe and catch any acetone and particulate matter that is brushed from the probe. Run the brush through the probe three or more times until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above. Between sampling runs, keep brushes clean and protected from contamination.

3.3.1.7.6.11 Clean the inside of the front half of the filter holder and cyclone by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. Rinse each surface three times, or more if needed, to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone and cyclone flask (if applicable). Brush and rinse any particulate material adhering to the inner surfaces of these components into the front-half rinse sample. After all rinses and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents.

3.3.1.7.6.12 Container No. 3 (knockout and acid impinger catch for moisture and HCl determination). Disconnect the impingers. Measure the liquid in the acid and knockout impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these impingers, connecting glassware (and tubing, if used); and the back half of the filter holder with water and add these rinses to the storage container. Seal the container, shake to mix, and label. The fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Retain rinse water

and acidic absorbing solution blanks and analyze with the samples.

3.3.1.7.6.13 Container No. 4 (alkaline impinger catch for Cl_2 and moisture determination). Measure and record the liquid in the alkaline impingers as described in section 3.3.1.7.6.12. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these two impingers and connecting glassware with water and add these rinses to the container. Seal the container, shake to mix, and label; mark the fluid level. Retain alkaline absorbing solution blank and analyze with the samples.

3.3.1.7.6.14 Container No. 5 (silica gel for moisture determination). Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the last impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere strongly to the impinger wall. Because the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the container and its contents to 0.5 g or better.

3.3.1.7.6.15 Prior to shipment, recheck all sample containers to ensure that the caps are well secured. Seal the lids of all containers around the circumference with Teflon tape. Ship all liquid samples upright and all particulate filters with the particulate catch facing upward.

3.3.1.7.7 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

3.3.1.7.7.1 Nomenclature.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_a = Acetone blank residue concentration, mg/mg.

C_d = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.

C_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).

I = Percent of isokinetic sampling.

m_a = Mass of residue of acetone after evaporation, mg.

M_n = Total amount of particulate matter collected, mg.

M_d = Stack-gas dry molecular weight, g/g-mole (lb/lb-mole).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack-gas pressure, ms Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3 (K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry-gas meter temperature (see Figure 2), °K (°R).

T_s = Absolute average stack-gas temperature (see Figure 2), °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_{lc} = Total volume of liquid collected in the impingers and silica gel, ml.

V_m = Volume of gas sample is measured by dry-gas meter, dscm (dscf).

$V_{m(std)}$ = Volume of gas sample measured by the dry-gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

V_s = Stack-gas velocity, calculated by Method 2, Equation 2–9, using data obtained from Method 5, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.

V_a = Volume of acetone blank, ml.

V_{aw} = Volume of acetone used in wash; ml.

Y = Dry-gas-meter calibration factor, dimensionless.

ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).

ρ_a = Density of acetone, mg/μl (see label on bottle).

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

3.3.1.7.7.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 3.3-2).

3.3.1.7.7.3 Dry gas volume. Correct the sample measured by the dry gas meter to standard conditions (20 °C, 760 mm Hg [68 °F, 29.92 in. Hg]) by using Equation 1:

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{P_{bar} + \Delta H/13.6}{P_{std}}$$

$$= K_1 V_m Y \frac{P_{bar} = \Delta H/13.6}{T_m} \quad (1)$$

where:

K_1 = 0.3858 K/mm Hg for metric units, or
K_1 = 17.64 °R/in. Hg for English units.

3.3.1.7.7.4 Volume of water vapor.

$$V_{w(std)} = V_{lc} \frac{P_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{lc} \quad (2)$$

where:

K_2 = 0.001333 m^3/ml for metric units, or
K_2 = 0.04707 m^3/ml for English units.

3.3.1.7.7.5 Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \quad (3)$$

Note: In saturated or water-droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 3) and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure

for determining the moisture content based upon assumption of saturated conditions is given in the Note to section 1.2 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ± 1 °C (2 °F).

3.3.1.7.7.6 Acetone blank concentration. For particulate determination.

$$C_a = \frac{m_a}{V_a \rho_a} \quad (4)$$

3.3.1.7.7.7 Acetone wash blank. For particulate determination.

$$W_a = C_a V_{aw} \Delta_a \quad (5)$$

3.3.1.7.7.8 Total particulate weight. Determine the total particulate catch from the sum of the weights obtained from Container Nos. 1 and 2 less the acetone blank (W_a).

3.3.1.7.7.9 Particulate concentration.

$$c_s = (0.001 \text{ g/mg})(m_n/V_{m(std)}) \quad (6)$$

3.3.1.7.7.10 Isokinetic variation.
3.3.1.7.7.10.1 Calculation from raw data.

$$I = \frac{100 \, T_s [K_3 P_{lc} + (V_m/T_m)(P_{bar} + H/13.6)]}{60 \, \theta \, V_s P_s A_n} \quad (7)$$

where:

K_3 = 0.003454 mm Hg-m^3/ml-K for metric units, or
K_3 = 0.002669 in. Hg-ft^3/ml °R for English units.

3.3.1.7.7.10.2 Calculation for intermediate values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} V_s \theta A_n P_s 60(1 - B_{ws})}$$

$$= K_4 \frac{T_s V_{m(std)}}{P_s V_s A_n \, \theta (1 - B_{ws})} \quad (8)$$

where:

K_4 = 4.320 for metric units, or
K_4 = 0.09450 for English units.

3.3.1.7.7.10.3 Acceptable units. If 90 percent < I < 110 percent, the results are acceptable. If the results are low in comparison with the standard and I is beyond the acceptable range, or if I is less than 90 percent, the Administrator may opt to accept the results.

3.3.1.8 Quality Control.

3.3.1.8.1 Sampling. See EPA Manual 600/4–77–027b for Method 5 quality control.

3.3.1.8.2 Analysis. At the present time, a validated audit material does not exist for this method. Analytical quality control procedures are detailed in Method 9057.

3.3.1.9 Method Performance.

3.3.1.9.1 The in-stack detection limit for the method is approximately 0.02 μg of HCl per liter of stack gas. The method has a negative bias below 20 ppm HCl (Reference 6).

3.3.1.9.2 It is preferable to include the cyclone in the sampling train to protect the filter from any moisture present. There is research in progress regarding the necessity of the cyclone at low moisture sources and the use of Ascarite II in the drying procedure (Section 3.3.1.7.5.12).

References

1. U.S. Environmental Protection Agency, 40 CFR part 60, appendix A, Methods 1–5.
2. U.S. Environmental Protection Agency, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods," Publication No. EPA–600/4–77–027b, August 1977.
3. Shigehara, R.T., Adjustments in the EPA Nomography for Different Pitot Tube Coefficients and Dry Molecular Weights, Stack Sampling News, 2:4–11 (October 1974).
4. Steinsberger, S.C. and J.H. Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U.S. Environmental Protection Agency, Office of Research and Development, Report No. EPA 600/3–89/064, NTIS PB89 220586–AS.
5. State of California, Air Resources Board, method 421, "Determination of Hydrochloric Acid emissions from Stationary Sources," March 18, 1987.
6. Entropy Environmentalists, Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride Emissions from Stationary Sources: Interim Report," EPA Contract No. 68–02–4442, Research Triangle Park, North Carolina, January 22, 1988.

3.3.2 *Midget Impinger HCl/Cl₂ Emission Sampling Train (Method 0051)*

3.3.2.1 Scope and Application.

3.3.2.1.1 This method describes the collection of hydrogen chloride (HCl, CAS Registry Number 7647–01–0) and chlorine (Cl₂, CAS Registry Number 7782–50–5) in stack gas emission samples from hazardous waste incinerators, municipal waste combustors, and boilers and industrial furnaces. The collected samples are analyzed using method 9057. This method is designed to collect HCl/Cl₂ in their gaseous forms. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter (e.g., HCl dissolved in water droplets) must be sampled using an isokinetic HCl/Cl₂ sampling train (see Method 0050).

3.3.2.2 Summary of Method.

3.3.2.2.1 An integrated gas sample is extracted from the stack and passes through a particulate filter, acidified water, and finally through an alkaline solution. The filter serves to remove particulate matter such as chloride salts which could potentially react and form analyte in the absorbing solutions. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride ions (Cl^-) as follows:

$$HCl + H_2O = H_3O^+ + Cl^-$$

The Cl₂ gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H^+), Cl^-, and hypochlorous acid (HClO) as follows:

$$H_2O + Cl_2 = H^+ + Cl^- + HClO$$
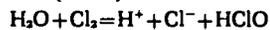
The Cl^- ions in the separate solutions are measured by ion chromatography (Method 9057).

3.3.2.3 Interferences.

3.3.2.3.1 Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferant for HCl is diatomic chlorine (Cl₂) gas which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water. Cl₂ gas exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present. Sampling a 400 ppm HCl gas stream containing 50 ppm Cl₂ with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl₂ results in a positive bias of 3.4 percent in the HCl measurement.

3.3.2.3.2 Reducing agents such as SO₂ may cause a positive bias in the Cl₂ measurement by the following reaction:

$$HClO + HSO_3^- = H_2SO_4 + Cl^-$$
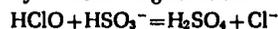
3.3.2.4 Apparatus and Materials.

3.3.2.4.1 Sampling Train. The sampling train is shown in Figure 1 and component parts are discussed below.

3.3.2.4.1.1 Probe. Borosilicate glass, approximately ⅜-in (9-mm) inside diameter, with a heating system to prevent condensation. When the concentration of alkaline particulate matter in the emissions is high, a ⅜-in (9-mm) inside diameter Teflon elbow should be attached to the inlet of the probe; a 1-in (25-mm) length of Teflon tubing with a ⅜-in (9-mm) inside diameter should be attached at the open end of the elbow to permit the opening of the probe to be burned away from the gas stream, thus reducing the amount of particulate entering the train. When high concentrations of particulate matter are not present, the Teflon elbow is not necessary, and the probe inlet can be perpendicular to the gas stream. When sampling at locations where gas temperatures are greater than approximately 400 °F, such as wet scrubber inlets, glass or quartz elbows must be used. In no case should a glass wool plug be used to remove particulate matter; use of such a filtering device could result in a bias in the data.(1) Instead, a Teflon filter should be used as specified in section 3.3.2.5.5:

3.3.2.4.1.2 Three-way stopcock. A borosilicate, three-way glass stopcock with a heating system to prevent condensation. The heated stopcock should connect directly to the outlet of the probe and filter assembly and the inlet of the first impinger. The heating system should be capable of preventing condensation up to the inlet of the first impinger. Silicone grease may be used, if necessary, to prevent leakage.

3.3.2.4.1.3 Impingers. Five 30-ml midget impingers with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. For sampling at high moisture sources or for extended sampling times greater than one hour, a midget impinger with a shortened stem (such that the gas sample does not bubble through the collected condensate) should be used in front of the first impinger.

3.3.2.4.1.4 Mae West impinger or drying tube. Mae West design impinger (or drying tube, if a moisture determination is not to be conducted) filled with silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump.

3.3.2.4.1.5 Sample Line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

3.3.2.4.1.6 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for the elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

3.3.2.4.1.7 Purge pump, purge line, drying tube, needle valve, and rate meter. Pump capable of purging sample probe at 2 liters/min, with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter, 0 to 5 liters/min.

3.3.2.4.1.8 Metering system. The following items comprise the metering system which is identical to that used for EPA Method 6 (see Reference 5).

3.3.2.4.1.8.1 Valve. Needle valve, to regulate sample gas flow rate.

3.3.2.4.1.8.2 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through train. Install a small surge tank between the pump and the rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

3.3.2.4.1.8.3 Rate meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of selected flow rate of 2 liters/min.

3.3.2.4.1.8.4 Volume meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions encountered during sampling, and equipped with a temperature gauge (dial thermometer or equivalent) capable of measuring temperature to within 3 °C (5.4 °F).

3.3.2.4.1.8.5 Vacuum gauge. At least 760 mm Hg (30 in. Hg) gauge to be used for leak check of the sampling train.

3.3.2.4.2 Sample Recovery.

3.3.2.4.2.1 Wash bottles. Polyethylene or glass, 500 ml or larger, two.

3.3.2.4.2.2 Storage bottles. Glass, with Teflon-lined lids, 100 ml, to store impinger samples (two per sampling run).

3.3.2.5 Reagents.

3.3.2 5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit

its use without lessening the accuracy of the determination.

3.3.2.5.2 ASTM Type II Water (ASTM D1193–77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified. It is advisable to analyze a blank sample of this reagent *prior* to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see method 9057).

3.3.2.5.3 Sulfuric acid (0.1 N), H_2SO_4. Used as the HCl absorbing reagent. To prepare 100 ml, slowly add 0.28 ml of concentrated H_2SO_4 to about 90 ml of water while stirring, and adjust the final volume to 100 ml using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent *prior* to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see method 9057).

3.3.2.5.4 Sodium hydroxide (0.1 N), NaOH. Used as the Cl_2 absorbing reagent. To prepare 100 ml, dissolve 0.40 g of solid NaOH in about 90 ml of water and adjust the final volume to 100 ml using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent *prior* to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see method 9057).

3.3.2.5.5 Filter. Teflon mat Pallflex® TX40HI75 or equivalent. Locate in a glass, quartz, or Teflon filter holder with a Teflon filter support in a filter box heated to 250 °F.

3.3.2.5.6 Stopcock grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

3.3.2.5.7 Silica gel. Indicating type, 6- to 16-mesh. If the silica gel has been used previously, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

3.3.2.6 Sample Collection, Preservation, and Handling.

3.3.2.6.1 Sample collection is described in this method. The analytical procedures are described in method 9057.

3.3.2.6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

3.3.2.7 Procedure.

3.3.2.7.1 Calibration. Section 3.5.2 of EPA's Quality Assurance Handbook, Volume III (Reference 4) may be used as a guide for these operations.

3.3.2.7.1.1 Dry Gas Metering System.

3.3.2.7.1.1.1 Initial calibration. Before its initial use in the field, first leak check the metering system (sample line, drying tube, if used, vacuum gauge, needle valve, pump, rate meter, and dry gas meter) as follows: plug the inlet end of the sampling line, pull a vacuum of 250 mm (10 in) Hg, plug off the outlet of the dry gas meter, and turn off the pump. The vacuum should remain stable for 30 seconds. Carefully release the vacuum from the system by slowly removing the plug from the sample line inlet. Remove the sampling line (and drying tube, if applicable), and connect the dry gas metering system to an appropriately sized wet test meter (e.g., 1 liter per revolution). Make three independent calibration runs, using at least five revolutions of the dry gas meter per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the dry gas meter volume, with both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y value deviates by more than 2 percent from the average, the metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

3.3.2.7.1.1.2 Post-test calibration check. After each field test series, conduct a calibration check as in section 3.3.2.7.1.1.1 above, except for the following variations: (a) The leak check is not to be conducted, (b) three or more revolutions of the dry gas meter may be used, (c) only two independent runs need to be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in section 3.3.2.7.1.1.1), the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as section 3.3.2.7.1.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

3.3.2.7.1.2 Thermometer(s). Prior to each field test, calibrate against mercury-in-glass thermometers at ambient temperature. If the thermometer being calibrated reads within 2 °C (2.6 °F) of the mercury-in-glass thermometer, it is acceptable. If not, adjust the thermometer or use an appropriate correction factor.

3.3.2.7.1.3 Rate meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

3.3.2.7.1.4 Barometer. Prior to each field test, calibrate against a mercury barometer. The field barometer should agree within 0.1 in. Hg with the mercury barometer. If it does not, the field barometer should be adjusted.

3.3.2.7.2 Sampling.

3.3.2.7.2.1 Preparation of collection train. Prepare the sampling train as follows: The first or knockout impinger should have a shortened stem and be left empty to condense moisture in the gas stream. The next two midget impingers should each be filled with 15 ml of 0.1 N H_2SO_4, and the fourth and fifth impingers should each be filled with 15 ml of 0.1 N NaOH. Place a fresh charge of silica gel, or equivalent, in the Mae West impinger (or the drying tube). Connect the impingers in series with the knockout impinger first, followed by the two impingers containing the acidified reagent, the two impingers containing the alkaline reagent, and the Mae West impinger containing the silica gel. If the moisture will be determined, weigh the impinger assembly to the nearest ±0.5 g and record the weight.

3.3.2.7.2.2 Leak check procedures. Leak check the probe and three-way stopcock prior to inserting the probe into the stack. Connect the stopcock to the outlet of the probe, and connect the sample line to the needle valve. Plug the probe inlet, turn on the sample pump, and pull a vacuum of at least 250 mm Hg (10 in. Hg). Turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Place the probe in the stack at the sampling location, and adjust the filter heating system to 250 °F and the probe and stopcock heating systems to a temperature sufficient to prevent water condensation. Connect the first impinger to the stopcock, and connect the sample line to the last impinger and the needle valve. Upon completion of a sampling run, remove the probe from the stack and leak check as described above. If a leak has occurred, the sampling run must be voided. Alternatively, the portion of the train behind the probe may be leak checked between multiple runs at the same site as follows: Close the stopcock to the first impinger (see Figure 3.3–3A), and turn on the sample pump. Pull a vacuum of at least 250 mm Hg (10 in. Hg), turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Release the vacuum on the impinger train by turning the stopcock to the vent position to permit ambient air to enter (see Figure 3.3–3B). If this procedure is used, the full train leak check described above must be conducted following the final run and all preceding sampling runs voided if a leak has occurred.

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Federal Register / Vol. 56, No. 137 / Wednesday, July 17, 1991 / Rules and Regulations   **32739**
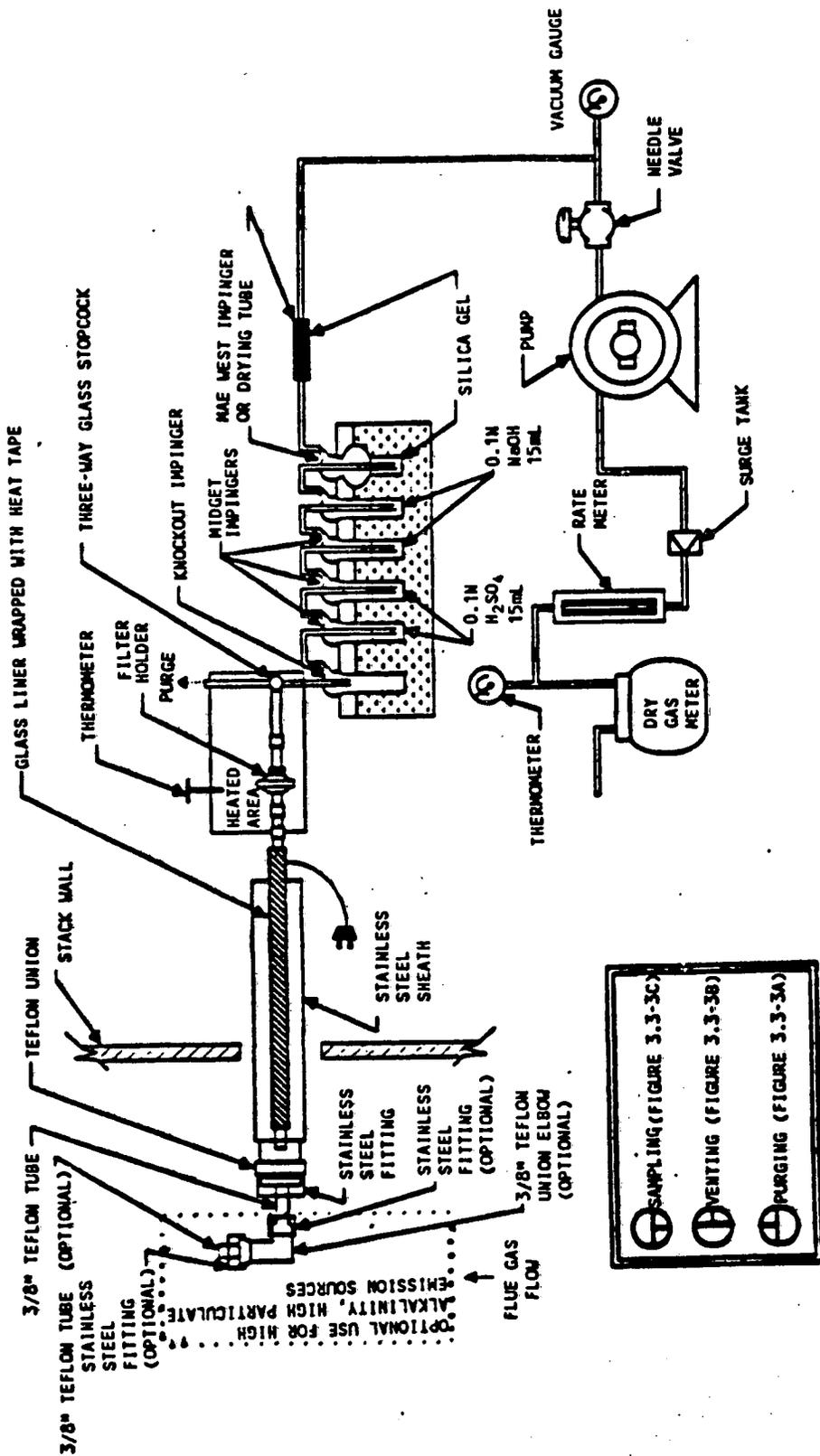
Figure 3.3-3 Midget Impinger HCl/Cl$_2$ Sampling Train

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3.3.2.7.2.3 Purge procedure. Immediately prior to sampling, connect the purge line to the stopcock and turn the stopcock to permit the purge pump to purge the probe (see Figure 3.3–3A). Turn on the purge pump, and adjust the purge rate to 2 liters/min. Purge for at least 5 minutes prior to sampling.

3.3.2.7.2.4 Sample collection. Turn on sample pump, pull a slight vacuum of approximately 25 mm Hg (1 in. Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure 3.3–3C). Adjust the sampling rate to 2 liters/min, as indicated by the rate meter, and maintain this rate within 10 percent during the entire sampling run. Take readings of the dry gas meter, the dry gas meter temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of one hour is recommended. However, if the expected condensate catch for this sampling run duration will exceed the capacity of the sampling train, (1) a larger knockout impinger may be used or (2) two sequential half-hour runs may be conducted. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak check as described in section 3.3.2.7.2.2.

3.3.2.7.3 Sample recovery. Following sampling, disconnect the impinger train from the remaining sampling equipment at the inlet to the knockout impinger and the outlet to the last impinger. If performing a moisture determination, wipe off any moisture on the outside of the train and any excess silicone grease at the inlet and outlet openings; weigh the train to the nearest 0.5 g and record this weight. Then disconnect the impingers from each other. Quantitatively transfer the contents of the first three impingers (the knockout impinger and the two 0.1 N H$_2$SO$_4$ impingers) to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware from the second set of impingers (containing the 0.1 N NaOH) should be recovered in a similar manner if a Cl$_2$ analysis is desired. The sample bottle should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Save portions of the 0.1 N H$_2$SO$_4$ and 0.1 N NaOH used as impinger reagents as reagent blanks. Take 50 ml of each and place in separate leak-free storage bottles. Label and mark the fluid levels as previously described.

3.3.2.7.4 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

3.3.2.7.4.1 Nomenclature.

B_{ws} = Water vapor in the gas stream, proportion by volume.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/°K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Average dry gas meter absolute temperature, °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_{lc} = Total volume of liquid collected in impingers and silica gel, ml (equivalent to the difference in weight of the impinger train before and after sampling, 1 mg = 1 ml).

V_m = Dry gas volume as measured by the dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

Y = Dry gas meter calibration factor.

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

3.3.2.7.4.2 Sample volume, dry basis, corrected to standard conditions. Calculate as described below:

$$V_{m(std)} = V_m Y \left[\frac{T_{std}}{T_m} \right]\left[\frac{P_{bar}}{P_{std}} \right]$$

$$= K_1 Y \frac{V_m P_{bar}}{T_m} \tag{1}$$

where:

K_1 = 0.3858 °K/mm Hg for metric units.
K_1 = 17.64 °R/in. Hg for English units.

3.3.2.7.4.3 Volume of water vapor.

$$V_{w(std)} = V_{lc} \frac{P_w}{M_w} \frac{RT_{std}}{P_{std}}$$

$$= K_2 V_{lc} \tag{2}$$

where:

K_2 = 0.0013333 m^3/ml for metric units.
K_2 = 0.04707 ft^3/ml for English units.

3.3.2.7.4.4 Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \tag{3}$$

3.3.2.8 Quality Control.
3.3.2.8.1 At the present time, a validated audit material does not exist for this method. Analytical quality control procedures are detailed in Method 9057.

3.3.2.9 Method Performance.
3.3.2.9.1 The in-stack detection limit for the method is approximately 0.08 µg of HCl per liter of stack gas for a 1-hour sample.
3.3.2.9.2 The precision and bias for measurement of HCl using this sampling protocol combined with the analytical protocol of method 9057 have been determined. The within laboratory relative standard deviation is 6.2 percent and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit any bias for HCl when sampling at Cl$_2$ concentrations less than 50 ppm.

References

1. Steinsberger, S.C. and J.H. Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U.S. Environmental Protection Agency, Office of Research and Development, Report No. EPA 600/3– 89/064, NTIS PB 89 220586–AS.

2. State of California, Air Resources Board, Method 421, "Determination of Hydrochloric Acid Emissions from Stationary Sources," March 18, 1987.

3. Entropy Environmentalists, Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride Emissions from Stationary Sources: Interim Report," EPA Contract No. 68–02–4442, Research Triangle Park, North Carolina, January 22, 1988.

4. U.S. Environmental Protection Agency, "Quality Assurance Handbook for Air Pollution Measurement Systems, volume III, Stationary Source Specific Methods," Publication No. EPA–600/4–77–027b, August 1977.

5. U.S. Environmental Protection Agency, 40 CFR part 60, appendix A, method 6.

3.3.3 *Protocol for Analysis of Samples from HCl/Cl$_2$ Emission Sampling Train (Method 9057)*

3.3.3.1 Scope and Application.
3.3.3.1.1 This method describes the analytical protocol for determination of hydrogen chloride (HCl, CAS Registry Number 7647–01–0) and chloride (Cl$_2$, CAS Registry Number 7782–50–5) in stack gas emission samples collected from hazardous waste and municipal waste incinerators using the midget impinger HCl/Cl$_2$ sampling train (method 0051) or the isokinetic HCl/Cl$_2$ sampling train (method 0050).

3.3.3.1.2 The lower detection limit is 0.1 µg of chloride (Cl$^-$) per ml of sample solution. Samples with concentrations which exceed the linear range of the analytical instrumentation may be diluted.

3.3.3.1.3 This method is recommended for use only by analysts experienced in the use of ion chromatography and in the interpretation of ion chromatograms.

3.3.3.2 Summary of Method.
3.3.3.2.1 The stoichiometry of HCl and Cl$_2$ collection in the sampling train (see methods 0050 and 0051) is as follows: In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride ions (Cl$^-$) according to the following formula:
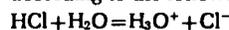
$HCl + H_2O = H_3O^+ + Cl^-$

The Cl$_2$ gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H$^+$), Cl$^-$, and hypochlorous acid (HClO) as shown:

$H_2O + Cl_2 = H^+ + Cl^- + HClO$
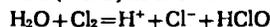
Non-suppressed or suppressed ion chromatography (IC) is used for analysis of the Cl$^-$.

3.3.3.3 Interferences.
3.3.3.3.1 Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One likely interferant is diatomic chlorine (Cl$_2$) gas which disproportionates to HCl and hypochlorous acid (HOCl) upon dissolution in water. Cl$_2$ gas

exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present. Sampling a 400 ppm HCl gas stream containing 50 ppm Cl_2 with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl_2 results in a positive bias of 3.4 percent in the HCl measurement. Other interferants have not been encountered.

3.3.3.3.2 Reducing agents such as SO_2 may cause a positive bias in the Cl_2 measurement by the following reaction:

$$HClO + HSO_3^- = H_2SO_4 + Cl^-$$
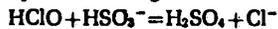
3.3.3.4 Apparatus and Materials.

3.3.3.4.1 Volumetric Flasks. Class A, various sizes.

3.3.3.4.2 Volumetric Pipettes. Class A, assortment, to dilute samples to calibration range of the IC.

3.3.3.4.3 Ion Chromatograph. Suppressed or non-suppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, a strip chart recorder, and peak heights may be used provided the 5 percent repeatability criteria for sample analysis and the linearity criteria for the calibration curve can be met.

3.3.3.5 Reagents.

3.3.3.5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

3.3.3.5.2 ASTM Type II Water (ASTM D1193–77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

3.3.3.5.3 Sulfuric acid (0.1 N), H_2SO_4. To prepare 100 ml, slowly add 0.28 ml of concentrated H_2SO_4 to about 90 ml of water while stirring, and adjust the final volume to 100 ml using additional water. Shake well to mix the solution.

3.3.3.5.4 Sodium hydroxide (0.1 N), NaOH. To prepare 100 ml, dissolve 0.40 g of solid NaOH in about 90 ml of water and adjust the final volume to 100 ml using additional water. Shake well to mix the solution.

3.3.3.5.5 Reagent blank solutions. A separate blank solution of each sampling train reagent used and collected in the field (0.1 N H_2SO_4 and 0.1 N NaOH) should be prepared for analysis with the field samples. For midget impinger train sample analysis, dilute 30 ml of each reagent with rinse water collected in the field as a blank to the final volume of the samples; for isokinetic train sample analysis, dilute 200 ml to the same final volume as the field samples also using the blank sample of rinse water.

3.3.3.5.6 Sodium chloride, NaCl, stock standard solution. Solutions containing a nominal certified concentration of 1000 mg/L NaCl are commercially available as convenient stock solutions from which working standards can be made by appropriate volumetric dilution. Alternately,

concentrated stock solutions may be produced from reagent grade NaCl that has been dried at 110 °C for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. The exact Cl^- concentration can be calculated using the equation:

$$\mu g\ Cl^-/ml = g\ of\ NaCl \times 10^3 \times 35.453/58.44$$

Refrigerate the stock standard solutions and store no longer than one month.

3.3.3.5.7 Chromatographic eluent. Effective eluents for non-suppressed ion chromatography using a resin- or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution, adjusted to a pH of 4.0 using a saturated sodium borate solution, and a mM 4-hydroxy benzoate solution, adjusted to a pH of 8.6 using 1 N sodium hydroxide. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH that contain no ions interfering with the chromatographic analysis may be used. If, using suppressed ion chromatography, the "water dip" resulting from sample injection is interfering with the chlorine peak, use a 2 mM sodium hydroxide/2.4 mM sodium bicarbonate eluent.

3.3.3.6 Sample Collection, Preservation, and Handling.

3.3.3.6.1 Sample collection using the midget impinger HCl/Cl_2 train or the isokinetic HCl/Cl_2 train is described in Method 0051 or 0050, respectively.

3.3.3.6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

3.3.3.7 Procedure.

3.3.3.7.1 Sample preparation for analysis. Check the liquid level in each sample, and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume can be determined from the difference between the initial and final solution levels, and this value can be used to correct the analytical results. For midget impinger train samples, quantitatively transfer each sample solution to a 100 ml volumetric flask and dilute to 100 ml with water. For isokinetic sampling train samples, quantitatively transfer each sample to a volumetric flask or graduated cylinder and dilute with water to a final volume appropriate for all samples.

3.3.3.7.2 Calibration of Ion Chromatograph.

3.3.3.7.2.1 The ion chromatographic conditions will depend on the type of analytical column used and whether suppressed or non-suppressed ion chromatography is used. Prior to calibration and sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^- appears in the chromatogram. If Cl^- is present, repeat the load/injection procedure until no Cl^- is present.

3.3.3.7.2.2 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solution to

convenient volumes, using 0.1 H_2SO_4 or 0.1 NaOH as appropriate. Prepare at least four standards that are within the linear range of the field samples. Inject the calibration standards, starting with the lowest concentration standard first, both before and after injection of the quality control check sample, reagent blank, and field samples. This allows compensation for any instrument drift occurring during sample analysis.

3.3.3.7.2.3 Determine the peak areas, or heights, of the standards and plot individual values versus Cl^- concentrations in $\mu g/ml$. Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

3.3.3.7.3 Sample analysis. Between injections of the series of calibration standards, inject in duplicate the reagent blanks and the field samples, including a matrix spike sample. Measure the areas or heights (same as done for the calibration standards) of the Cl^- peaks. Use the average response to determine the concentrations of the field samples, matrix spike, and reagent blanks using the linear calibration curve. The results for a reagent blank should not exceed 10 percent of the corresponding value for a field sample.

3.3.3.7.4 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

3.3.3.7.4.1 Total μg HCl per sample. Calculate as described below:

$$^mHCl = (S - B) \times V_s \times 36.46/35.453 \tag{1}$$

where:

^mHCl = Mass of HCl in sample, μg,

S = Analysis of sample, $\mu g\ Cl^-/ml$,

B = Analysis of reagent blank, $\mu g\ Cl^-/ml$,

V_s = Volume of filtered and diluted sample, ml,

36.46 = Molecular weight of HCl, $\mu g/\mu g$-mole, and

35.45 = Atomic weight of Cl^-, $\mu g/\mu g$-mole.

3.3.3.7.4.2 Total $\mu g\ Cl_2$ per sample. Calculate as described below:

$$^MCl_2 = (S - B) \times V_2 \times 70.91/35.45 \tag{2}$$

where:

$^MCl_2$ = Mass of Cl_2 in sample, μg,

70.91 = Molecular weight of Cl_2, $\mu g/\mu g$-mole, and

35.45 = Atomic weight of Cl^-, $\mu g/\mu g$-mole.

3.3.3.7.4.3 Concentration of HCl in the flue gas. Calculate as described below:

$$C = K \times m/V_{m(std)} \tag{3}$$

where:

C = Concentration of HCl or Cl_2, dry basis, mg/dscm,

K = 10^{-3} mg/μg,

m = Mass of HCl or Cl_2 in sample, μg, and

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (from Method 0050 or Method 0051).

3.3.3.8 Quality Control.

3.3.3.8.1 At the present time, a validated audit material does not exist for this method. However, it is strongly recommended that a quality control check sample and a matrix spike sample be used.

3.3.3.8.1.1 Quality control check sample. Chloride solutions of reliably known

concentrations are available for purchase from the National Bureau of Standards (SRM 3182). The QC check sample should be prepared in the appropriate absorbing reagent at a concentration approximately equal to the mid range calibration standard. The quality control check sample should be injected in duplicate immediately after the calibration standards have been injected for the first time. The Cl⁻ value obtained for the check sample using the final calibration curve should be within 10 percent of the known value for the check sample.

3.3.3.8.1.2 Matrix spike sample. A portion of at least one field sample should be used to prepare a matrix spike sample. Spike the sample aliquot in the range of the expected concentration. Analyze the matrix spike sample in duplicate along with the field samples. Based on the matrix spike results, determine the recovery for the spiked material. This should be within 10 percent of the known spike value.

3.3.3.9 Method Performance.

3.3.3.9.1 The lower detection limit of the analytical method is 0.1 μg of Cl⁻ per ml of sample solution. Samples with concentrations which exceed the linear range of the IC may be diluted.

3.3.3.9.2 The precision and bias for analysis of HCl using this analytical protocol have been measured in combination with the midget impinger HCl/Cl₂ train (method 0051) for sample collection. The within-laboratory relative standard deviation is 6.2 percent and 3.2 percent at HCl concentrations of 3.9 and

15.3 ppm, respectively. The method does not exhibit any bias for HCl when sampling at Cl₂ concentrations less than 50 ppm.

References

1. Steinsberger, S.C. and J.H. Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U.S. Environmental Protection Agency, Office of Research and Development, Report No. EPA 600/3–89/064, NTIS PB89 220586–AS.
2. State of California, Air Resources Board, Method 421, "Determination of Hydrochloric Acid Emissions from Stationary Sources" March 18, 1987.
3. Entropy Environmentalists, Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride emissions from Stationary Sources: Interim Report," EPA Contract No. 68–02–4442, Research Triangle Park, North Carolina, January 22, 1988.

3.4 *Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) From Stationary Sources (Method 23)*

3.4.1 *Applicability and Principle*

3.4.1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from stationary sources.

3.4.1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDDs and PCDFs are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

3.4.2 *Apparatus*

3.4.2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 3.4–1. Sealing greases may not be used in assembling the train. The train is identical to that described in Section 2.1 of Method 5 (40 CFR part 60, appendix A) with the following additions:

3.4.2.1.1 Reagents. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

3.4.2.1.2 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

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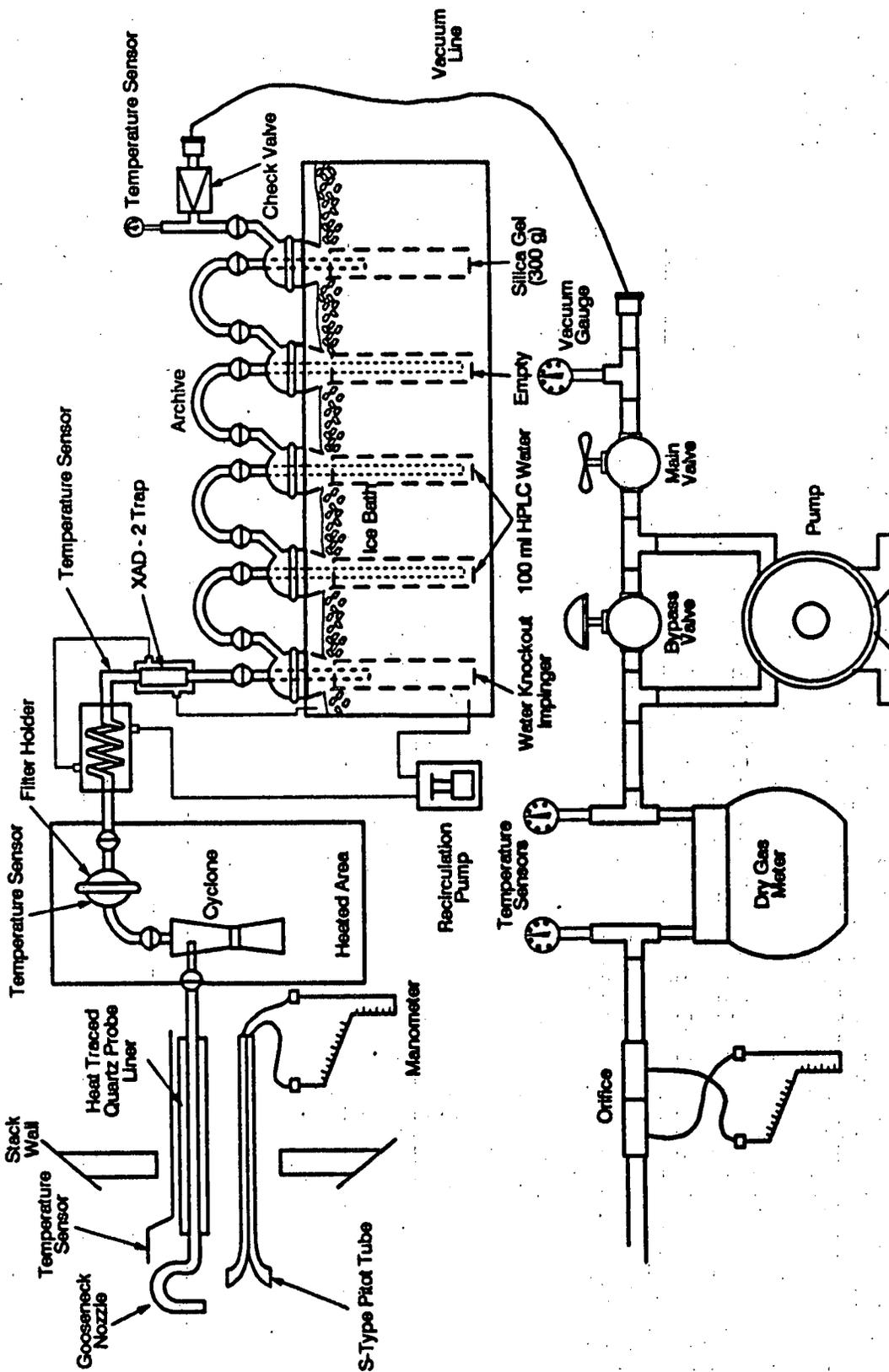
Figure 3.4-1 Sampling Train

3.4.2.1.3 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat-traced, heavy walled TFE (½ in. OD with ⅛ in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

3.4.2.1.4 Filter Support. Teflon or Teflon-coated wire.

3.4.2.1.5 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 3.4–2.

3.4.2.1.6 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

3.4.2.1.7 Adsorbent Module. Glass container to hold the solid adsorbent. A schematic diagram is shown in Figure 3.4–2. Other physical configurations of the resin

trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.
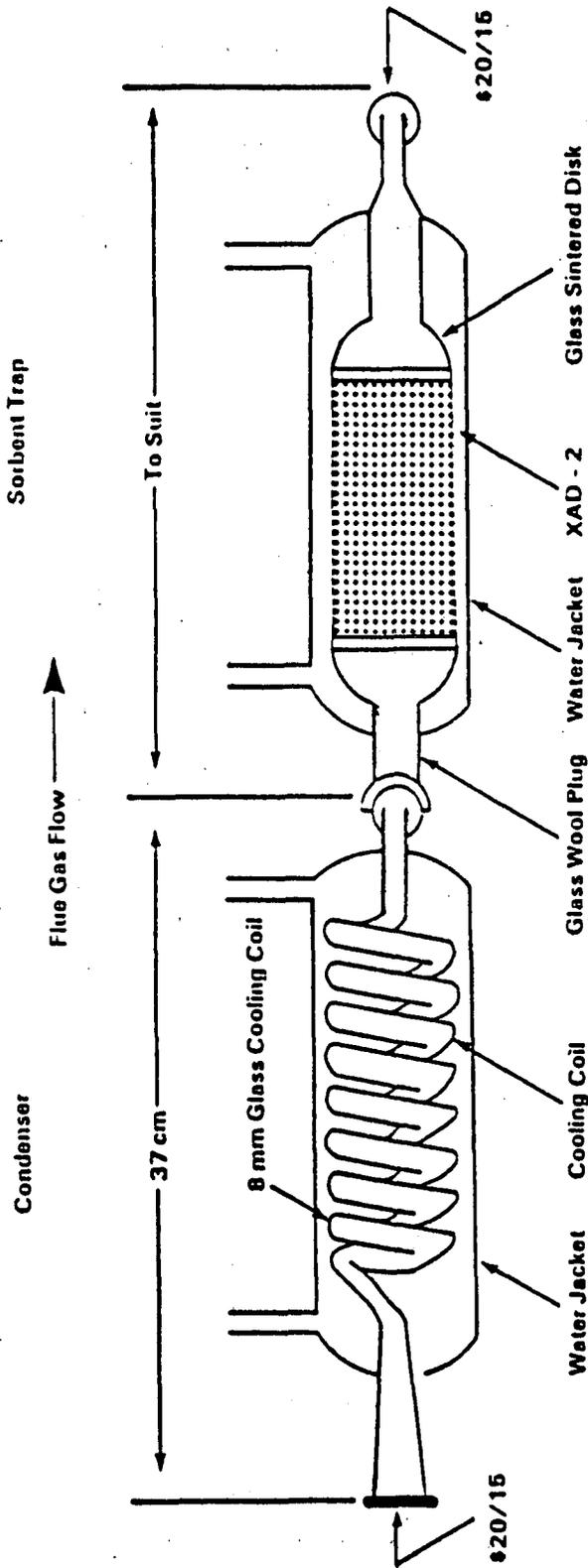
Figure 3.4-2 Condenser and adsorbent trap

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3.4.2.2   Sample Recovery.

3.4.2.2.1   Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 3.4.2.2.6) to cap off the sample-exposed sections of the train.

3.4.2.2.2   Wash Bottles. Teflon, 500-ml.

3.4.2.2.3   Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

3.4.2.2.4   Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

3.4.2.2.5   Balance. Triple beam.

3.4.2.2.6   Aluminum Foil. Heavy duty, hexane-rinsed.

3.4.2.2.7   Metal Storage Container. Air-tight container to store silica gel.

3.4.2.2.8   Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

3.4.2.2.9   Glass sample Storage container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak-free Teflon-lined caps.

3.4.2.3   Analysis.

3.4.2.3.1   Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

3.4.2.3.2   Test Tube. Glass.

3.4.2.3.3   Soxhlet Extraction Apparatus. Capable of holding 43 × 123 mm extraction thimbles.

3.4.2.3.4   Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

3.4.2.3.5   Pasteur Pipettes. For preparing liquid chromatographic columns.

3.4.2.3.6   Reacti-vials. Amber glass, 2-ml, silanized prior to use.

3.4.2.3.7   Rotary Evaporator. Buchi/Brinkman RF–121 or equivalent.

3.4.2.3.8   Nitrogen Evaporator Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

3.4.2.3.9   Separatory Funnels. Glass, 2-liter.

3.4.2.3.10   Gas Chromatograph. Consisting of the following components:

3.4.2.3.10.1   Oven. Capable of maintaining the separation column at the proper operating temperature ±1 °C and performing programmed increases in temperature at rates of at least 3 °C/min.

3.4.2.3.10.2   Temperature Gauge. To monitor column, oven, detector, and exhaust temperatures ±1 °C.

3.4.2.3.10.3   Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

3.4.2.3.10.4   Capillary Columns. A fused silica column, 60 × 0.25 mm inside diameter (ID), coated with DB.5 and a fused silica column, 30 m × 0.25 mm ID coated with DB–225. Other similar systems may be used provided that the user is able to demonstrate, using calibration and performance checks, that the column system is able to meet the specifications of section 3.4.6.1.2.2.

3.4.2.3.11   Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

3.4.2.3.12   Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

3.4.2.3.13   Analytical Balance. To measure within 0.1 mg.

3.4.3   *Reagents*

3.4.3.1   Sampling.

3.4.3.1.1   Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986–71 (Reapproved 1978) (incorporated by reference—see § 60.17).

3.4.3.1.1.1   Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble, 1 g of silica gel, and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the toluene extract, and retain it for analysis. Remove the filters and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.4.3.1.2   Adsorbent Resin. Amberlite XAD–2 resin, thoroughly cleaned before initial use.

3.4.3.1.2.1   Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-coarse frit is used for extraction of XAD–2. The frit is recessed 10–15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order:

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride.	Extract for 22 hours.
Methylene Chloride (fresh).	Extract for 22 hours.

3.4.3.1.2.2   Drying.

3.4.3.1.2.2.1   Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.4.3.1.2.2.2   Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as to cause the particles to fracture.

3.4.3.1.2.3   Quality Control Check. The adsorbent must be checked for residual methylene chloride as well as PCDDs and PCDFs.

3.4.3.1.2.3.1   Extraction. Weigh a 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.4.3.1.2.3.2   Analysis. Inject a 2-μl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft × ⅛ in. stainless steel containing 10 percent OV–101 on 100/120 Supelcoport.

Carrier Gas: Helium at a rate of 30 ml/min.

Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.

Injection Port Temperature: 250 °C.

Detector Temperature: 305 °C.

Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injecting 2.5 μl of methylene chloride into 100 ml of toluene. This corresponds to 100 μg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 μg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.4.3.1.2.3.3   Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.4.3.1.3   Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven. and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.4.3.1.4   Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.4.3.1.5   Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.4.3.1.6   Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.4.3.2   Sample Recovery.

3.4.3.2.1   Acetone. Pesticide quality.

3.4.3.2.2   Methylene Chloride. Pesticide quality.

3.4.3.2.3   Toluene. Pesticide quality.

3.4.3.3   Analysis.

3.4.3.3.1   Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.4.3.3.2   Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying.

Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.4.3.3.3 Sulfuric Acid. Reagent grade.

3.4.3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.4.3.3.5 Hexane. Pesticide grade.

3.4.3.3.6 Methylene Chloride. Pesticide grade.

3.4.3.3.7 Benzene. Pesticide grade.

3.4.3.3.8 Ethyl Acetate.

3.4.3.3.9 Methanol. Pesticide grade.

3.4.3.3.10 Toluene. Pesticide grade.

3.4.3.3.11 Nonane. Pesticide grade.

3.4.3.3.12 Cyclohexane. Pesticide grade.

3.4.3.3.13 Basic Alumina. Activity grade 1, 100–200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.4.3.3.14 Silica Gel. Bio-Sil A, 100–200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, and then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.4.3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw-capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.4.3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw-capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.4.3.3.17 Carbon/Celite. Combine 10.7 g of AX-21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.4.3.3.18 Nitrogen. Ultra high purity.

3.4.3.3.19 Hydrogen. Ultra high purity.

3.4.3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labeled PCDDs and PCDFs at the concentrations shown in Table 3.4–1 under the heading "Internal Standards" in 10 ml of nonane.

3.4.3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labeled PCDDs and PCDFs at the concentrations shown in Table 1 under the heading "Surrogate Standards" in 10 ml of nonane.

3.4.3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the isotopically labeled PCDDs and PCDFs at the concentrations shown in Table 1 under the heading "Recovery Standards" in 10 ml of nonane

TABLE 3.4–1.—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/μl)
Internal Standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCCD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards:	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,7,8,9-HpCDF	100
Recovery Standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

3.4.4 Procedure

3.4.4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, analysts should be trained and experienced with the analytical procedures.

3.4.4.1.1 Preparation Prior to Analysis.

3.4.4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in Section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

3.4.4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD-2. Follow the XAD-2 with glass wool and tightly cap both ends of the trap. Add 100 μl of the surrogate standard solution (Section 3.4.3.3.21) to each trap.

3.4.4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD–0578.

3.4.4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air-tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sample holder just prior to sampling.

3.4.4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

3.4.4.1.2 Preliminary Determinations. Same as Section 4.1.2 of Method 5.

3.4.4.1.3 Preparation of Collection Train.

3.4.4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

Note: Do not use sealant grease in assembling the train.

3.4.4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

3.4.4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

3.4.4.1.3.4 Assemble the train as shown in Figure 3.4–1.

3.4.4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD–2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD–2 temperature must not exceed 20 °C for efficient capture of the PCDDs and PCDFs.

3.4.4.1.4 Leak-Check Procedure. Same as method 5, section 4.1.4.

3.4.4.1.5 Sample Train Operation. Same as method 5, section 4.1.5.

3.4.4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

3.4.4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

3.4.4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

3.4.4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter

holder, and the cyclone, if used, first, by brushing while rinsing three times each with acetone, and then by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

3.4.4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in section 3.4.4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

3.4.4.2.5 Impinger Water. Measure the liquid in the first three impingers to with ± 1 ml by using a graduated cylinder or by weighing it to within ± 0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

3.4.4.2.6 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal.

3.4.5 *Analysis*

All glassware shall be cleaned as described in section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

3.4.5.1 Sample Extraction.

3.4.5.1.1 Extraction System. Place an extractable thimble (section 3.4.2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

3.4.5.1.2 Container No. 1 (Filter). Transfer the contents of container number 1 directly to the glass thimble of the extraction system and extract them simultaneously with the XAD-2 resin.

3.4.5.1.3 Adsorbent Module. Suspend the adsorbent module directly over the extraction thimble in the beaker (see section 3.4.5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD-2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD-2 glass wool plug to the thimble.

3.4.5.1.4 Container No. 2 (Acetone and Methylene Chloride Rinse). Concentrate the sample to a volume of about 1-5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD-2 resin in the Soxhlet apparatus described in section 3.4.5.1.1.

3.4.5.1.5 Extraction. Add 100 μl of the internal standard solution (section 3.4.3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 3.4.5.1.3. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD-2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately $\frac{2}{3}$ full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 3.4.5.2 and 3.4.5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

3.4.5.1.6 Container No. 3 (Toluene Rinse). Add 100 μl of the Internal Standard solution (section 3.4.3.3.20) to the contents of the container. Concentrate the sample to a volume of about 1-5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 3.4.5.2 and 3.4.5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

3.4.5.2 Sample Cleanup and Fractionation.

3.4.5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm × 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 3.4.2.3.8).

3.4.5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

3.4.5.2.3 AX-21 Carbon/Celite 545 Column. Remove the bottom 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases, AX-21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 μl using a stream of N$_2$. Store extracts at room temperature, shielded from light, until the analysis is performed.

3.4.5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 3.4.5.3.1 and 3.4.5.3.2. Immediately prior to analysis, add a 20-μl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2-μl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB-5 capillary column to determine the concentration of each isomer of PCDDs and PCDFs (tetra- through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB-225 column to measure the 2,3,7,8-tetrachlorodibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate, using calibration and performance checks, that the column system is able to meet the specifications of Section 3.4.6.1.2.2.

3.4.5.3.1 Gas Chromatograph Operating Conditions.

3.4.5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

3.4.5.3.1.2 Carrier Gas. Helium, 1-2 ml/min.

3.4.5.3.1.3 Oven. Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then at 3 °C/min up to 300 °C.

3.4.5.3.2 High Resolution Mass Spectrometer.

3.4.5.3.2.1 Resolution. 10000 m/e.

3.4.5.3.2.2 Ionization Mode. Electron impact.

3.4.5.3.2.3 Source Temperature 250 °C.

3.4.5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.4–2.

TABLE 3.4–2.—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTIONS MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor no.	Accurate mass *	Ion type	Elemental composition	Analyte
1	[Not used]			
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}C13{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_{337}ClO_2$	TCDD
	327.8847	M	$C_{12}H_{437}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$_{13}C_{12}H_{435}Cl_4O_2$	TCDD (S)
	333.9339	M+2	$_{13}C_{12}H_{436}Cl^{37}ClO_2$	TCDD (S)
	339.8597	M+2	$C_{12}H_{335}Cl_{437}ClO$	PECDF
	341.6587	M+4	$C_{12}H_{335}Cl_5{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_{335}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_{335}Cl_5{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_{335}Cl_{337}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_{335}Cl_{337}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_{335}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_{335}Cl_5{}^{37}ClO_2$	PeCDD (S)
	375.8364	M+2	$C_{12}H_{335}Cl_{437}ClO$	HxCDPE
	409.7974	M+2	$C_{12}H_{335}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M+2	$C_{12}H_{235}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_{235}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_{235}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_{335}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M+2	$C_{12}H_{235}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_{335}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_{235}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_{235}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	445.7555	M+4	$C_{12}H_{235}Cl_4{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H^{35}Cl_4{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H_{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H_{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M+2	$C_{12}H_{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H_{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H_{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H_{35}Cl_6{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H_{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M+2	$C_{1235}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{1235}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{1235}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{1235}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{1235}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{1235}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M+4	$C_{1235}Cl_6{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

* The following nuclidic masses were used: $H = 1.007825$, $O = 15.994915$, $C = 12.000000$, $^{35}Cl = 34.968853$, $^{13}C = 13.003355$, $_{37}Cl = 36.965903$, $F = 18.9984$, $S = $ Labeled Standard, $QC = $ Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 3.4–3.—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

Number of Chlorine atoms	Ion type	Theoretical ratio	Control limits Lower	Control limits Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6ª	M/M+2	0.51	0.43	0.59
7ᵇ	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

* Used only for ^{13}C-HxCDF
ᵇ Used only for ^{13}C-HpCDF

3.4.5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M+2 or M+2/M+4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 3.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions, shown in Table 3.4-2 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRTs found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

6. The confirmation of 2,3,7,8-TCDD and 2,3,7,8-TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDFs, no signal may be found in the corresponding PCDPE channels.

3.4.5.3.2.6 Quantitation. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantitate the indigenous PCDDs or PCDFs in its homologous series. For example, the [13]C_{12}-2,3,7,8-tetrachlorodibenzodioxin is used to calculate the concentrations of all other tetrachlorinated isomers. Recoveries of the tetra- and penta-internal standards are calculated using the [13]C_{12}-1,2,3,4-TCDD. Recoveries of the hexa- through octa-internal standards are calculated using [13]C_{12}-1,2,3,7,8,9-HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

3.4.6 Calibration

Same as Method 5 with the following additions.

3.4.6.1 GC/MS System.

3.4.6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 3.4-4. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 4) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 3.4-5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 3.4-3.

3.4.6.1.2 Daily Performance Check.

3.4.6.1.2.1 Calibration Check. Inject one µl of solution Number 3 from table 4. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRFs for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 3.4-5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 3.4-3.

3.4.6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDDs and PCDFs that documents resolution between 2,3,7,8-TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

TABLE 3.4-4.—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Solution No.	Concentrations (pg/µL)			
		1	2	3	4
Unlabeled Analytes					
2,3,7,8-TCDD	0.5	1	5	50	100
2,3,7,8-TCDF	0.5	1	5	50	100
1,2,3,7,8-PeCDD	2.5	5	25	250	500
1,2,3,7,8-PeCDF	2.5	5	25	250	500
2,3,4,7,8-PeCDF	2.5	5	25	250	500
1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
1,2,3,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,7,8,9-HxCDD	2.5	5	25	250	500
1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
1,2,3,6,7,8-HxCDF	2.5	5	25	250	500
1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
2,3,4,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDF	2.5	5	25	250	500
1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
OCDD	5.0	10	50	500	1000
OCDF	5.0	10	50	500	1000
Internal Standards					
[13]C_{12}-2,3,7,8-TCDD	100	100	100	100	100
[13]C_{12}-1,2,3,7,8-PeCDD	100	100	100	100	100
[13]C_{12}-1,2,3,6,7,8,-HxCDD	100	100	100	100	100
[13]C_{12}-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
[13]C_{12}-OCDD	200	200	200	200	200
[13]C_{12}-2,3,7,8-TCDF	100	100	100	100	100
[13]C_{12}-1,2,3,7,8-PeCDF	100	100	100	100	100
[13]C_{12}-1,2,3,6,7,8-HxCDF	100	100	100	100	100
[13]C_{12}-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
Surrogate Standards					
[37]Cl_4-2,3,7,8-TCDD	0.5	1	5	50	100
[13]C_{12}-2,3,4,7,8-PeCDF	2.5	5	25	250	500
[13]C_{12}-1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
[13]C_{12}-1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
[13]C_{12}-1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
Alternative Standard					
[13]C_{12}-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
Recovery Standards					
[13]C_{12}-1,2,3,4-TCDD	100	100	100	100	100
[13]C_{12}-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 3.4-5.—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative Response Factors	
	Initial Calibration RSD	Daily Calibration % Difference
Unlabeled Analytes		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{14}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HXCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8-TCDF and other TCDF isomers.

3.4.6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3.4-3. Monitor the quality control check channels specified in Table 3.4-3 to verify instrument stability during the analysis.

3.4.7 *Quality Control*

3.4.7.1 Sampling Train Collection Efficiency Check. Add 100 μl of the surrogate standards in Table 3.4-1 to the adsorbent cartridge of each train before collecting the field samples.

3.4.7.2 Internal Standard Percent Recoveries. A group of nine carbon-labeled PCDDs and PCDFs representing the tetra- through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantitate the native PCDDs and PCDFs present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra- through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.

3.4.7.3 Surrogate Recoveries. The five surrogate compounds in Table 3.4-4 are added to the resin the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDDs and PCDFs. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of samples.

3.4.7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

3.4.8 *Quality Assurance*

3.4.8.1 Applicability. When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

3.4.8.2 Audit Procedure. Analyze an audit sample with each set of compliance samples. The audit sample contains tetra through octa isomers of PCDD and PCDF. Concurrently, analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for the compliance samples and the EPA audit sample.

3.4.8.3 Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing: Source Test Audit Coordinator (MD-77B), Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711. or by calling the Source Test Audit Coordinator (STAC) at (919) 541-7834. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

3.4.8.4 Audit Results. Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency and a

second copy to the STAC. The EPA Regional Office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

3.4.9 Calculations

Same as method 5, section 6 with the following additions.

3.4.9.1 Nomenclature.

A_{al} = Integrated ion current of the noise at the retention time of the analyte.

A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A_{cij} = Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.

A^*_{cij} = Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.

A_{csi} = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

A_i = Integrated ion current of the two ions characteristic of compound in the sample.

A^*_i = Integrated ion current of the two ions characteristic of internal standard i in the sample.

A_{rs} = Integrated ion current of the two ions characteristic of the recovery standard.

A_{si} = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_i = Concentration of PCDD or PCDF i in the sample, pg/M³.

C_T = Total concentration of PCDDs or PCDFs in the sample, pg/M³.

m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.

m^*_{ci} = Mass of labeled compound i in the calibration standard injected into the analyzer, pg.

m^*_i = Mass of internal standard i added to the sample, pg.

m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.

m_{si} = Mass of surrogate compound i in the calibration standard, pg.

RRF_i = Relative response factor.

RRF_{rs} = Recovery standard response factor.

RRF_s = Surrogate compound response factor.

3.4.9.2 Average Relative Response Factor.

$$RRF_i = 1/n \sum_{j=1}^{n} [A_{cij} m^*_{ci}/(A^*_{cij} m_{ci})] \quad Eq.\ 23-1$$

3.4.9.3 Concentration of the PCDDs and PCDFs.

$$C_i = m^*_i A_i/(A^*_i RRF_i V_{m(std)}) \quad Eq.\ 23-2$$

3.4.9.4 Recovery Standard Response Factor.

$$RRF_{rs} = A^*_{ci} m_{rs}/(A_{rs} m^*_{ci}) \quad Eq.\ 23-3$$

3.4.9.5 Recovery of Internal Standards (R*).

$$R^* = (A^*_i m_{rs}/A_{rs} RF_{rs} m^*_i) \times 100\% \quad Eq.\ 23-4$$

3.4.9.6 Surrogate Compound Response Factor.

$$RRF_s = A^*_{ci} m_s/(A_{cis} m^*_{ci}) \quad Eq.\ 23-5$$

3.4.9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = (A_s m^*_i/A^*_i RRF_s m_s) \times 100\% \quad Eq.\ 23-6$$

3.4.9.8 Minimum Detectable Limit (MDL).

$$MDL = 2.5 A_{al} m^*_i/(A^*_{ci} RRF_i) \quad Eq.\ 23-7$$

3.4.9.9 Total Concentration of PCDDs and PCDFs in the Sample.

$$C_T = \sum_{i=1}^{n} C_i \quad Eq.\ 23-8$$

3.4.10 Bibliography

1. American Society of Mechanical Engineers. Sampling for the Determination of Chlorinated Organic Compounds in Stack Emissions. Prepared for U.S. Department of Energy and U.S. Environmental Protection Agency. Washington, DC December 1984. 25 p.

2. American Society of Mechanical Engineers. Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF). Prepared for the U.S. Department of Energy and U.S. Environmental Protection Agency. Washington, DC December 1984. 23 p.

3. Thompson, J.R. (ed.) Analysis of Pesticide Residues in Human and Environmental Samples. U.S. Environmental Protection Agency. Research Triangle Park, NC 1974.

4. Triangle Laboratories. Case Study: Analysis of Samples for the Presence of Tetra Through Octachloro-p-Dibenzodioxins and Dibenzofurans. Research Triangle Park, NC 1988. 26 p.

5. U.S. Environmental Protection Agency. Draft Method 8290—The Analysis of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofurans by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry. In: Test Methods for Evaluating Solid Waste. Washington, DC SW–846.

3.5 Sampling for Aldehyde and Ketone Emissions from Stationary Sources (Method 0011)

3.5.1 Scope and Application

This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of formaldehyde, CAS Registry number 50–00–0, and possibly other aldehydes and ketones from stationary sources as specified in the regulations. The methodology has been applied specifically to formaldehyde; however, many laboratories have extended the application to other aldehydes and ketones. Compounds derivatized with 2,4-dinitrophenyl-hydrazine can be detected as low as 6.4 x 10⁻⁸ lbs/cu ft (1.8 ppbv) in stack gas over a 1 hr sampling period, sampling approximately 45 cu ft.

3.5.2 Summary of Method

3.5.2.1 Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and are collected in aqueous acidic 2,4-dinitrophenyl-hydrazine. Formaldehyde present in the emissions reacts with the 2,4-dinitrophenyl-hydrazine to form the formaldehyde dinitrophenylhydrazone derivative. The dinitrophenylhydrazone derivative is extracted, solvent-exchanged, concentrated, and then analyzed by high performance liquid chromatography.

3.5.3 Interferences

3.5.3.1 A decomposition product of 2,4-dinitrophenyl-hydrazine, 2,4-dinitroaniline, can be an analytical interferant if concentrations are high. 2,4-Dinitroaniline can coelute with 2,4-dinitrophenylhydrazone of formaldehyde under high performance liquid chromatography conditions, which may be used for the analysis. High concentrations of highly-oxygenated compounds, especially acetone, that have the same retention time or nearly the same retention time as the dinitrophenylhydrazone of formaldehyde, and that also absorb at 360 nm, will interfere with the analysis.

Formaldehyde, acetone, and 2,4-dinitroaniline contamination of the aqueous acidic 2,4-dinitrophenyl-hydrazine (DNPH) reagent is frequently encountered. The reagent must be prepared within five days of use in the field and must be stored in an uncontaminated environment both before and after sampling in order to minimize blank problems. Some concentration of acetone contamination is unavoidable, because acetone is ubiquitous in laboratory and field operations. However, the acetone contamination must be minimized.

3.5.4 Apparatus and Materials

3.5.4.1 A schematic of the sampling train is shown in Figure 3.5–1. This sampling train configuration is adapted from EPA method 4 procedures. The sampling train consists of the following components: Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Metering System, Barometer, and Gas Density Determination Equipment.

3.5.4.1.1 Probe Nozzle: Quartz or glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant inner diameter. The nozzle shall be buttonhook or elbow design. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.15 cm(1/16 in), e.g., 0.32 to 1.27 cm (⅛ to ½ in), of larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in section 3.5.8.1.

3.5.4.1.2 Probe Liner: Borosilicate glass or quartz shall be used for the probe liner. The tester should not allow the temperature in the probe to exceed 120 ± 14 °C (248 ± 25°F).

3.5.4.1.3 Pitot Tube: The Pitot tube shall be Type S, as described in section 2.1 of EPA method 2, or any other appropriate device. The pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plan (see EPA method 2, Figure 26b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in section 4 of EPA method 2.

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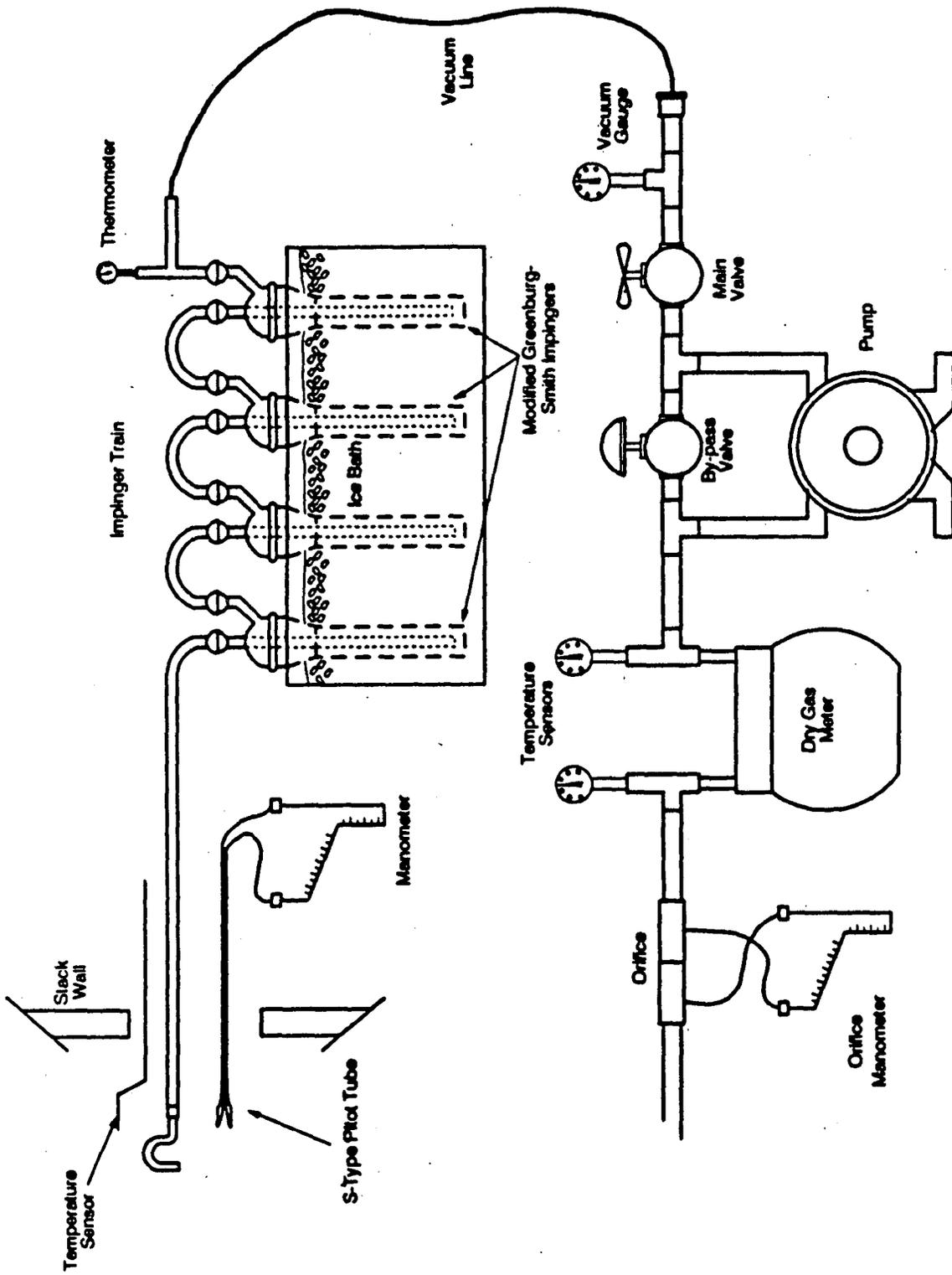
Formaldehyde Sampling Train

Figure 3.5-1

BILLING CODE 6560-50-C

3.5.4.1.4 Differential Pressure Gauge: The differential pressure gauge shall be an inclined manometer or equivalent device as described in section 2.2 of EPA method 2. One manometer shall be used for velocity-head reading and the other for orifice differential pressure readings.

3.5.4.1.5 Impingers: The sampling train requires a minimum of four impingers, connected as shown in Figure 3.5-1, with ground glass (or equivalent) vacuum-tight fittings. For the first, third, and fourth implngers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm inside diameter (½ in) glass tube extending to 1.3 cm (½ in) from the bottom of the flask. For the second impinger, use a Greenburg-Smith Impinger with the standard tip. Place a thermometer capable of measuring temperature to within 1 °C (2 °F) at the outlet of the fourth impinger for monitoring purposes.

3.5.4.1.6 Metering System: The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperature within 3 °C (5.4 °F), dry-gas meter capable of measuring volume to within 1%, and related equipment as shown in Figure 3.5-1. At a minimum, the pump should be capable of 4 cfm free flow, and the dry gas meter should have a recording capacity of 0-999.9 cu ft with a resolution of 0.005 cu ft. Other metering systems may be used which are capable of maintaining sample volumes to within 2%. The metering system may be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.

3.5.4.1.7 Barometer: The barometer may be mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service Station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in Hg) per 30 m (100 ft) elevation increases (vice versa for elevation decrease).

3.5.4.1.8 Gas Density Determination Equipment: Temperature sensor and pressure gauge (as described in sections 2.3 and 2.3 of EPA method 2), and gas analyzer, if necessary (as described in EPA method 3). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot openings (see EPA method 2, Figure 2-7). As a second alternative, if a difference of no more than 1% in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube.

3.5.4.2 Sample Recovery.

3.5.4.2.1 Probe Liner: Probe nozzle and brushes; Teflon bristle brushes with stainless steel wire handles are required. The probe

brush shall have extensions of stainless steel, Teflon, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner, the probe nozzle, and the impingers.

3.5.4.2.2 Wash Bottles: Three wash bottles are required. Teflon or glass wash bottles are recommended; polyethylene wash bottles should not be used because organic contaminants may be extracted by exposure to organic solvents used for sample recovery.

3.5.4.2.3 Graduate Cylinder and/or Balance: A graduated cylinder or balance is required to measure condensed water to the nearest 1 ml or 1 g. Graduated cylinders shall have division not >2 ml. Laboratory balances capable of weighing to ±0.5 g are required.

3.5.4.2.4 Amber Glass Storage Containers: One-liter wide-mouth amber flint glass bottles with Teflon-lined caps are required to store impinger water samples. The bottles must be sealed with Teflon tape.

3.5.4.2.5 Rubber Policeman and Funnel: A rubber policeman and funnel are required to aid in the transfer of material into and out of containers in the field.

3.5.4.3 Reagent Preparation.

3.5.4.3.1 Bottles/Caps: Amber 1- or 4-L bottles with Teflon-lined caps are required for storing cleaned DNPH solution. Additional 4-L bottles are required to collect waste organic solvents.

3.5.4.3.2 Large Glass Container: At least one large glass (8 to 16 L) is required for mixing the aqueous acidic DNPH solution.

3.5.4.3.3 Stir Plate/Large Stir Bars/Stir Bar Retriever: A magnetic stir plate and large stir bar are required for the mixing of aqueous acidic DNPH solution. A stir bar retriever is needed for removing the stir bar from the large container holding the DNPH solution.

3.5.4.3.4 Buchner Filter/Filter Flask/Filter Paper: A large filter flask (2-4 L) with a buchner filter, appropriate rubber stopper, filter paper, and connecting tubing are required for filtering the aqueous acidic DNPH solution prior to cleaning.

3.5.4.3.5 Separatory Funnel: At least one large separatory funnel (2 L) is required for cleaning the DNPH prior to use.

3.5.4.3.6 Beakers: Beakers (150 ml, 250 ml, and 400 ml) are useful for holding/measuring organic liquids when cleaning the aqueous acidic DNPH solution and for weighing DNPH crystals.

3.5.4.3.7 Funnels: At least one large funnel is needed for pouring the aqueous acidic DNPH into the separator funnel.

3.5.4.3.8 Graduated Cylinders: At least one large graduated cylinder (1 to 2 L) is required for measuring organic-free reagent water and acid when preparing the DNPH solution.

3.5.4.3.9 Top-Loading Balance: A one-place top loading balance is needed for weighing out the DNPH crystals used to prepare the aqueous acidic DNPH solution.

3.5.4.3.10 Spatulas: Spatulas are needed for weighing out DNPH when preparing the aqueous DNPH solution.

3.5.4.4 Crushed Ice: Quantities ranging from 10-50 lb may be necessary during a sampling run, depending upon ambient temperature. Samples which have been taken must be stored and shipped cold; sufficient Ice for this purpose must be allowed.

3.5.5 *Reagents*

3.5.5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

3.5.5.2 Organic-free reagent water: All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

3.5.5.3 Silica Gel: Silica gel shall be indicating type, 6-16 mesh. If the silica gel has been used previously, dry at 175°C (350 °F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

3.5.5.4 2,4-dinitrophenylhydrazine (DNPH), $[2,4-(O_2N)_2C_6H_3]NHNH_2$—The quantity of water may vary from 10 to 30%.

3.5.5.4.1 The 2,4-dinitrophenylhydrazine reagent must be prepared in the laboratory within five days of sampling use in the field. Preparation of DNPH can also be done in the field, with consideration of appropriate procedures required for safe handling of solvent in the field. When a container of prepared DNPH reagent is opened in the field, the contents of the opened container should be used within 48 hours. All laboratory glassware must be washed with detergent and water and rinsed with water, methanol, and methylene chloride prior to use.

Note: DNPH crystals or DNPH solution should be handled with plastic gloves at all times with prompt and extensive use of running water in case of skin exposure.

3.5.5.4.2 Preparation of Aqueous Acidic DNPH Derivatizing Reagent: Each batch of DNPH reagent should be prepared and purified within five days of sampling, according to the procedures described below.

Note: Reagent bottles for storage of cleaned DNPH derivatizing solution must be rinsed with acetonitrile and dried before use. Baked glassware is not essential for preparation of DNPH reagent. The glassware must not be rinsed with acetone or an unacceptable concentration of acetone contamination will be introduced. If field preparation of DNPH is performed, caution must be exercised in avoiding acetone contamination.

3.5.5.4.2.1 Place an 8 L container under a fume hood on a magnetic stirrer. Add a large stir bar and fill the container half full of organic-free reagent water. Save the empty bottle from the organic-free reagent water. Start the stirring bar and adjust the stir rate to be as fast as possible. Using a graduated cylinder, measure 1.4 ml of concentrated hydrochloric acid. Slowly pour the acid into the stirring water. Fumes may be generated and the water may become warm. Weight the DNPH crystals on a one-place balance (see Table 3.5-1 for approximate amounts) and add to the stirring acid solution. Fill the 8-L

container to the 8–L mark with organic-free reagent water and stir overnight. If all of the DNPH crystals have dissolved overnight, add additional DNPH and stir for two more hours. Continue the process of adding DNPH with additional stirring until a saturated solution has been formed. Filter the DNPH solution using vacuum filtration. Gravity filtration may be used, but a much longer time is required. Store the filtered solution in an amber bottle at room temperature.

3.5.5.4.2.2 Within five days of proposed use, place about 1.6 L of the DNPH reagent in a 2–L separatory funnel. Add approximately 200 ml of methylene chloride and stopper the funnel. Wrap the stopper of the funnel with paper towels to absorb any leakage. Invert and vent the funnel. Then shake vigorously for 3 minutes. Initially, the funnel should be vented frequently (every 10–15 sec). After the layers have separated, discard the lower (organic) layer.

3.5.5.4.2.3 Extract the DNPH a second time with methylene chloride and finally with cyclohexane. When the cyclohexane layer has separated from the DNPH reagent, the cyclohexane layer will be the top layer in the separatory funnel. Drain the lower layer (the cleaned extract DNPH reagent solution) into an amber bottle that has been rinsed with acetonitrile and allowed to dry.

3.5.5.4.3 Quality Control: Take two aliquots of the extracted DNPH reagent. The size of the aliquots is dependent upon the exact sampling procedure used, but 100 ml is reasonably representative. To ensure that the background in the reagent is acceptable for field use, analyze one aliquot of the reagent according to the procedure of method 8315. Save the other aliquot of aqueous acidic DNPH for use as a method blank when the analysis is performed.

TABLE 3.5–1.—APPROXIMATE AMOUNT OF CRYSTALLINE DNPH USED TO PREPARE A SATURATED SOLUTION

Amount of moisture in DNPH	Weight required per 8 L of solution
10 weight percent	31 g
15 weight percent	33 g
30 weight percent	40 g

TABLE 3.5–2.—INSTRUMENT DETECTION LIMITS AND REAGENT CAPACITY FOR FORMALDEHYDE ANALYSIS [1]

Analyte	Detection limit, ppb [2]	Reagent capacity, ppmv
Formaldehyde	1.8	66
Acetaldehyde	1.7	70
Acrolein	1.5	75
Acetone/ Propionaldehyde	1.5	75
Butyraldehyde	1.5	79
Methyl ethyl ketone	1.5	79
Valeraldehyde	1.5	84
Isovaleraldehyde	1.4	84
Hexaldehyde	1.3	88
Benzaldehyde	1.4	84

TABLE 3.5–2.—INSTRUMENT DETECTION LIMITS AND REAGENT CAPACITY FOR FORMALDEHYDE ANALYSIS [1]—Continued

Analyte	Detection limit, ppb [2]	Reagent capacity, ppmv
o-/m-/p-Tolualdehyde	1.3	89
Dimethylbenzaldehyde	1.2	93

[1] Oxygenated compounds in addition to formaldehyde are included for comparison with formaldehyde; extension of the methodology to other compounds is possible.
[2] Detection limits are determined in solvent. These values therefore represent the optimum capability of the methodology.

3.5.5.4.4 Shipment to the Field: Tightly cap the bottle containing extracted DNPH reagent using a Teflon-lined cap. Seal the bottle with Teflon tape. After the bottle is labeled, the bottle may be placed in a friction-top can (paint can or equivalent) containing a 1-2 inch layer of granulated charcoal and stored at ambient temperature until use.

3.5.5.4.4.1 If the DNPH reagent has passed the Quality Control criteria, the reagent may be packaged to meet necessary shipping requirements and sent to the sampling area. If the Quality Control criteria are not met, the reagent solution may be re-extracted or the solution may be re-prepared and the extraction sequence repeated.

3.5.5.4.4.2 If the DNPH reagent is not used in the field within five days of extraction, an aliquot may be taken and analyzed as described in method 0011A. If the reagent meets the Quality Control requirements, the reagent may be used. If the reagent does not meet the Quality Control requirements, the reagent must be discarded and new reagent must be prepared and tested.

3.5.5.4.5 Calculation of Acceptable Concentrations of Impurities in DNPH Reagent: The acceptable impurity concentration (AIC, μg/ml) is calculated from the expected analyte concentration in the sampled gas (EAC, ppbv), the volume of air that will be sampled at standard conditions (SVOL, L), the formula weight of the analyte (FW, g/mol), and the volume of DNPH reagent that will be used in the impingers (RVOL, ml):

$$AIC = 0.1 \times [EAC \times SVOL \times FW / 22.4 \times (FW + 180)/FW](RVOL \times 1,000)$$

where:
0.1 is the acceptable contaminant concentration,
22.4 is a factor relating ppbv to g/L,
180 is a facto relating underivatized to derivatized analyte
1,000 is a unit conversion factor.

3.5.5.4.6 Disposal of Excess DNPH Reagent: Excess DNPH reagent may be returned to the laboratory and recycled or treated as aqueous waste for disposal purposes. 2,4-dinitrophenylhydrazine is a flammable solid when dry, so water should not be evaporated from the solution of the reagent.

3.5.5.5 Field Spike Standard Preparation: To prepare a formaldehyde field spiking standard at 4.01 mg/ml, use a 500 μl syringe to transfer 0.5 ml to 37% by weight of

formaldehyde (401 mg/ml) to a 50 ml volumetric flask containing approximately 50 ml of methanol. Dilute to 50 ml with methanol.

3.5.5.6 Hydrochloric Acid, HCL: Reagent grade hydrochloric acid (approximately 12N) is required for acidifying the aqueous DNPH solution.

3.5.5.7 Methylene Chloride, CH_2Cl_2: Methylene chloride (suitable for residue and pesticide analysis, GC/MS, HPLC, GC, Spectrophotometry or equivalent) is required for cleaning the aqueous acidic DNPH solution, rinsing glassware, and recovery of sample trains.

3.5.5.8 Cyclohexane, C_6H_{12}: Cyclohexane (HPLC grade) is required for cleaning the aqueous acidic DNPH solution.

NOTE: Do not use spectroanalyzed grades of cyclohexane if this sampling methodology is extended to aldehydes and ketones with four or more carbon atoms.

3.5.5.9 Methanol, CH_3OH: Methanol (HPLC grade or equivalent) is required for rinsing glassware.

3.5.5.10 Acetonitrile, CH_3CN: Acetonitrile (HPLC grade or equivalent) is required for rinsing glassware.

3.5.5.11 Formaldehyde, HCHO: Analytical grade or equivalent formaldehyde is required for preparation of standards. If other aldehydes or ketones are used, analytical grade or equivalent is required.

3.5.6 *Sample Collection, Preservation, and Handling*

3.5.6.1 Because of the complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

3.5.6.2 Laboratory Preparation:

3.5.6.2.1 All the components shall be maintained and calibrated according to the procedure described in APTD–0576, unless otherwise specified.

3.5.6.2.2 Weigh several 200 to 300 g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may instead be weighed directly in the impinger or sampling holder just prior to train assembly.

3.5.6.3 Preliminary Field Determinations:

3.5.6.3.1 Select the sampling site and the minimum number of sampling point according to EPA method 1 or other relevant criteria. Determine the stack pressure, temperature, and range of velocity heads using EPA method 2. A leak-check of the pitot lines according to EPA method 2, section 3.1, must be performed. Determine the stack gas moisture content using EPA Approximation method 4 or its alternatives to establish estimates of isokinetic sampling-rate settings. Determine the stack gas dry molecular weight, as described in EPA method 2, section 3.6. If integrated EPA method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

3.5.6.3.2 Select a nozzle size based on the range of velocity heads so that is not

necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 L/min (1.0 cfm). During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see section 2.2. of EPA method 2).

3.5.6.3.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

3.5.6.3.4 A minimum of 45 ft³ of sample volume is required for the determination of the Destruction and Removal Efficiency (DRE) of formaldehyde from incineration systems (45 ft³ is equivalent to one hour of sampling at 0.75 dscf). Additional sample volume shall be collected as necessitated by the capacity of the DNPH reagent and analytical detection limit constraints. To determine the minimum sample volume required, refer to sample calculations in section 10.

3.5.6.3.5 Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by EPA method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus 0.5 min.

3.5.6.3.6 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas-volume samples. In these cases, careful documentation must be maintained in order to allow accurate calculation of concentrations.

3.5.6.4 Preparation of Collection Train:

3.5.6.4.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon film or aluminum foil until just prior to assembly or until sampling is about to begin.

3.5.6.4.2 Place 100 ml of cleaned DNPH solution in each of the first two impingers, and leave the third impinger empty. If additional capacity is required for high expected concentrations of formaldehyde in the stack gas, 200 ml of DNPH per impinger may be used or additional impingers may be used for sampling. Transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the fourth impinger. Care should be taken to ensure that the silica gel is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place or later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

3.5.6.4.3 With a glass or quartz liner, install the selected nozzle using a Viton-A O-ring with stack temperatures are <260 °C (500 °F) and a woven glass-fiber gasket when temperatures are higher. See APTD-0576 (Rom, 1972) for details. Other connection systems utilizing either 316 stainless steel or Teflon ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

3.5.6.4.4 Assemble the train as shown in Figure 3.5-1. During assembly, do not use any

silicone grease on ground-glass joints upstream of the impingers. Use Teflon tape, if required. A very light coating of silicone grease may be used on ground-glass joints downstream of the impingers, but the silicone grease should be limited to the outer portion (see APTD-0576) of the ground-glass joints to minimize silicone grease contamination. If necessary, Teflon tape may be used to seal leaks. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperatures.

3.5.6.4.5 Place crushed ice all around the impingers.

3.5.6.4.6 Turn on and set the probe heating system at the desired operating temperature. Allow time for the temperature to stabilize.

3.5.6.5 Leak-Check Procedures:

3.5.6.5.1 Pre-test Leak Check.

3.5.6.5.1.1 After the sampling train has been assembled, turn on and set the probe heating system at the desired operating temperature. Allow time for the temperature to stabilize. If a Viton-A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak check the train at the sampling site by plugging the nozzle and pulling a 381 mm Hg (15 in Hg) vacuum.

Note: A lower vacuum may be used, provided that the lower vacuum is not exceeded during the test.

3.5.6.5.1.2 If an asbestos string is used, do not connect the probe to the train during the leak check. Instead, leak-check the train by first attaching a carbon-filled leak check impinger to the inlet and then plugging the inlet and pulling a 381 mm Hg (15 in Hg) vacuum. (A lower vacuum any be used if this lower vacuum is not exceeded during the test.) Next connect the probe to the train and leak-check at about 25 mm Hg (1 in Hg) vacuum. Alternatively, leak-check the probe with the rest of the sampling train in one step at 381 mm Hg (15 in Hg) vacuum. Leakage rates in excess of (a) 4% of the average sampling rate or (b) >0.00057 m³/min (0.02 cfm), are unacceptable.

3.5.6.5.1.3 The following leak check instructions for the sampling train described In ADPT-0576 and APTD-0581 may be helpful. Start the pump with the fine-adjust valve fully open and coarse-valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached. Do *not* reverse direction of the fine-adjust valve, as liquid will back up into the train. If the desired vacuum is exceeded, either perform the leak check at this higher vacuum or end the leak check, as shown below, and start over.

3.5.6.5.1.4 When the leak check is completed, first slowly remove the plug from the inlet to the probe. When the vacuum drops to 127 mm (5 in) Hg or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed to prevent the liquid in the impingers from being forced backward in the sampling line and silica gel from being entrained backward into the third impinger.

3.5.6.5.2 Leak Checks During Sampling Run:

3.5.6.5.2.1 If, during the sampling run, a component change (i.e., impinger) becomes necessary, a leak check shall be conducted immediately after the interruption of sampling and before the change is made. The leak check shall be done according to the procedure described in section 3.5.6.5.1, except that is shall be done at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm or 4% of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester must void the sampling run.

Note: Any correction of the sample volume by calculation reduces the integrity of the pollutant concentration data generated and must be avoided.

3.5.6.5.2.2 Immediately after a component change and before sampling is reinitiated, a leak check similar to a pre-test leak check must also be conducted.

3.5.6.5.3 Post-test Leak Check:

3.5.6.5.3.1 A leak check is mandatory at the conclusion of each sampling run. The leak check shall be done with, the same procedures as the pre-test leak check, except that the post-test leak check shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester shall record the leakage rate and void the sampling run.

3.5.6.6 Sampling Train Operation:

3.5.6.6.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic, below 20 L/min (1.0 cfm). Maintain a temperature around the probe of 120 °C (248 °±25 °F).

3.5.6.6.2 For each run, record the data on a data sheet such as the one shown in Figure 3.5-2. Be sure to record the initial dry-gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted. Take other readings required by Figure 2 at least once at each sample point during each time increment and additional readings when significant adjustments 20% variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

3.5.6.6.3 Clean the stack access ports prior to the test run to eliminate the change of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are at the specified temperature, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid

adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use when the Type S pitot tube coefficient is 0.84 ± 0.02 and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4. APTD-0576 details the procedure for using the nomographs. If the stack gas molecular weight and the pitot tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps are taken to compensate for the deviations.

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Plant

Location

Operator

Date

Run No.

Sample Box No.

Meter Box No.

Meter H@

C Factor

Pilot Tube Coefficient C$_p$

Ambient Temperature

Barometric Pressure

Assumed Moisture %

Probe Length, m(ft)

Nozzle Identification No.

Average Calibrated Nozzle Diameter, cm (in)

Probe Heating Setting

Leak Rate, m³/min. (cfm)

Probe Liner Material

Static Pressure, mm Hg (in. Hg)

Filter No.

Schematic of Stack Cross Section

Traverse Point Number	Sampling Time (θ) Min.	Vacuum mm Hg (in. Hg)	Stack Temperature (T$_s$) °C (°F)	Velocity Head (P$_s$) mm (in) H$_2$O	Pressure Differential Across Orifice Meter mm (H$_2$O) (in H$_2$O)	Gas Sample Volume m³ (ft³)	Gas Sample Temp. at Dry Gas Meter		Filter Holder Temperature °C (°F)	Temperature of Gas Leaving Last Impinger °C (°F)
							Inlet °C(°F)	Outlet °C(°F)		
Total										
Average					Avg.	Avg.				

Figure 3.5-2 Field Data Sheet

BILLING CODE 6560-50-C

3.5.6.6.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse-adjust valve before inserting the probe into the stack in order to prevent liquid from backing up through the train. If necessary, the pump may be turned on with the coarse-adjust valve closed.

3.5.6.6.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

3.5.6.6.6 Traverse the stack cross section, as required by EPA Method 1, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.

3.5.6.6.7 During the test run, make periodic adjustments to keep the temperature around the probe at the proper levels. Add more ice and, if necessary, salt, to maintain a temperature of $>20\,^\circ C\,(68\,^\circ F)$ at the silica gel outlet. Also, periodically check the level and zero of the manometer.

3.5.6.6.8 A single train shall be used for the entire sampling run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. An additional train or additional trains may also be used for sampling when the capacity of a single train is exceeded.

3.5.6.6.9 When two or more trains are used, separate analyses of components from each train shall be performed. If multiple trains have been used because the capacity of a single train would be exceeded, first impingers from each train may be combined, and second impingers from each train may be combined.

3.5.6.6.10 At the end of the sampling run, turn off the coarse-adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak check. Also, leak check the pitot lines as described in EPA method 2. The lines must pass this leak check in order to validate the velocity-head data.

3.5.6.6.11 Calculate percent isokineticity (see method 2) to determine whether the run was valid or another test should be made.

3.5.7 Sample Recovery

3.5.7.1 Preparation.

3.5.7.1.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When the probe can be handled safely, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling because a vacuum will be created, drawing liquid from the impingers back through the sampling train.

3.5.7.1.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet, being careful not to lose any condensate that might be present. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used, let any condensed

water or liquid drain into the impingers. Cap off any open impinger inlets and outlets. Ground glass stoppers, Teflon caps or caps of other inert materials may be used to seal all openings.

3.5.7.1.3 Transfer the probe and impinger assembly to an area that is clean and protected from wind so that the chances of contaminating or losing the sample are minimized.

3.5.7.1.4 Inspect the train before and during disassembly, and note any abnormal conditions.

3.5.7.1.5 Save a portion of all washing solution (methylene chloride, water) used for cleanup as a blank. Transfer 200 ml of each solution directly from the wash bottle being used and place each in a separate, prelabeled sample container.

3.5.7.2 Sample Containers.

3.5.7.2.1 Container 1: Probe and Impinger Catches. Using a graduated cylinder, measure to the nearest ml, and record the volume of the solution in the first three impingers. Alternatively, the solution may be weighed to the nearest 0.5 g. Include any condensate in the probe in this determination. Transfer the impinger solution from the graduated cylinder into the amber flint glass bottle. Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, clean all surfaces to which the sample is exposed (including the probe nozzle, probe fitting, probe liner, first impinger, and impinger connector) with methylene chloride. Use less than 500 ml for the entire wash (250 ml would be better, if possible). Add the washing to the sample container.

3.5.7.2.1.1 Carefully remove the probe nozzle and rinse the inside surface with methylene chloride from a wash bottle. Brush with a Teflon bristle brush, and rinse until the rinse shows no visible particles or yellow color, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok fitting with methylene chloride in a similar way.

3.5.7.2.1.2 Rinse the probe liner with methylene chloride. While squirting the methylene chloride into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with methylene chloride. Let the methylene chloride drain from the lower end into the sample container. The tester may use a funnel (glass or polyethylene) to aid in transferring the liquid washes to the container. Follow the rinse with a Teflon brush. Hold the probe in an inclined position, and squirt methylene chloride into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any methylene chloride, water, and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since there may be small crevices in which particulate matter can be entrapped. Rinse the brush with methylene chloride or water, and quantitatively collect these washing in the sample container. After the brushing, make a final rinse of the probe as described above.

Note: Two people should clean the probe in order to minimize sample losses. Between sampling runs, brushes must be kept clean and free from contamination.

3.5.7.2.1.3 Rinse the inside surface of each of the first three impingers (and connecting tubing) three separate times. Use a small portion of methylene chloride for each rinse, and brush each surface to which the sample is exposed with a Teflon bristle brush to ensure recovery of fine particulate matter. Water will be required for the recovery of the impingers in addition to the specified quantity of methylene chloride. There will be at least two phases in the impingers. This two-phase mixture does not pour well, and a significant amount of the impinger catch will be left on the walls. The use of water as a rinse makes the recovery quantitative. Make a final rinse of each surface and of the brush, using both methylene chloride and water.

3.5.7.2.1.4 After all methylene chloride and water washing and particulate matter have been collected in the sample container, tighten the lid so the solvent, water, and DNPH reagent will not leak out when the container is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Seal the container with Teflon tape. Label the container clearly to identify its contents.

3.5.7.2.1.5 If the first two impingers are to be analyzed separately to check for breakthrough, separate the contents and rinses of the two impingers into individual containers. Care must be taken to avoid physical carryover from the first impinger to the second. The formaldehyde hydrazone is a solid which floats and froths on top of the impinger solution. Any physical carryover of collected moisture into the second impinger will invalidate a breakthrough assessment.

3.5.7.2.2 Container 2: Sample Blank. Prepare a blank by using an amber flint glass container and adding a volume of DNPH reagent and methylene chloride equal to the total volume in Container 1. Process the blank in the same manner as Container 1.

3.5.7.2.3 Container 3: Silica Gel. Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. The impinger containing the silica gel may be used as a sample transport container with both ends sealed with tightly fitting caps or plugs. Ground-glass stoppers or Teflon caps may be used. The silica gel impinger should then be labeled, covered with aluminum foil, and packaged on ice for transport to the laboratory. If the silica gel is removed from the impinger, the tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use water or other liquids to transfer the silica gel. If a balance is available in the field, the spent silica gel (or silica gel plus impinger) may be weighed to the nearest 0.5 g.

3.5.7.2.4 Sample containers should be placed in a cooler, cooled by (although not in contact with) ice. Sample containers must be

placed vertically and, since they are glass, protected from breakage during shipment. Samples should be cooled during shipment so they will be received cold at the laboratory.

3.5.8 *Calibration*

3.5.8.1 Probe Nozzle: Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in). When the nozzles become nicked or corroded, they shall be replaced and calibrated before use. Each nozzle must be permanently and uniquely identified.

3.5.8.2 Pitot Tube: The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2 or assigned a nominal coefficient of 0.84 if it is not visibly nicked or corroded and if it meets design and intercomponent spacing specifications.

3.5.8.3 Metering System.

3.5.8.3.1 Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak check be conducted. For metering systems having diaphragm pumps, the normal leak check procedure will not detect leakages with the pump. For these cases, the following leak check procedure will apply: make a ten-minute calibration run at 0.00057 m³/min (0.02 cfm). At the end of the run, take the difference of the measured wettest and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m³/min (0.02 cfm).

3.5.8.3.2 After each field use, check the calibration of the metering system by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). Set the vacuum at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet-test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5%, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

3.5.8.3.3 Leak check of metering system: The portion of the sampling train from the pump to the orifice meter (see Figure 1) should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the following procedure: Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13–18 cm (5–7 in) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 min. A loss

of pressure on the manometer indicates a leak in the meter box. Leaks must be corrected.

Note: If the dry-gas-meter coefficient values obtained before and after a test series differ by >5%, either the test series must be voided or calculations for test series must be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

3.5.8.4 Probe Heater: The probe heating system must be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

3.5.8.5 Temperature gauges: Each thermocouple must be permanently and uniquely marked on the casting. All mercury-in-glass reference thermometers must conform to ASTM E-1 63C or 63F specifications. Thermocouples should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the thermocouple readings at the ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change >1.5%.

3.5.8.5.1 Impinger and dry-gas meter thermocouples: For the thermocouples used to measure the temperature of the gas leaving the impinger train, three-point calibration at ice water, room air, and boiling water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree to ±2C (3.60 °F) with those of the absolute value of the reference thermometer.

3.5.8.5.2 Probe and stack thermocouple: For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice water, boiling water, and hot oil bath temperatures must be performed. Use of a point at room air temperature is recommended. The thermometer and thermocouple must agree to within 1.5% at each of the calibration points. A calibration curve (equation) may be constructed (calculated) and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

3.5.8.6 Barometer: Adjust the barometer initially and before each test series to agree to within ±2.5 mm Hg (0.1 in Hg) of the mercury barometer or the correct barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).

3.5.8.7 Triple-beam balance: Calibrate the triple-beam balance before each test series, using Class S standard weights. The weights must be within ±0.5% of the standards, or the balance must be adjusted to meet these limits.

3.5.9 *Calculations*

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

3.5.9.1 Calculation of Total Formaldehyde: To determine the total formaldehyde in mg, use the following equation:

$$\text{Total mg formaldehyde} = C_d \times V \times DF$$
$$\times \frac{[g/\text{mole aldehyde}]}{[g/\text{mole DNPH derivative}]} \times 10^3 \text{ mg}/\mu g$$

where:

C_d = measured concentration of DNPH—formaldehyde derivative, $\mu g/ml$.
V = organic extract volume ml.
DF = dilution factor.

3.5.9.2 Formaldehyde concentration in stack gas.

Determine the formaldehyde concentration in the stack gas using the following equation:

$$C_f = K \text{ [total formaldehyde, mg] } V_{m(std)}$$

where:

K = 35.31 ft³/m³ if $V_{m(std)}$ is expressed in English units
= 1.00 m³/m³ if $V_{m(std)}$ is expressed in metric units.
$V_{m(std)}$ volume of gas sample a measured by dry gas meter, corrected to standard conditions, dscm (dscf).

3.5.9.3 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop are obtained from the data sheet.

3.5.9.4 Dry Gas Volume: Calculate $V_{m(std)}$ and adjust for leakage, if necessary, using the equation in section 6.3 of EPA method 5.

3.5.9.5 Volume of Water Vapor and Moisture Content: Calculate the volume of water vapor and moisture content from equations 5-2 and 5-3 of EPA method 5.

3.5.10 *Determination of Volume to be Sampled*

To determine the minimum sample volume to be collected, use the following sequence of equations.

3.5.10.1 From prior analysis of the waste feed, the concentration of formaldehyde (FORM) introduced into the combustion system can be calculated. The degree of destruction and removal efficiency that is required is used to determine the amount of FORM allowed to be present in the effluent. This amount may be expressed as:

$$\text{Max FORM Mass} = [(WF) (FORM conc) (100 - \%DRE)]/100$$

where:

WF = mass flow rate of waste feed per h, g/h (lb/h).
FORM = concentration of FORM (wt %) introduced into the combustion process.
DRE = percent Destruction and Removal Efficiency required.
Max FORM = mass flow rate (g/h [lb/]) of FORM emitted from the combustion sources.

3.5.10.2 The average discharge concentration of the FORM in the effluent gas is determined by comparing the Max FORM with the volumetric flow rate being exhausted from the source. Volumetric flow rate data are available as a result of preliminary EPA method 1–4 determinations:

$$\text{Max FORM conc} = [\text{Max FORM Mass}] / DV_{eff(std)}$$

where:

$DV_{eff(std)}$ = volumetric flow rate of exhaust gas, dscm (dscf).

FORM conc=anticipated concentration of the FORM in the exhaust gas stream, g/dscm (lb/dscf).

3.5.10.3 In making this calculation, it is recommended that a safety margin of at least ten be included.

[LDL$_{FORM}$ × 10 / FORM conc] V$_{tbc}$

where:

LDL$_{FORM}$=detectable amount of FORM in entire sampling train.

V$_{tbc}$=minimum dry standard volume to be collected at dry-gas meter.

3.5.10.4 The following analytical detection limits and DNPH Reagent Capacity (based on a total volume of 200 ml in two impingers) must also be considered in determining a volume to be sampled.

3.5.11 *Quality Control*

3.5.11.1 Sampling: See EPA Manual 600/4–77–02b for Method 5 quality control.

3.5.11.2 Analysis: The quality assurance program required for this method includes the analysis of the field and method blanks, procedure validations, and analysis of field spikes. The assessment of combustion data and positive identification and quantitation of formaldehyde are dependent on the integrity of the samples received and the precision and accuracy of the analytical methodology. Quality assurance procedures for this method are designed to monitor the performance of the analytical methodology and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.

3.5.11.2.1 Field Blanks: Field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents, methylene chloride and water, and unused DNPH reagent. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual sampling train). The probe of the blank train must be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the blank sampling train.

3.5.11.2.2 Method Blanks: A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

3.5.11.2.3 Field Spike: A field spike is performed by introducing 200 µL of the Field Spike Standard into an impinger containing 200 ml of DNPH solution. Standard impinger recovery procedures are followed and the spike is used as a check on field handling and recovery procedures. An aliquot of the field spike standard is retained in the laboratory for derivatization and comparative analysis.

3.5.12 *Method Performance*

3.5.12.1 Method performance evaluation: The expected method performance parameters for precision, accuracy, and detection limits are provided in Table 3.5–3.

Addition of a Filter to the Formaldehyde Sampling Train

As a check on the survival of particulate material through the impinger system, a filter can be added to the impinger train either after the second impinger or after the third impinger. Since the impingers are in an ice bath, there is no reason to heat the filter at this point.

Any suitable medium (e.g., paper, organic membrane) may be used for the filter if the material conforms to the following specifications:

(1) the filter has at least 95% collection efficiency (<5% penetration) for 3 µm dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986–71. Test data from the supplier's quality control program are sufficient for this purpose.

(2) the filter has a low aldehyde blank value (<0.015 mg formaldehyde/cm^2 of filter area). Before the test series, determine the average formaldehyde blank value of at least three filters (from the lot to be used for sampling) using the applicable analytical procedures.

TABLE 3.5–3.— EXPECTED METHOD PERFORMANCE FOR FORMALDEHYDE

Parameter	Preci-sion [1]	Accura-cy [2]	Detection limits [3]
Matrix: Dual trains.	±15% RPD	±20%	1.5×10^{-7} lb/ft^3 (1.8 ppbv).

[1] Relative percent difference limit for dual trains.
[2] Limit for field spike recoveries.
[3] The lower reporting limit having less than 1% probability of false positive detection.

Recover the exposed filter into a separate clean container and return the container over ice to the laboratory for analysis. If the filter is being analyzed for formaldehyde, the filter may be recovered into a container or DNPH reagent for shipment back to the laboratory. If the filter is being examined for the presence of particulate material, the filter may be recovered into a clean dry container and returned to the laboratory.

3.6 *Analysis for Aldehydes and Ketones by High Performance Liquid Chromatography (HPLC) (Method 0011A)*

3.6.1 *Scope and Application*

3.6.1.1 Method 0011A covers the determination of free formaldehyde in the aqueous samples and leachates and derived aldehydes/ketones collected by method 0011.

Compound name	CAS No.[1]
Formaldehyde	50–00–0
Acetaldehyde	75–07–0

[1] Chemical Abstract Services Registry Number

3.6.1.2 Method 0011A is a high performance liquid chromatographic (HPLC) method optimized for the determination of formaldehyde and acetaldehyde in aqueous environmental matrices and leachates of solid samples and stack samples collected by

method 0011. When this method is used to analyze unfamiliar sample matrices, compound identification should be supported by at least one additional qualitative technique. A gas chromatograph/mass spectrometer (GC/MS) may be used for the qualitative confirmation of results from the target analytes, using the extract produced by this method.

3.6.1.3 The method detection limits (MDL) are listed in Tables 3.6–1 and 3.6–2. The MDL for a specific sample may differ from that listed, depending upon the nature of interferences in the sample matrix and the amount of sample used in the procedure.

3.6.1.4 The extraction procedure for solid samples is similar to that specified in method 1311 (1). Thus, a single sample may be extracted to measure the analytes included in the scope of other appropriate methods. The analyst is allowed the flexibility to select chromatographic conditions appropriate for the simultaneous measurement of contaminations of these analytes.

TABLE 3.6–1.—HIGH PERFORMANCE LIQUID CHROMATOGRAPHY CONDITIONS AND METHOD DETECTION LIMITS USING SOLID SORBENT EXTRACTION

Analyte	Retention time (minutes)	MDL (µg/L) [1]
Formaldehyde	7.1	7.2

HPLC conditions: Reverse phase C18 column, 4.6 × 250 mm; isocratic elution using methanol/water (75:25, v/v); flow rate 1.0 mL/min.; detector 360 nm.
[1] After correction for laboratory blank.

TABLE 3.6–2.—HIGH PERFORMANCE LIQUID CHROMATOGRAPHY CONDITIONS AND METHOD DETECTION LIMITS USING METHYLENE CHLORIDE EXTRACTION

Analyte	Retention time (minutes)	MDL (µg/L) [1]
Formaldehyde	7.1	7.2
Acetaldehyde	8.6	171 [1]

HPLC conditions: Reverse phase C18 column, 4.6 × 250 mm; isocratic elution using methanol/water (75:25, v/v); flow rate 1.0 mL/min.; detector 360 nm.
[1] These values include reagent blank concentrations of approximately 13 µg/L formaldehyde and 130 µg/L acetaldehyde.

3.6.1.5 This method is restricted to use by, or under the supervision of analysts experienced in the use of chromatography and in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

3.6.1.6 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current

awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.

3.6.1.7 Formaldehyde has been tentatively classified as a known or suspected, human or mammalian carcinogen.

3.6.2 Summary of Method

3.6.2.1 Environmental Liquids and Solid Leachates.

3.6.2.1.1 For wastes comprised of solids or for aqueous wastes containing significant amounts of solid material, the aqueous phase, if any, is separated from the solid phase and stored for later analysis. If necessary, the particle size of the solids in the waste is reduced. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase of the waste. A special extractor vessel is used when testing for volatiles. Following extraction, the aqueous extract is separated from the solid phase by filtration employing 0.6 to 0.8 μm glass fiber filters.

3.6.2.1.2 If compatible (i.e., multiple phases will not form on combination), the initial aqueous phase of the waste is added to the aqueous extract, and these liquids are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume weighted average concentration.

3.6.2.1.3 A measured volume of aqueous sample or an appropriate amount of solids leachate is buffered to pH 5 and derivatized with 2,4-dinitrophenylhydrazine (DNPH), using either the solid sorbent or the methylene derivatization/extraction option. If the solid sorbent option is used, the derivative is extracted using solid sorbent cartridges, followed by elution with ethanol. If the methylene chloride option is used, the derivative is extracted with methylene chloride. The methylene chloride extracts are concentrated using the Kuderna-Danish (K–D) procedure and solvent exchanged into methanol prior to HPLC analysis. Liquid chromatographic conditions are described which permit the separation and measurement of formaldehyde in the extract by absorbance detection at 360 nm.

3.6.2.2 Stack Gas Samples Collected by Method 0011.

3.6.2.2.1 The entire sample returned to the laboratory is extracted with methylene chloride and the methylene chloride extract is brought up to a known volume. An aliquot of the methylene chloride extract is solvent exchanged and concentrated or diluted as necessary.

3.6.2.2.2 Liquid chromatographic conditions are described that permit the separation and measurement of formaldehyde in the extract by absorbance detection at 360 nm.

3.6.3 Interferences

3.6.3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/ or elevated baselines in the chromatograms. All of these materials must be routinely

demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks.

3.6.3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing with hot water, and rinses with tap water and distilled water. It should then be drained, dried. and heated in a laboratory oven at 130°C for several hours before use. Solvent rinses with methanol may be substituted for the oven heating. After drying and cooling, glassware should be stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.6.3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.6.3.2 Analysis for formaldehyde is especially complicated by its ubiquitous occurrence in the environment.

3.6.3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. No interferences have been observed in the matrices studied as a result of using solid sorbent extraction as opposed to liquid extraction. If interferences occur in subsequent samples, some additional cleanup may be necessary.

3.6.3.4 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although the HPLC conditions described allow for a resolution of the specific compounds covered by this method, other matrix components may interfere.

3.6.4 Apparatus and Materials

3.6.4.1 Reaction vessel—250 ml Florence flask.

3.6.4.2 Separatory funnel—205 ml, with Teflon stopcock.

3.6.4.3 Kuderna-Danish (K–D) apparatus.

3.6.4.3.1 Concentrator tube—10 ml graduated (Kontes K–570050–1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

3.6.4.3.2 Evaporation flask—500 ml (Kontes K–570001–500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

3.6.4.3.3 Snyder column—Three ball macro (Kontes K–503000–0121 or equivalent).

3.6.4.3.4 Snyder column—Two ball macro (Kontes K–569001–0219 or equivalent).

3.6.4.3.5 Springs—½ inch (Kontes K–662750 or equivalent).

3.6.4.4 Vials—10, 25 ml, glass with Teflon lined screw caps or crimp tops.

3.6.4.5 Boiling chips—Solvent extracted with methylene chloride, approximately 10/ 40 mesh (silicon carbide or equivalent).

3.6.4.6 Balance—Analytical, capable of accurately weighing to the nearest 0.0001 g.

3.6.4.7 pH meter—Capable of measuring to the nearest 0.01 units.

3.6.4.8 High performance liquid chromatograph (modular).

3.6.4.8.1 Pumping system—Isocratic, with constant flow control capable of 1.00 ml/min.

3.6.4.8.2 High pressure injection valve with 20 μL loop.

3.6.4.8.3 Column—250 mm $\times$ 4.6 mm ID, 5 μm particle size, C18 (or equivalent).

3.6.4.8.4 Absorbance detector—360 nm.

3.6.4.8.5 Strip-chart recorder compatible with detector—Use of a data system for measuring peak areas and retention times is recommended.

3.6.4.9 Glass fiber filter paper.

3.6.4.10 Solid sorbent cartridges—Packed with 500 mg C18 (Baker or equivalent).

3.6.4.11 Vacuum manifold—Capable of simultaneous extraction of up to 12 samples (Supelco or equivalent).

3.6.4.12 Sample reservoirs—60 ml capacity (Supelco or equivalent).

3.6.4.13 Pipet—Capable of accurately delivering 0.10 ml solution (Pipetman or equivalent).

3.6.4.14 Water bath—Heated, with concentric ring cover, capable of temperature control (($\pm$) 2 °C). The bath should be used under a hood.

3.6.4.15 Volumetric Flasks—250 or 500 ml.

3.6.5 Reagents

3.6.5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

3.6.5.2 Organic-free water—All references to water in this method refer to organic-free reagent water, as defined in chapter I SW–846.

3.6.5.3 Methylene chloride, CH_2Cl_2—HPLC grade or equivalent.

3.6.5.4 Methanol, CH_3OH—HPLC grade or equivalent.

3.6.5.5 Ethanol (absolute), CH_3CH_2OH—HPLC grade or equivalent.

3.6.5.6 2,4-Dinitrophenylhydrazine (DNPH) (70% (W/W)), $[2,4-(O_2N)_2C_6H_3]$ $NHNH_2$, in organic-free reagent water.

3.6.5.7 Formalin (37.6 percent (w/w)), formaldehyde in organic-free reagent water.

3.6.5.8 Acetic acid (glacial), CH_3CO_2H.

3.6.5.9 Sodium hydroxide solutions NaOH, 1.0 N and 5 N.

3.6.5.10 Sodium chloride, NaCl.

3.6.5.11 Sodium sulfite solution, Na_2SO_3, 0.1 M.

3.6.5.12 Hydrochloric Acid, HCl, 0.1 N.

3.6.5.13 Extraction fluid—Dilute 64.3 ml of 1.0 N NaOH and 5.7 ml glacial acetic acid to 900 ml with organic-free reagent water. Dilute to 1 liter with organic-free reagent water. The pH should be 4.93 $\pm$0.02.

3.6.5.14 Stock standard solutions.

3.6.5.14.1 Stock formaldehyde (approximately 1.00 mg/ml)—Prepare by diluting 265 μl formalin to 100 ml with organic-free reagent water.

3.6.5.14.1.1 Standardization of formaldehyde stock solution—Transfer a 25 ml aliquot of a 0.1 M Na_2SO_3 solution to a beaker and record the pH. Add a 25.0 ml aliquot of the formaldehyde stock solution (section 3.6.5.14.1) and record the pH. Titrate

this mixture back to the original pH using 0.1 N HCl. The formaldehyde concentration is calculated using the following equation:

Concentration (mg/ml) = 30.03×(N HCl)×(ml HCl) 25.0

where:

N HCl = Normality of HCl solution used.
ml HCl = ml of standardized HCl solution used.
30.03 = MW of formaldehyde.

3.6.5.14.2 Stock formaldehyde and acetaldehyde—Prepare by adding 265 μL formalin and 0.1 g acetaldehyde to 90 ml of water and dilute to 100 mL. The concentration of acetaldehyde in this solution is 1.00 mg/mL. Calculate the concentration of formaldehyde in this solution using the results of the assay performed in section 3.6.5.14.1.1.

3.6.5.14.3 Stock standard solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

3.6.5.15 Reaction Solutions.

3.6.5.15.1 DNPH (1.00 μg/L)—Dissolve 142.9 mg of 70% (w/w) reagent in 100 ml absolute ethanol. Slight heating or sonication may be necessary to effect dissolution.

3.6.5.15.2 Acetate buffer (5 N) Prepare by neutralizing glacial acetic acid to pH 5 with 5 N NaOH solution. Dilute to standard volume with water.

3.6.5.15.3 Sodium chloride solution (saturated) Prepare by mixing of the reagent grade solid with water.

3.6.6 *Sample Collection, Preservation, and Handling.*

3.6.6.1 See the introductory material to this Chapter, Organic Analytes, section 4.1 of SW-846.

3.6.6.2 Environmental liquid and leachate samples must be refrigerated at 4 °C, and must be derivatized within 5 days of sample collection and analyzed within 3 days of derivatization.

3.6.6.3 Stack gas samples collected by Method 0011 must be refrigerated at 4 °C. It is recommended that samples be extracted within 30 days of collection and that extracts be analyzed within 30 days of extraction.

3.6.7 *Procedure*

3.6.7.1 Extraction of Solid Samples.

3.6.7.1.1 All solid samples should be homogeneous. When the sample is not dry, determine the dry weight of the sample, using a representative aliquot.

3.6.7.1.1.1 Determination of dry weight—In certain cases, sample results are desired based on a dry weight basis. When such data is desired, or required, a portion of sample for dry weight determination should be weighed out at the same time as the portion used for analytical determination.

Warning: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated hazardous waste sample.

3.6.7.1.1.2 Immediately after weighing the sample for extraction, weigh 5–10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105 °C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

3.6.7.1.2 Measure 25 g of solid into a 500 ml bottle with a Teflon lined screw cap or crimp top, and add 500 ml of extraction fluid (section 3.6.5.13). Extract the solid by rotating the bottle at approximately 30 rpm for 18 hours. Filter the extract through glass fiber paper and store in sealed bottles at 4 °C. Each ml of extract represents 0.050 g solid.

3.6.7.2 Cleanup and Separation.

3.6.7.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedures recommended in this method have been used for the analysis of various sample types. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of formaldehyde is no less than 85% of recoveries specified in Table 3.6–3. Recovery may be lower for samples which form emulsions.

3.6.7.2.2 If the sample is not clean, or the complexity is unknown, the entire sample should be centrifuged at 2500 rpm for 10 minutes. Decant the supernatant liquid from the centrifuge bottle, and filter through glass fiber filter paper into a container which can be tightly sealed.

3.6.7.3 Derivatization.

3.6.7.3.1 For aqueous samples, measure a 50 to 100 ml aliquot of the sample. Quantitatively transfer the sample aliquot to the reaction vessel (section 3.6.4.1).

3.6.7.3.2 For solid samples, 1 to 10 ml of leachate (section 3.6.7.1) will usually be required. The amount used for a particular sample must be determined through preliminary experiments.

TABLE 3.6–3.—SINGLE OPERATOR ACCURACY AND PRECISION USING SOLID SORBENT EXTRACTION.

Analyte	Matrix type	Average percent recovery	Standard deviation percent	Spike range (μg/L)	No. of analyses
Formaldehyde	Reagent water	86	9.4	15–1430	39
	Final effluent	90	11.0	46.8–1430	16
	Phenol formaldehyde sludge	93	12.0	457–1430	15

Note: For all reactions, the total volume of the aqueous layer should be adjusted to 100 ml with water.

3.6.7.3.3 Derivatization and extraction of the derivative can be accomplished using the solid sorbent (section 3.6.7.3.4) or methylene chloride option (section 3.6.7.3.5).

3.6.7.3.4 Solid Sorbent Option.

3.6.7.3.4.1 Add 4 ml of acetate buffer and adjust the pH to 5.0±0.1 with glacial acetic acid or 5 N NaOH. Add 6 ml of DNPH reagent, seal the container, and place on a wrist-action shaker for 30 minutes.

3.6.7.3.4.2 Assemble the vacuum manifold and connect to a water aspirator or vacuum pump. Assemble solid sorbent cartridges containing a minimum of 1.5 g of C18 sorbent, using connectors supplied by the manufacturer, and attach the sorbent train to the vacuum manifold. Condition each cartridge by passing 10 ml dilute acetate buffer (10 ml 5 N acetate buffer dissolved in

250 ml water), through the sorbent cartridge train.

3.6.7.3.4.3 Remove the reaction vessel from the shaker and add 10 ml saturated NaCl solution to the vessel.

3.6.7.3.4.4 Add the reaction solution to the sorbent train and apply a vacuum so that the solution is drawn through the cartridges at a rate of 3 to 5 ml/min. Release the vacuum after the solution has passed through the sorbent.

3.6.7.3.4.5 Elute each cartridge train with approximately 9 ml of absolute ethanol, directly into a 10 ml volumetric flask. Dilute the solution to volume with absolute ethanol, mixed thoroughly, and place in a tightly sealed vial until analyzed.

3.6.7.3.5 Methylene Chloride Option.

3.6.7.3.5.1 Add 5 m of acetate buffer and adjust the pH to 5.0±0.5 with glacial acetic acid or 5 N NaOH. Add 10 ml of DNPH

reagent, seal the container, and place on a wrist-action shaker for 1 hour.

3.6.7.3.5.2 Extract the solution with three 20 ml portions of methylene chloride, using a 250 ml separatory funnel, and combine the methylene chloride layers. If an emulsion forms upon extraction, remove the entire emulsion and centrifuge at 2000 rpm for 10 minutes. Separate the layers and proceed with the next extraction.

3.6.7.3.5.3 Assemble a Kuderna-Danish (K–D) concentrator by attaching a 10 ml concentrator tube to a 500 ml evaporator flask. Wash the K–D apparatus with 25 ml of extraction solvent to complete the quantitative transfer.

3.6.7.3.5.4 Add one to two clean boiling chips to the evaporative flask and attach a three ball Snyder column. Preset the Snyder column by adding about 1 ml methylene chloride to the top. Place the K–D apparatus

on a hot water bath (80–90 °C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10–15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 10 ml, remove the K–D apparatus and allow it to drain and cool for a least 10 min.

3.6.7.3.5.5 Prior to liquid chromatographic analysis, the solvent must be exchanged to methanol. The analyst must ensure quantitative transfer of the extract concentrate. The exchange is performed as follows:

3.6.7.3.5.5.1 Following K–D concentration of the methylene chloride extract to <10 ml using the macro Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

3.6.7.3.5.5.2 Momentarily remove the Snyder column, add 5 ml of the methanol, a new glass bed, or boiling chip, and attach the micro Snyder column. Concentrate the extract using 1 ml of methanol to prewet the Snyder column. Place the K–D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches <5 ml, remove the K–D apparatus and allow it to drain and cool for at least 10 minutes.

3.6.7.3.5.5.3 Remove the Snyder column and rinse the flask and its lower joint with 1–2 ml of methanol and add to concentrator tube. A 5-ml syringe is recommended for this operation. Adjust the extract volume to 10 ml. Stopper the concentrator tube and store refrigerated at 4 °C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon-lined screw cap or crimp top. Proceed with liquid chromatographic analysis if further cleanup is not required.

3.6.7.4 Extraction of Stack Gas Samples Collected by Method 0011.

3.6.7.4.1 Measure the aqueous volume of the sample prior to extraction (for moisture determination in case the volume was not measured in the field). Pour the sample into a separatory funnel and drain the methylene chloride into a volumetric flask.

3.6.7.4.2 Extract the aqueous solution with two or three aliquots of methylene chloride. Add the methylene chloride extracts to the volumetric flask.

3.6.7.4.3 Fill the volumetric flask to the line with methylene chloride. Mix well and remove an aliquot.

3.6.7.4.4 If high levels of formaldehyde are present, the extract can be diluted with mobile phase, otherwise the extract must be solvent exchanged as described in section 3.6.7.5.3.3. If low levels of formaldehyde are present, the sample should be concentrated during the solvent exchange procedure.

3.6.7.5 Chromatographic Conditions.

Column.....................	C18, 250 mm×4.6 mm ID, 5 μm particle size
Mobile Phase	methanol/water, 75:25 (v/v), isocratic
Flow Rate	1.0 ml/min
UV Detector.............	360 nm
Injection Volume	20 μl

3.6.7.6 Calibration.

3.6.7.6.1 Establish liquid chromatographic operating parameters to produce a retention time equivalent to that indicated in Table 3.6–1 for the solid sorbent options, or in Table 3.6–2 for methylene chloride option. Suggested chromatographic conditions are provided in section 3.6.7.5. Prepare derivatized calibration standards according to the procedure in section 3.6.7.6.1.1. Calibrate the chromatographic system using the external standard technique (section 3.6.7.6.1.2).

3.6.7.6.1.1 Preparation of calibration standards.

3.6.7.6.1.1.1 Prepare calibration standard solutions of formaldehyde and acetaldehyde in water from the stock standard (section 3.6.5.14.2). Prepare these solutions at the following concentrations (in μg/ml) by serial dilution of the stock standard solution: 50, 20, 10. Prepare additional calibration standard solutions at the following concentrations, by dilution of the appropriate 50, 20, or 10 μg/ml standard: 5, 0.5, 2, 0.2, 1, 0.1.

3.6.7.6.1.1.2 Process each calibration standard solution through the derivatization option used for sample processing (section 3.6.7.3.4 or 3.6.7.3.5).

3.6.7.6.1.2 External standard calibration procedure.

3.6.7.6.1.2.1 Analyze each derivatized calibration standard using the chromatographic conditions listed in Tables 3.6–1 and 3.6–2, and tabulate peak area against concentration injected. The results may be used to prepare calibration curves for formaldehyde and acetaldehyde.

3.6.7.6.1.2.2 The working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the previously established responses by more the 10%, the test must be repeated using a fresh calibration standard after it is verified that the analytical system is in control. Alternatively, a new calibration curve may be prepared for that compound. If an autosampler is available, it is convenient to prepare a calibration curve daily by analyzing standards along with test samples.

3.6.7.7 Analysis.

3.6.7.7.1 Analyze samples by HPLC, using conditions established in section 3.6.7.6.1. Tables 3.6–1 and 3.6–2 list the retention times and MDLs that were obtained under these conditions. Other HPLC columns, chromatographic conditions, or detectors may be used if the requirements for section 3.6.8.1 are met, or if the data are within the limits described in Tables 3.6–1 and 3.6–2.

3.6.7.7.2 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over

the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of the chromatograms.

3.6.7.7.3 If the peak area exceeds the linear range of the calibration curve, a smaller sample volume should be used. Alternatively, the final solution may be diluted with ethanol and reanalyzed.

3.6.7.7.4 If the peak area measurement is prevented by the presence of observed interferences, further cleanup is required. However, none of the 3600 method series have been evaluated for this procedure.

3.6.7.8 Calculations.

3.6.7.8.1 Calculate each response factor as follows (mean value based on 5 points):

$$RF = \frac{\text{concentration of standard}}{\text{area of the signal}}$$

$$\text{mean} = RF = \overline{RF} = \frac{(\sum_{i}^{5} RF_i)}{5}$$

3.6.7.8.2 Calculate the concentration of formaldehyde and acetaldehyde as follows:

$\mu g/ml = (\overline{RF})$ (area of signal) (concentration factor)

where:

$$\text{concentration factor} = \frac{\text{Final Volume of Extract}}{\text{Initial Extract Volume}}$$

Note: For solid samples, a dilution factor must be included in the equation to account for the weight of the sample used.

3.6.7.8.3 Calculate the total weight of formaldehyde in the stack gas sample as follows:

total $\mu g/ml = (RF)$ (area of signal) (concentration factor)

where:

$$\text{concentration factor} = \frac{\text{Final Volume of Extract}}{\text{Initial Extract Volume}}$$

3.6.8 *Quality Control*

3.6.8.1 Refer to Chapter One of SW–846 for guidance on quality control procedures.

3.6.9 *Method Performance*

3.6.9.1 The MDL concentrations listed in Table 3.6–1 were obtained using organic-free water and solid sorbent extraction. Similar results were achieved using a final effluent and sludge leachate. The MDL concentrations listed in Table 3.6–2 were obtained using

organic-free water and methylene chloride extraction. Similar results were achieved using representative matrices.

3.6.9.2 This method has been tested for linearity of recovery from spiked organic-free water and has been demonstrated to be applicable over the range from $2 \times MDL$ to $200 \times MDL$.

3.6.9.3 In a single laboratory evaluation using several spiked matrices, the average recoveries presented in Tables 3.6–3 and 3.6–

4 were obtained using solid sorbent and methylene chloride extraction, respectively. The standard deviations of the percent recovery are also included in Tables 3.6–3 and 3.6–4.

3.6.9.4 A representative chromatogram is presented in Figure 3.6–1.

3.6.10 *References*

1. Federal Register, 1986, 51, 40643–40652; November 7.

2. EPA Methods 6010, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, Test Methods for Evaluating Solid Waste: Physical/ Chemical Methods. SW–846, Third Edition. September 1988. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC 20460.

TABLE 3.6–4.— SINGLE OPERATOR ACCURACY AND PRECISION USING METHYLENE CHLORIDE EXTRACTION

| Analyte	Matrix type	Average percent recovery (x)	Standard deviation percent (p)	Spike range (µg/L)	No. of analyses
Formaldehyde	Reagent Water	91	2.5	50–1000	9
	Groundwater	92.5	8.2	50	6
	Liquids	69.6	16.3	250	12
Acetaldehyde	Reagent Water	60.3	3.2	50–1000	9
	Groundwater	63.6	10.9	50	12
	Liquids (2 types)	44.0	20.2	250	12
	Solids	58.4	2.7	0.10–1.0ª	12

* Spike range in units of mg/g.
x = Average recovery expected for this method.
p = Average standard deviation expected for this method.

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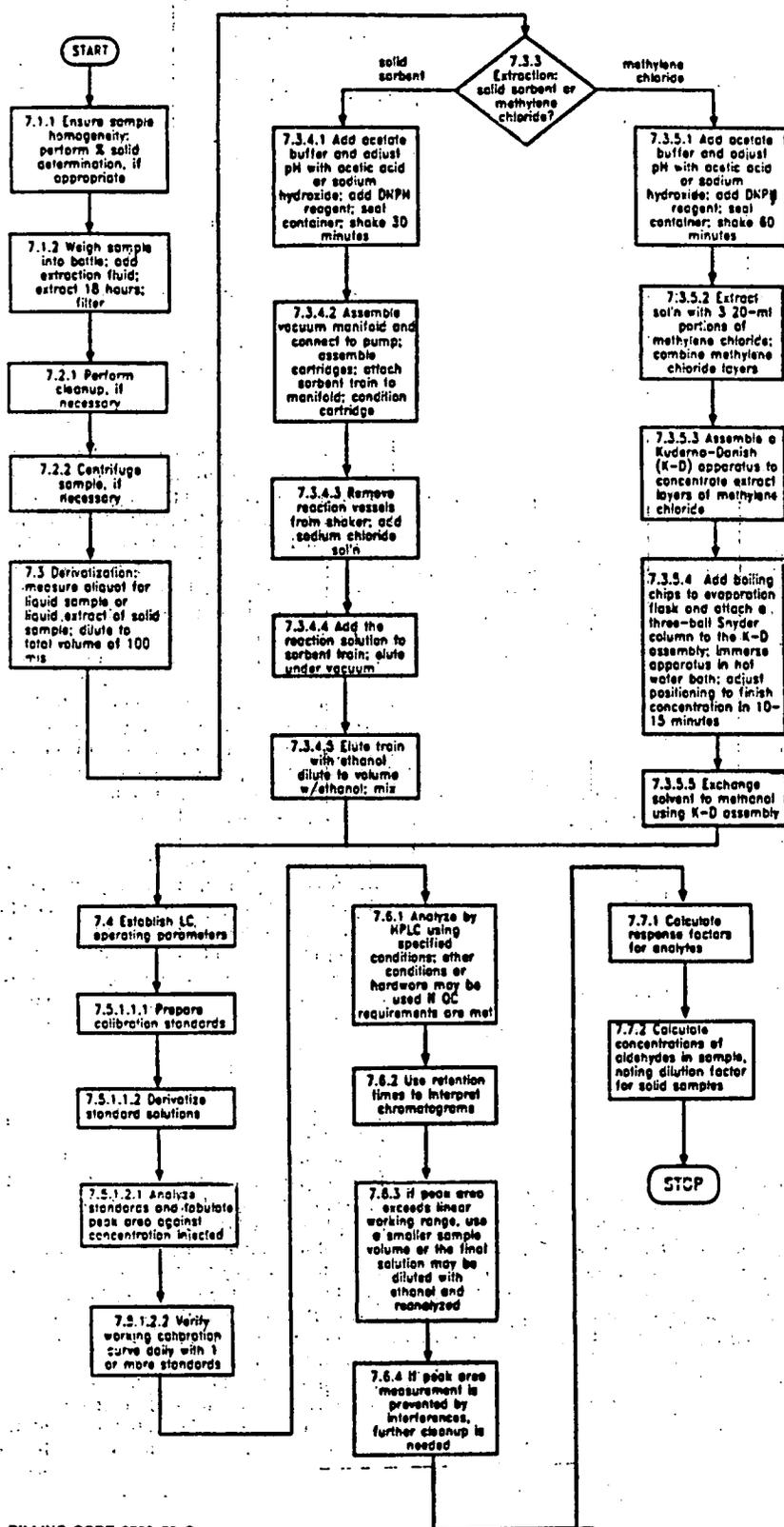FIGURE 3.6-1

REPRESENTATIVE CHROMATOGRAM OF A 50 µg/L SOLUTION OF FORMALDEHYDE
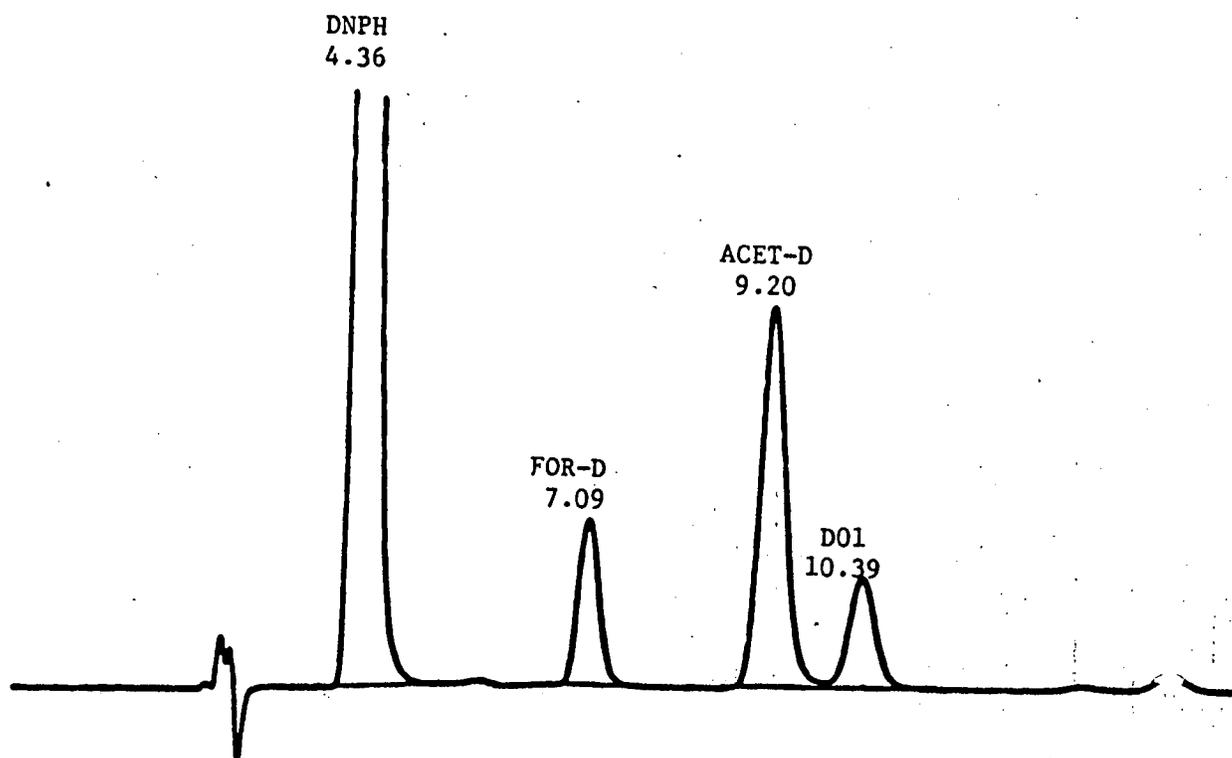
FOR-D = **Formaldehyde derivative**
ACET-D = **Acetaldehyde derivative**

FIGURE 3.6-2

FORMALDEHYDE BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

SECTION 4.0 PROCEDURE FOR ESTIMATING THE TOXICITY EQUIVALENCY OF CHLORINATED DIBENZO-P-DIOXIN AND DIBENZOFURAN CONGENERS

PCDDs and PCDFs must be determined using the method given in section 3.4 of this document. In this method, individual congeners or homologues [1] are measured and then summed to yield a total PCDD/PCDF value. No toxicity factors are specified in the method to compute risks from such emissions.

For the purpose of estimating risks posed by emissions from boilers and industrial furnaces, however, specific congeners and homologues must be measured using the specified method and then multiplied by the assigned toxicity equivalence factors (TEFs), using procedures described in "Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzofurans (CDDs and CDFs) and 1989 Update," EPA/625/3–89/016, March 1989. The resulting 2,3,7,8–TCDD equivalents value is used in the subsequent risk calculations and modeling efforts as discussed in the BIF final rule.

The procedure for calculating the 2,3,7,8–TCDD equivalent is as follows:

1. Using method 23, determine the concentrations of 2,7,3,8-congeners of various PCDDs and PCDFs in the sample.

2. Multiply the congener concentrations in the sample by the TEF listed in Table 4.0–1 to express the congener concentrations in terms of 2,3,7,8–TCDD equivalent. Note that congeners not chlorinated at 2,3,7, and 8 positions have a zero toxicity factor in this table.

3. Add the products obtained in step 2, to obtain the total 2,3,7,8–TCDD equivalent in the sample.

Sample calculations are provided in EPA document No. EPA/625/3–89/016, March 1989, which can be obtained from the EPA, ORD Publications Office, Cincinnati, Ohio (Phone no. 513–569–7562).

TABLE 4.0–1.—2,3,7,8–TCDD TOXICITY EQUIVALENCE FACTORS (TEFs) [1]

Compound	I-TEFs, 89
Mono-, Di-, and TriCDDs	0
2,3,7,8–TCDD	1
Other TCDDs	0
2,3,7,8–PeCDD	0.5
Other PeCDDs	0
2,3,7,8–HxCDD	0.1
Other HxCDDs	0
2,3,7,8–HpCDD	0.01

[1] The term "congener" refers to any one particular member of the same chemical family; e.g., there are 75 congeners of chlorinated dibenzo-p-dioxins. The term "homologue" refers to a group of structurally related chemicals that have the same degree of chlorination. For example, there are eight homologues of CDs, monochlorinated through octachlorinated. Dibenzo-p-dioxins and dibenzofurans that are chlorinated at the 2,3,7, and 8 positions are denoted as "2378" congeners, except when 2,3,7,8–TCDD is uniquely referred to: e.g., 1,2,3,7,8–PeCDF and 2,3,4,7,8–PeCDF are both referred to as "2378-PeCDFs."

TABLE 4.0–1.—2,3,7,8–TCDD TOXICITY EQUIVALENCE FACTORS (TEFs) [1]—Continued

Compound	I-TEFs, 89
Other HpCDDs	0
OCDD	0.001
Mono-, Di-, and TriCDFs	0
2,3,7,8–TCDF	0.1
Other TCDFs	0
1,2,3,7,8–PeCDF	0.05
2,3,4,7,8–PeCDF	0.5
Other PeCDFs	0
2378–HxCDFs	0.1
Other HxCDFs	0
2378–HpCDFs	0.01
Other HpCDFs	0
OCDF	0.001

Reference: Adapted from NATO/CCMS, 1988a.
[1] Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzofurans (CDDs and CDFs) 1989 Update EPA/625/3–89/016, March 1989.

SECTION 5.0 HAZARDOUS WASTE COMBUSTION AIR QUALITY SCREENING PROCEDURE

The HWCAQSP is a combined calculation/ reference table approach for conservatively estimating short-term and annual average facility impacts for stack emissions. The procedure is based on extensive short-term modeling of 11 generic source types and on a set of adjustment factors for estimating annual average concentrations from short-term concentrations. Facility impacts may be determined based on the selected worst-case stack or on multiple stacks, in which the impacts from each stack are estimated separately and then added to produce the total facility impact.

This procedure is most useful for facilities with multiple stacks, large source-to-property boundary distances, and complex terrain between 1 and 5 km from the facility. To ensure a sufficient degree of conservatism, the HWCAQSP may not be used if any of the five screening procedure limitations listed below are true:

• The facility is located in a narrow valley less than 1 km wide;
• The facility has a stack taller than 20 m and is located such that the terrain rises to the stack height within 1 km of the facility;
• The facility has a stack taller than 20 m and is located within 5 km of the shoreline of a large body of water;
• The facility property line is within 200 m of the stack and the physical stack height is less than 10 m; or
• On-site receptors are of concern, and stack height is less than 10 m.

If any of these criteria are met or the Director determines that this procedure is not appropriate, then detailed site-specific modeling or modeling using the "Screening Procedures for Estimating the Air Quality Impact of Stationary Sources," EPA –450/4– 88–010, Office of Air Quality Planning and Standards, August 1988, is required. Detailed site-specific dispersion modeling must conform to the EPA "Guidance on Air Quality Models (Revised)", EPA 450/2–78–027R, Office of Air Quality Planning and Standards,

Research Triangle Park, North Carolina, July 1986. This document provides guidance on both the proper selection and regulatory application of air quality models.

Introduction

The Hazardous Waste Combustion Air Quality Screening Procedure (HWCAQSP) (also referred to hereafter as "the screening procedure" or "the procedure") provides a quick, easy method for estimating maximum (hourly) and annual average ambient air impacts associated with the combustion of hazardous waste. The methodology is conservative in nature and estimates dispersion coefficients [1] based on facility-specific information.

The screening procedure can be used to determine emissions limits at sites where the nearest meteorological (STAR) station is not representative of the meteorology at the site. If the screen shows that emissions from the site are adequately protective, then the need to collect site-specific meteorological data can be eliminated.

The screening procedure is generally most helpful for facilities meeting one or more of the following conditions:

• Multiple stacks with substantially different release specifications (e.g., stack heights differ by >50 percent, exit temperatures differ by >50 °K, or the exit flow rates differ by more than a factor of 2).

• Terrain located between 1 km and 5 km from the site increases in elevation by more than the physical height of the shortest stack (i.e., the facility is located in complex terrain), or

• Significant distance between the facility's stacks and the site boundary [guidance on determining whether a distance is "significant" is provided in Step 6(B) of the procedure].

Steps 1 through 9 of the screening procedure present a simplified method for determining emissions based on the use of the "worst-case" stack. If the simplified method shows that desired feed rates result in emissions that exceed allowable limits for one or more pollutants, a refined analysis to examine the emissions from each stack can be conducted. This multiple-stack method is presented in Step 10.

The steps involved in screening methodology are as follows:

Step 1. Define Source Characteristics

Step 2. Determine the Applicability of the Screening Procedure

Step 3. Select the Worst-Case Stack

Step 4. Verify Good Engineering Practice (GEP) Criteria

Step 5. Determine the Effective Stack Height and Terrain-Adjusted Effective Stack Height

Step 6. Classify the Site as Urban or Rural

Step 7. Determine Maximum Dispersion Coefficients

Step 8. Estimate Maximum Ambient Air Concentrations

[1] The term dispersion coefficient refers to the change in ambient air concentration ($\mu g/m^3$) resulting from a source with an emission rate of 1 g/sec.

Step 9. Determine Compliance With
   Regulatory Limits
Step 10. Multiple Stack Method

Step 1: Define Source Characteristics

Provide the following source data: [a]

Stack Data:	Stack No. 1	Stack No. 2	Stack No. 3
Physical stack height (m)			
Exhaust temperature (°K).................			
Flow rate (m³/sec)..........			

Nearby Building Dimensions

Consider all buildings within five building heights or five maximum projected widths of the stack(s). For the building with the greatest height, fill in the spaces below.
Building Height (m) ————————
Maximum projected building width (m) ———

Nearby Terrain Data

Determine maximum terrain rise for the following three distance ranges from the facility (not required if the highest stack is less than 10 m in height):

———————(m)———————(m)————————(m)
  0–0.5 km   0–2.5 km   0–5 km

Distance from facility to nearest shoreline (km) ————————————————
Valley width (km) ————————————

Step 2: Determine the Applicability of the Screening Procedure

Fill in the following data:

	Yes	No
Is the facility in a valley < km in width?......................................		
Is the terrain rise within 1 km of the facility greater than the physical stack height of the tallest stack? (Only applies to stacks ≥ 20 meters in height)		
Is the distance to the nearest shoreline <5 km? (Only applies to facilities with stacks ≥ 20 meters in height)		
For the building listed in Step 1, is the closest property boundary <5 times the building height or <5 times the maximum projected building width? (Only applies to facilities with a stack height <2.5 times the building height)		

If the answer is "no" to all the preceding questions, then the HWCAQSP is acceptable. If the answer to any question is "yes", the procedure is not acceptable.

Step 3: Select the Worst-Case Stack

If the facility has several stacks, a worst-case stack must be chosen to conservatively represent release conditions at the facility. Follow the steps below to identify the worst-case stack.

Apply the following equation to each stack:

$$K = HVT$$

where:

K = an arbitrary parameter accounting for the relative influence of the stack height and plume rise.
H = Physical stack height (m)
V = Flow rate (m³/sec)
T = Exhaust temperature (°K)

Complete the following table to compute the "K" value for each stack:

Stack No.	Stack height (m)	×	Flow rate (m³/sec)	×	Exit temp (°K)	=	K
1............................	————————	×	———————	×	———————	=	————————
2............................	————————	×	———————	×	———————	=	————————
3............................	————————	×	———————	×	———————	=	————————

Select the stack with the lowest "K" value. This is the worst-case stack that will be used for Steps 4 through 9.

Worst-Case Stack is identified as Stack No.
————

Step 4: Verify Good Engineering Practice (GEP) Criteria

Confirm that the selected worst-case stack meets Good Engineering Practice (GEP) criteria. The stack height to be used in the subsequent steps of this procedure must not be greater than the maximum GEP. Maximum and minimum GEP stack heights are defined as follows:

CEP (minimum) = $H + (1.5 \times L)$
GEP (maximum) = greater of 65 m or
   $H + (1.5 \times L)$

where:

H = height of the building selected in Step 1 measured from ground level elevation at the base of the stack
L = the lesser dimension of the height or projected width of the building selected in Step 1

Record the following data for the worst-case stack:

Stack height (m) = ————————
H(m) = ————————
L(m) = ————————

Then compute the following:

GEP (minimum) (m) = ————————
GEP (maximum) (m) = ————————

• If the physical height of the worst-case stack exceeds the maximum GEP, then use the maximum GEP stack height for the subsequent steps of this analysis;
• If the physical height of the worst-case stack is less than the minimum GEP, then use generic source number 11 as the selected source for further analysis and proceed directly to Step 6;
• If the physical height of the worst-case stack is between the minimum and maximum GEP, then use the actual physical stack height for the subsequent steps of this analysis.

Step 5: Determine the Effective Stack Height and the Terrain-Adjusted Effective Stack Height (TAESH)

The effective stack height is an important factor in dispersion modeling. The effective stack height is the physical height of the stack plus plume rise. As specified in Step 4, the stack height used to estimate the effective stack height must not exceed GEP requirements. Plume rise is a function of the stack exit gas temperature and flow rate.

In this analysis, the effective stack height is used to select the generic source that represents the dispersion characteristics of the facility. For facilities located in flat

terrain and for all facilities with worst-case stacks less than or equal to 10 meters in height, generic source numbers are selected strictly on the basis of effective stack height. In all other cases, the effective stack height is further adjusted to take into account the terrain rise near the facility. This "terrain-adjusted effective stack height" (TAESH) is then used to select the generic source number that represents the dispersion characteristics of the facility. Follow the steps below to identify the effective stack height, the TAESH (where applicable), and the corresponding generic source number.

(A) Go to Table 5.0–1 and find the plume rise value corresponding to the stack temperature and exit flow rate for the worst-case stack determined in Step 3.

Plume rise = ————(m)

(B) Add the plume rise to the GEP stack height of the worst-case stack determined in Steps 3 and 4.

GEP stack height (m)	+	Plume rise (m)	=	Effective stack height (m)
————————	+	————————	=	————————

(C) Go to the first column of Table 5.0–2 and identify the range of effective stack

———

[a] Worksheet space is provided for three stacks. If the facility has additional stacks, copy the form and revise stack identification numbers for 4, 5, etc.

heights that includes the effective stack height estimated in Step 5(B). Record the generic source number that corresponds to this range.

Generic source number=_____

(D) If the source is located in flat terrain [3], or if the generic source number identified in Step 5(C) above is 1 or 11 (regardless of terrain classification), use the generic source number determined in Step 5(C) and proceed directly to Step 6. Otherwise, continue to Step 5(E).

(E) For those situations where the conditions in Step 5(D) do not apply, the effective stack height must be adjusted for terrain. The TAESH for each distance range is computed by subtracting the terrain rise within the distance range from the effective stack height.[4]

[3] The terrain is considered flat and terrain adjustment factors are not used if the maximum terrain rise within 5 km of the facility (see Step 1) is less than 10 percent of the physical stack height of the worst-case stack.

[4] Refer to Step 1 for terrain adjustment data. Note that the distance from the source to the outer radii of each range is used. For example, for the range >0.5–2.5 km, the maximum terrain rise in the range 0.0–2.5 km is used.

TABLE 5.0-1.—ESTIMATED PLUME RISE (IN METERS) BASED ON STACK EXIT FLOW RATE AND GAS TEMPERATURE

Flow rate (m³/s)	Exhaust Temperature (°K)										
	<325	325–349	350–399	400–449	450–499	500–599	600–699	700–799	800–999	1000–1499	>1499
<0.5	0	0	0	0	0	0	0	0	0	0	0
0.5–0.9	0	0	0	0	0	0	0	0	1	1	1
1.0–1.9	0	0	0	0	1	1	2	3	3	3	4
2.0–2.9	0	0	1	3	4	4	6	6	7	8	9
3.0–3.9	0	1	2	5	6	7	9	10	11	12	13
4.0–4.9	1	2	4	6	8	10	12	13	14	15	17
5.0–7.4	2	3	5	8	10	12	14	16	17	19	21
7.5–9.9	3	5	8	12	15	17	20	22	22	23	24
10.0–12.4	4	6	10	15	19	21	23	24	25	26	27
12.5–14.9	4	7	12	18	22	23	25	26	27	28	29
15.0–19.9	5	8	13	20	23	24	26	27	28	29	31
20.0–24.9	6	10	17	23	25	27	29	30	31	32	34
25.0–29.9	7	12	20	25	27	29	31	32	33	35	36
30.0–34.9	8	14	22	26	29	31	33	35	36	37	39
35.0–39.9	9	16	23	28	30	32	35	36	37	39	41
40.0–49.9	10	17	24	29	32	34	36	38	39	41	42
50.0–59.9	12	21	26	31	34	36	39	41	42	44	46
60.0–69.9	14	22	27	33	36	39	42	43	45	47	49
70.0–79.9	16	23	29	35	38	41	44	46	47	49	51
80.0–89.9	17	25	30	36	40	42	46	48	49	51	54
90.0–99.9	19	26	31	38	42	44	48	50	51	53	56
100.0–119.9	21	26	32	39	43	46	49	52	53	55	58
120.0–139.9	22	28	35	42	46	49	52	55	56	59	61
140.0–159.9	23	30	36	44	48	51	55	58	59	62	65
160.0–179.9	25	31	38	46	50	54	58	60	62	65	67
180.0–199.9	26	32	40	48	52	56	60	63	65	67	70
>199.9	26	33	41	49	54	58	62	65	67	69	73

TABLE 5.0-2—Selection of Generic Source Number

Effective stack height (m)	Generic source No.
<10.0	1
10.0–14.9	2
15.0–19.9	3
20.0–24.9	4
25.0–30.9	5
31.0–41.9	6
42.0–52.9	7
53.0–64.9	8
65.0–122.9	9
113.0+	10
Downwash	11

TABLE 5.0-3.—Classification of Land Use Types

Type [1]	Description	Urban or rural designation [2]
I1	Heavy Industrial	Urban
I2	Light/Moderate Industrial	Urban
CI	Commercial	Urban
R1	Common Residential (Normal Easements).	Rural
R2	Compact Residential (Single Family).	Urban
R3	Compact Residential (Multi-Family).	Rural
R4	Estate Residential (Multi-Acre Plots).	Rural
A1	Metropolitan Natural	Rural
A2	Agricultural	Rural
A3	Undeveloped (Grasses/Weeds).	Rural
A4	Undeveloped (Heavily Wooded).	Rural
A5	Water Surfaces	Rural

[1] EPA, Guideline on Air Quality Models (Revised), EPA-450/2-78-027, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, July, 1986.

[2] Auer, August H. Jr., "Correlation of Land Use and Cover with meteorological Anomalies," *Journal of Applied Meteorology*, pp. 636–643, 1978.

Distance range (km)	Effective stack—height (m) [see step 5(B)]	_	Maximum terrain—rise (m) (see step 1)	=	TAESH(m)
0.0–0.5	_____	-	_____	=	_____
>0.5–2.5	_____	-	_____	=	_____
>2.5–5.0	_____	-	_____	=	_____

If the terrain rise for any of the distance ranges is greater than the effective stack height, set the TAESH equal to zero and use generic source number 1 for that distance range.

Record the generic source numbers from Table 5.0–2 based on each of the TAESH values.

Distance range (km)	Generic source No. (after terrain adjustment)
0.0–0.5	_____
>0.5–2.5	_____
>2.5–5.0	_____

Step 6: Classify the Site as Urban or Rural

(A) Classify the land use near the facility as either urban or rural by determining the percentage of urban land use types (as defined in Table 3; for further guidance see the footnoted references) that fall within 3 km of the facility.[5]

Method Used to Estimate Percent Urban Land Use:	Visual	Planimeter
	_____	_____
Estimated Percentages.	Urban	Rural
	_____	_____

If the urban land use percentage is less than or equal to 30 percent based on a visual estimate, or 50 percent based on a planimeter, the local land use is considered rural. Otherwise, the local land use is considered urban.

Classification	Urban	Rural
(check applicable space).	_____	_____

(B) Based on the TAESH and the urban/rural classification of surrounding land use, use the following table to determine the threshold distance between any stack and the nearest facility boundary.

Terrain adjusted effective stack height range (m)	Distance (m) Urban	Distance (m) Rural
1–9.9	200	200
10–14.9	200	250
15–19.9	200	250
20–24.9	200	350
25–30.9	200	450
31–41.9	200	550
42–52.9	250	800
53–64.9	300	1000
65–112.9	400	1200
113+	700	2500

Record the following information:

Threshold distance from the table (m):

_____

Minimum distance from any stack to property boundary (m): _____

If the minimum distance between any stack and the nearest facility boundary is greater than the threshold distance, the surrounding buffer distance is considered significant and the facility is likely to benefit from use of the HWCAQSP relative to the Tier I and II limits (see discussion of benefits from using HWCAQSP in Introduction section).

Step 7: Determine Maximum Dispersion Coefficients

(A) Determine maximum average hourly dispersion coefficients. Based on the results of Step 6(A), select either Table 5.0–4 (urban) or Table 5.0–5 (rural) to determine the maximum average hourly dispersion coefficient.[6] For flat terrain [defined in Step 5(D)] and for all sites with generic source numbers 1 or 11, use Step 7(A) (1). For rolling or complex terrain (excluding generic sources numbers 1 and 11), use Step 7(A) (2).

(1) Search down the appropriate generic source number column [based on Step 5(C)], beginning at the minimum fenceline distance listed in Step 6(B).[7] Record the maximum average hourly dispersion coefficient encountered. Maximum Average Hourly Dispersion

Coefficient = _____ $(\mu g/m^3/g/sec)$

(2) For each of the three distance-based generic source numbers listed in Step 5(E), search down the appropriate generic source number columns, beginning at the minimum fenceline distance listed in Step 6(B). Note that different columns may be used for each of the three distance ranges if there is a need for terrain adjustment. Record the maximum dispersion coefficient for each generic source number.

Distance range (km)	Generic source No. [from Step 5(E)]	Maximum dispersion coefficient ($\mu g/m^3/m/sec$)
0.0–0.5	_____	_____
>0.5–2.5	_____	_____
>2.5–5.0	_____	_____
>5.0–20.0	_____	_____

TABLE 5.0–4.—ISCT PREDICATED MAXIMUM CONCENTRATIONS ($\mu G/M^3$)[a] FOR HAZARDOUS WASTE COMBUSTORS USING URBAN CONDITIONS

Distance (KM)	Generic Source #1 (<10M)	Generic Source #2 (10M)	Generic Source #3 (15M)	Generic Source #4 (20M)	Generic Source #5 (25M)	Generic Source #6 (31M)	Generic Source #7 (42M)	Generic Source #8 (53M)	Generic Source #9 (65M)	Generic Source #10 (113M)	Generic Source #11 (Down-wash)
0.20	680.1	517.5	368.7	268.7	168.5	129.8	63.4	30.1	18.4	1.6	662.3
0.25	521.9	418.2	303.7	232.6	163.0	124.2	67.6	38.5	19.8	3.2	500.0

[a] The delineation of urban and rural areas, can be difficult for the residential-type areas listed in Table 5.0–3. The degree of resolution in Table 5.0–3 for residential areas often cannot be identified without conducting site area inspections. This process can require extensive analysis, which, for many applications, can be greatly streamlined without sacrificing confidence in selecting the appropriate urban or rural classification. The fundamental simplifying assumption is based on the premise that many applications will have clear-cut urban/rural designations, i.e., most will be in rural settings that can be definitively characterized through a review of aerial photographs, zoning maps, or U.S. Geological Survey topographical maps.

[6] For the distance range 6 to 20 kilometers, generic source number 1 is used to conservatively represent the maximum dispersion coefficient.

[7] Exclude all distances that are closer to the facility than the property boundary. For example, if the actual distance to the nearest property boundary is 265 meters, begin at the 300 meter distance in Tables 5.0–4 and 5.0–5.

TABLE 5.0-4.—ISCT PREDICATED MAXIMUM CONCENTRATIONS (μG/M^3)* FOR HAZARDOUS WASTE COMBUSTORS USING URBAN CONDITIONS—CONTINUED

Distance (KM)	Generic Source #1 (<10M)	Generic Source #2 (10M)	Generic Source #3 (15M)	Generic Source #4 (20M)	Generic Source #5 (25M)	Generic Source #6 (31M)	Generic Source #7 (42M)	Generic Source #8 (53M)	Generic Source #9 (65M)	Generic Source #10 (113M)	Generic Source #11 (Down-wash)
0.30	407.7	351.7	256.2	199.0	147.0	118.3	63.5	41.5	25.0	4.2	389.3
0.35	326.2	304.2	221.6	172.7	130.2	107.9	60.0	40.5	27.3	5.4	311.9
0.40	268.5	268.5	195.6	152.5	115.7	97.1	59.6	37.8	27.4	5.8	268.5
0.45	240.8	240.7	175.4	136.7	103.9	87.6	56.6	37.2	26.3	5.8	240.8
0.50	218.5	218.5	159.2	124.1	94.4	79.7	52.9	36.7	24.7	5.8	218.5
0.55	200.3	200.3	145.9	113.8	88.5	73.1	49.2	35.4	24.5	6.6	200.3
0.60	185.1	185.1	134.9	105.1	80.0	67.6	45.8	33.8	24.3	7.1	185.1
0.65	172.2	172.2	125.5	97.8	74.4	62.9	42.7	32.0	23.7	7.4	172.2
0.70	161.2	161.2	117.4	91.6	69.6	58.9	40.1	30.2	22.9	7.5	161.2
0.75	151.6	151.6	110.5	86.1	65.5	55.4	37.7	28.6	22.0	7.5	151.6
0.80	143.2	143.2	104.4	81.4	61.9	52.3	35.6	27.1	21.1	7.4	143.2
0.85	135.8	135.8	99.0	77.2	58.7	49.6	33.8	25.7	20.2	7.2	135.8
0.90	129.2	129.2	94.2	73.4	55.8	47.2	32.1	24.5	19.3	7.0	129.2
0.95	123.3	123.3	89.9	70.1	53.3	45.0	30.7	23.4	18.5	6.8	123.3
1.00	118.0	118.0	86.0	67.0	51.0	43.1	29.4	22.4	17.7	6.5	118.0
1.10	108.8	108.0	79.3	61.8	47.0	39.7	27.1	20.6	16.4	8.5	108.8
1.20	101.1	101.1	73.7	57.4	43.7	36.9	25.2	19.2	15.2	6.4	101.1
1.30	94.6	94.6	68.9	53.7	40.9	34.5	23.5	18.0	14.2	6.3	94.6
1.40	89.0	89.0	64.8	50.6	38.5	32.5	22.1	16.9	13.4	6.1	89.0
1.50	64.1	84.1	61.3	47.8	36.3	30.7	20.9	16.0	12.7	5.9	84.1
1.60	79.8	79.8	58.2	45.4	34.5	29.2	19.9	15.2	12.0	5.6	79.8
1.70	76.0	76.0	55.4	43.2	32.9	27.8	18.9	14.4	11.4	5.4	76.0
1.80	72.7	72.7	53.0	41.3	31.4	28.5	18.1	13.8	10.9	5.2	72.7
1.90	69.6	69.6	50.7	39.6	30.1	25.4	17.3	13.2	10.5	5.0	69.8
2.00	66.9	66.9	48.6	38.0	28.9	24.4	16.7	12.7	10.1	4.8	66.9
2.25	61.1	61.1	44.5	34.7	26.4	22.3	15.2	11.6	9.2	4.4	61.1
2.50	56.4	56.4	41.1	32.1	24.4	20.6	14.0	10.7	8.5	4.1	56.4
2.75	52.6	52.6	38.3	29.9	22.7	19.2	10.0	10.0	7.9	3.8	52.6
3.00	49.3	49.3	35.9	28.0	21.3	18.0	9.4	9.4	7.4	3.8	49.3
4.00	40.2	40.2	29.3	22.8	17.4	14.7	7.6	7.8	6.1	2.9	40.2
5.00	34.5	34.5	25.2	19.6	14.9	12.6	6.6	6.6	5.2	2.5	34.5
6.00	30.7	30.7	30.7	30.7	30.7	30.7	30.7	30.7	30.7	30.7	30.7
7.00	27.8	27.8	27.8	37.8	27.8	27.8	27.8	27.6	27.8	27.6	27.8
8.00	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5	25.5
9.00	23.8	23.8	23.8	23.8	23.8	23.8	23.8	23.8	23.8	23.8	23.6
10.00	22.3	22.3	22.3	22.3	22.3	22.3	22.3	22.3	22.3	22.3	22.3
15.00	17.8	17.6	17.6	17.6	17.6	17.6	17.8	17.6	17.6	17.8	17.6
20.00	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.0	15.01	15.0

* Based on a 1 Gram/Second Emission Rate

TABLE 5.0-5.—ISCT PREDICATED MAXIMUM CONCENTRATIONS (μG/M^3)* FOR HAZARDOUS WASTE COMBUSTORS USING URBAN CONDITIONS

Distance (KM)	Generic source #1 (<10M)	Generic source #2 (10M)	Generic source #3 (15M)	Generic source #4 (20M)	Generic source #5 (25M)	Generic source #6 (31M)	Generic source #7 (42M)	Generic source #8 (53M)	Generic source #9 (65M)	Generic source #10 (113M)	Generic source #11 (Down-wash)
0.20	1771.1	670.3	308.6	176.8	102.8	76.5	26.0	10.1	3.5	0.0	1350.8
0.25	1310.6	676.4	316.9	183.6	104.6	71.8	36.0	17.6	7.9	0.2	1227.3
0.30	1002.3	629.2	303.4	199.1	100.4	75.0	39.7	24.0	12.6	0.6	1119.3
0.35	798.4	569.6	282.3	200.7	117.0	71.1	38.3	25.9	16.8	1.9	1023.8
0.40	656.9	516.5	278.7	194.4	125.2	82.7	25.3	24.8	18.1	3.1	938.9
0.45	621.5	471.1	277.6	184.3	127.5	89.7	35.6	21.7	17.6	4.3	651.6
0.50	633.5	432.4	272.0	172.7	125.7	92.9	34.4	21.6	15.9	5.5	787.8
0.55	630.1	399.2	263.6	168.0	121.6	93.3	36.6	22.1	13.6	6.5	730.6
0.60	618.6	370.4	254.0	189.1	118.2	91.8	42.6	21.7	14.3	6.7	676.4
0.65	596.7	345.4	243.6	168.1	110.3	89.2	45.3	20.9	14.7	6.4	633.4
0.70	573.2	323.4	232.9	165.6	104.5	85.6	47.0	23.3	14.6	5.9	592.0
0.75	546.9	304.0	222.3	162.0	98.8	82.2	47.7	25.5	14.3	5.5	554.6
0.60	520.9	286.6	212.1	157.7	98.8	76.5	47.8	27.1	13.8	5.1	522.1
0.85	495.7	271.5	202.4	153.0	99.0	74.9	47.4	28.3	15.0	4.7	491.6
0.90	471.5	257.8	193.3	148.1	98.6	71.4	46.6	29.1	16.3	4.5	464.2
0.95	448.5	245.4	184.7	143.1	97.6	72.3	45.6	29.6	17.3	4.2	438.9
1.00	426.6	234.2	176.6	136.1	96.3	72.6	44.4	29.6	16.2	4.0	415.6
1.10	367.5	214.7	162.5	128.2	91.9	71.1	41.8	29.5	19.3	3.9	375.0
1.20	353.5	196.4	150.3	119.3	87.4	69.1	39.1	26.8	19.6	4.1	340.3
1.30	323.0	189.6	139.9	111.5	82.9	66.7	36.8	27.5	19.6	4.2	310.4
1.40	296.6	182.2	130.8	104.5	78.7	64.2	34.3	26.2	19.5	4.2	284.6
1.50	273.3	174.6	122.9	98.3	74.7	61.6	32.3	24.9	19.0	4.2	262.0
1.60	252.7	167.0	115.9	92.6	71.0	59.1	31.8	23.6	18.4	4.2	242.2

TABLE 5.0–5.—ISCT PREDICATED MAXIMUM CONCENTRATIONS (μG/M³)ᵃ FOR HAZARDOUS WASTE COMBUSTORS USING URBAN CONDITIONS—CONTINUED

Distance (KM)	Generic source #1 (<10M)	Generic source #2 (10M)	Generic source #3 (15M)	Generic source #4 (20M)	Generic source #5 (25M)	Generic source #6 (31M)	Generic source #7 (42M)	Generic source #8 (53M)	Generic source #9 (65M)	Generic source #10 (113M)	Generic source #11 (Down-wash)
1.70	234.5	159.6	109.7	87.9	67.6	56.7	31.6	22.5	17.7	4.3	224.7
1.80	216.3	152.4	104.1	83.5	64.4	54.3	31.3	21.4	17.0	4.5	211.9
1.90	203.7	145.6	99.1	79.5	61.5	52.1	30.9	20.4	16.3	4.8	198.4
2.00	190.7	139.1	94.6	75.9	58.8	50.0	30.4	19.5	15.7	5.1	186.3
2.25	164.4	124.5	85.1	68.3	53.0	45.4	28.9	18.1	14.2	5.4	160.8
2.50	143.7	112.1	77.3	62.1	48.2	41.4	27.2	17.9	12.9	5.5	140.7
2.75	127.0	101.5	70.9	56.9	38.1	38.1	25.6	17.5	11.8	5.4	124.5
3.00	113.4	92.4	65.6	52.6	35.2	35.2	24.0	17.0	11.2	5.2	112.5
4.00	78.8	67.3	50.6	40.6	27.2	27.2	29.0	14.3	10.4	4.3	78.3
5.00	59.1	54.6	41.4	33.2	22.2	22.2	15.6	12.0	9.3	3.5	58.8
6.00	56.7	46.7	46.7	46.7	46.7	46.7	46.7	46.7	46.7	46.7	46.7
7.00	40.4	40.4	40.4	40.4	40.4	40.4	40.4	40.4	40.4	40.4	40.4
8.00	35.8	35.8	35.8	35.8	35.8	35.8	35.8	35.8	35.8	35.8	35.8
9.00	32.2	32.2	32.2	32.2	32.2	32.2	32.2	32.2	32.2	32.2	32.2
10.00	9.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4	29.4
15.00	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5
20.00	15.9	15.9	15.9	15.9	15.9	15.9	15.9	15.9	15.9	15.9	15.9

ᵃ Based on a 1 Gram/Second Emission Rate

(B) Determine annual/hourly ratio for rural analysis. The maximum average annual dispersion coefficient is approximated by multiplying the maximum hourly dispersion coefficient (identified in Step 7(A) by the appropriate ratio selection from Table 5.0–6. The generic source number(s) [from Steps 5(C) or 5(E)], urban/rural designation (from Step 6), and the terrain type are used to select the appropriate scaling factor. Use the noncomplex terrain designation for all sources located in flat terrain, for all sources where the physical stack height of the worst-case stack is less than or equal to 10 m, for all sources where the worst-case stack is less than the minimum GEP, and for those sources where all of the TAESH values in Step 5(E) are greater than zero. Use the complex terrain designation in all other situations.

(C) Determine maximum average annual dispersion coefficient. The maximum average annual dispersion coefficient is determined by multiplying the maximum hourly dispersion coefficient (Step 7(A)) by its corresponding annual/hourly ratio (Step 7(B)).

Terrain	Distance from stack (m)	Generic source No.	Maximum hourly dispersion coefficient (μg/m³/g/sec)	Annual hourly ratio	Maximum annual dispersion coefficient (μg/m³/g/sec) [1]
Flat	0–20.0 0–0.5 >0.5–2.5				
Rolling or Complex	>2.5–5.0 >5.0–20.0				

[1] Maximum hourly dispersion coefficient times annual/hourly ratio.

Step 8: Estimate Maximum Ambient Air Concentrations—see procedures prescribed in subpart H of 40 CFR part 266.

Step 9: Determine Compliance with Regulatory Limits—see procedures prescribed in subpart H of 40 CFR part 266.

Step 10: Multiple Stack Method (Optional)

This option is a special case procedure that may be helpful when (1) the facility exceeded the regulatory limits for one or more pollutants, as detailed in Step 9, and (2) the facility has multiple stacks with substantially different emission rates and effective release heights. Only those pollutants that fail the Step 9 screening limits need to be addressed in this exercise.

This procedure assesses the environmental impacts from each stack and then sums the results to estimate total impacts. This option is conceptually the same as the basic approach (Steps 1 through 9) and does not involve complex calculations. However, it is more time-consuming and is recommended only if the basic approach fails to meet the risk criteria. The procedure is outlined below.

(A) Compute effective stack heights for each stack.[8]

---

[8] Follow the procedure outlined in Step 4 of the basic screening procedure to determine the GEP for each stack. If a stack's physical height exceeds the maximum GEP, use the maximum GEP values. If a stack's physical height is less than the minimum GEP, use generic source number 11 in the subsequent steps of this analysis. Follow the procedure in Steps 5(A) and 5(B) to determine the effective height of each stack.

Stack No.	GEP stack height (m)	Flow rate (m³/sec)	Exit temp (°K)	Plume rise (m)	Effective stack height (m)
1..	——	——	——	——	——
2..	——	——	——	——	——
3..	——	——	——	——	——

Add an additional page if more than three stacks are involved. Circle the maximum and minimum effective stack heights.

(B) Determine if this multiple-stack screening procedure will likely produce less conservative results than the procedure in Steps 1 through 9. To do this, compute the ratio of maximum-to-minimum effective stack height:

$$\frac{\text{Maximum Effective Stack Height}}{\text{Minimum Effective Stack Height}} = \underline{\quad}$$

If the above ratio is greater than 1.25, proceed with the remaining steps. Otherwise, this option is less likely to significantly reduce the degree of conservatism in the screening method.

(C) Determine if terrain adjustment is needed and select generic source numbers. Select the shortest stack height and maximum terrain rise out to 5 km from Step 1 and determine if the facility is in flat terrain.

Shortest stack height (m) = _____
Maximum terrain rise in meters out to 5 km =

$$\frac{\text{Terrain Rise (m)}}{\text{Shortest Stack Height (m)}} \times 100 = \underline{\quad}\%$$

If the value above is greater than 10 percent, the terrain is considered nonflat; proceed to Step 10(D). If the ratio is less than or equal to 10 percent, the terrain is considered flat. Identify the generic source numbers based on effective stack heights computed in Step 10(A). Refer to Table 5.0–2 provided earlier to identify generic source numbers. Record the generic source numbers identified and proceed to Step 10(F).

	Stack No.		
	1	2	3
Generic Source Numbers.................	—	—	—

(D) Compute the TAESH and select generic source numbers (four sources located in nonflat terrain).

1. Compute the TAESH for all remaining stacks using the following equation:

HE−TR=TAESH
where:
  HE=effective stack height (m)
  TR=maximum terrain rise for each distance range (m)
  TAESH=terrain-adjusted effective stack height (m)

USE THE TABLE BELOW TO CALCULATE THE TAESH FOR EACH STACK [9]

Distance Range (km)	Stack No.								
	0–0.5			>0.5–2.5			>2.5–5.0		
	HE	− TR	= TAESH	HE	− TR	= TAESH	HE	− TR	= TAESH
1............	−	....	≈	−	....	=	−	....	= ....
2............	−	....	≈	−	....	=	−	....	= ....
3............	−	....	≈	−	....	=	−	....	= ....

[9] Refer to Step 1 for terrain adjustment data. Note that the distance from the source to the outer radii of each range is used. For example, for the range >0.5–2.5 km, the maximum terrain rise in the range 0.0–2.5 km is used.

For those stacks where the terrain rise within a distance range is greater than the effective stack height (i.e., HE−TR is less than zero), the TAESH for that distance range is set equal to zero, and generic source number 1 should be used for that distance range for *all* subsequent distance ranges. Additionally, for all stacks with a physical stack height of less than or equal to 10 meters, use generic source number 1 for all distance ranges.[10] For

[10] This applies to all stacks less than or equal to 10 meters regardless of the terrain classification.

the remaining stacks, proceed to Step 10(D)(2).

2. For the remaining stacks, refer to Table 5.0–2 and, for each distance range, identify the generic source number that includes the TAESH. Use the values obtained from Steps 10(D)(1) and 10(D)(2) to complete the following summary worksheet:

GENERIC SOURCE NUMBER AFTER TERRAIN ADJUSTED (IF NEEDED)

Stack No.	0–0.5 km	>0.5–2.5 km	>2.5–5.0 km
1............			
2............			
3............			

(E) Identify maximum average hourly dispersion coefficients. Based on the land use classification of the site (e.g., urban or rural), use either Table 5.0–4 or Table 5.0–5 to determine the appropriate

dispersion coefficient for each distance range for each stack. Begin at the minimum fenceline distance indicated in Step 7(B) and record on Worksheet 5.0-1 the dispersion coefficient for each stack/distance range. For stacks located in facilities in flat terrain, the generic source numbers were computed in Step 10(C). For stacks located in facilities in rolling and complex terrain, the generic source numbers were computed in Step 10(D). For flat terrain applications and for stacks with a physical height of less than or equal to 10 meters, only one generic source number is used per stack for all distance ranges. For other situations up to three generic source numbers may be needed per stack (i.e., a unique generic source number per distance range). In Tables 5.0-4 and 5.0-5, the dispersion coefficients for distances of 6 km to 20 km are the same for all generic source numbers in order to conservatively represent terrain beyond 5 km (past the limits of the terrain analysis).

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Worksheet 5.0-1　Dispersion Coefficient by Downwind Distance[1]

Distance	Stack 1	Stack 2	Stack 3
0.20			
0.25			
0.30			
0.35			
0.40			
0.45			
0.50			
0.55			
0.60			
0.65			
0.70			
0.75			
0.80			
0.85			
0.90			
0.95			
1.00			
1.10			
1.20			
1.30			
1.40			
1.50			
1.60			
1.70			
1.80			
1.90			
2.00			
2.25			
2.50			
2.75			
3.00			
4.00			
5.00			
6.00			
7.00			
8.00			
9.00			
10.00			
15.00			
20.00			

[1]Note: This procedure places all stacks at the same point, but allows for consideration of different effective stack heights. The distance to the closest boundary (extracted from Step 1) should be the closest distance to any stack.

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(F) Estimate maximum hourly ambient air concentrations. In this step, pollutant-specific emission rates are multiplied by appropriate dispersion coefficients to estimate ambient air concentrations. For each stack,

emissions are multiplied by the dispersion coefficient selected in Step 10(E) and summed across all stacks to estimate ambient air concentrations at various distances from the facility. From these summed concentrations, the

maximum hourly ambient air concentration is selected. First, select the maximum emission rate of the pollutant.[11] Record these data in the spaces provided below.[12]

MAXIMUM ANNUAL EMISSION RATES (G/SEC)

Pollutant	Stack 1	Stack 2	Stack 3

Complete a separate copy of Worksheet 5.0–2 for each pollutant and select the highest hourly concentration from the summation column at the far right of the worksheet. Record the maximum hourly air concentration for each pollutant analyzed (add additional lines if needed):

Pollutant	Maximum hourly air concentration

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Worksheet 5.0-2 Maximum Hourly Ambient Air Concentration

Pollutant _____

Total Distance (km)	Stack 1 ER x DC = C	Stack 2 ER x DC = C	Stack 3 ER x DC = C	Summed Concentration from all Stacks
0.20				
0.25				
0.30				
0.35				
0.40				
0.45				
0.50				
0.55				
0.60				
0.65				
0.70				
0.80				
0.85				
0.90				
0.95				
1.00				
1.10				
1.20				
1.30				
1.40				
1.50				

ER= Annual Average Emission Rate
DC= Hourly Dispersion Coefficient (from Worksheet 5.0-1)
C= Estimated Maximum Hourly Ambient Air Concentration

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Worksheet 5.0-2 Maximum Hourly Ambient Air Concentration

Pollutant _____

Total Distance (km)	Stack 1 ER × DC = C	Stack 2 ER × DC = C	Stack 3 ER × DC = C	Summed Concentration from all Stacks
1.60				
1.70				
1.80				
1.90				
2.00				
2.25				
2.50				
2.75				
3.00				
4.00				
5.00				
6.00				
7.00				
8.00				
9.00				
10.00				
15.00				
20.00				

ER = Annual Average Emission Rate
DC = Hourly Dispersion Coefficient (from Worksheet 5.0-1)
C = Estimated Maximum Hourly Ambient Air Concentration

Worksheet 5.0-2 Maximum Ambient Air Concentration

Pollutant _____

Total Distance (km)	Stack 1 ER x DC = C	Stack 2 ER x DC = C	Stack 3 ER x DC = C	Summed Concentration from all Stacks
1.60	__ x __ = __	__ x __ = __	__ x __ = __	
1.70	__ x __ = __	__ x __ = __	__ x __ = __	
1.80	__ x __ = __	__ x __ = __	__ x __ = __	
1.90	__ x __ = __	__ x __ = __	__ x __ = __	
2.00	__ x __ = __	__ x __ = __	__ x __ = __	
2.25	__ x __ = __	__ x __ = __	__ x __ = __	
2.50	__ x __ = __	__ x __ = __	__ x __ = __	
2.75	__ x __ = __	__ x __ = __	__ x __ = __	
3.00	__ x __ = __	__ x __ = __	__ x __ = __	
4.00	__ x __ = __	__ x __ = __	__ x __ = __	
5.00	__ x __ = __	__ x __ = __	__ x __ = __	
6.00	__ x __ = __	__ x __ = __	__ x __ = __	
7.00	__ x __ = __	__ x __ = __	__ x __ = __	
8.00	__ x __ = __	__ x __ = __	__ x __ = __	
9.00	__ x __ = __	__ x __ = __	__ x __ = __	
10.00	__ x __ = __	__ x __ = __	__ x __ = __	
15.00	__ x __ = __	__ x __ = __	__ x __ = __	
20.00	__ x __ = __	__ x __ = __	__ x __ = __	

ER = Annual average emission rate
DC = Hourly dispersion coefficient (from Worksheet 1)
C = Estimated maximum hourly ambient air concentration

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(G) Determine the complex/ noncomplex designation for each stack. For each stack, subtract the maximum terrain rise within 5 km of the site from the physical stack height and designate the stack as either complex or noncomplex. If the stack height minus the maximum terrain rise (within 5 km) is greater than zero or if the stack is less than 10 meters in physical height, then assign the stack a noncomplex designation. If the stack height minus the maximum terrain rise (within 5 km) is less than or equal to zero, then assign the stack a complex designation.

Perform the following computation for each stack and record the information in the spaces provided. Check in the spaces provided whether the stack designation is complex or noncomplex.

Stack No.	Stack height (m)	Maximum terrain rise (m)		Complex	Noncomplex
1		−	=	(m)	
2		−	=	(m)	
3		−	=	(m)	

(H) Identify annual/hourly ratios. Extract the annual/hourly ratios for each stack by referring to Table 5.0–6. Generic source numbers (from Steps 10(C) or 10(D), urban/rural designation (from Step 6)), and complex or noncomplex terrain designations (from Step 10(G)) are used to select the appropriate scaling factor needed to convert hourly maximum concentrations to estimates of annual average concentrations.

Complete the following table: [13]

[13] If any stack (excluding generic stack number 1 and 11) in Step 10(D) shows a negative terrain adjusted stack height, use the complex terrain annual/hourly ratios.

Stack No.	Generic source No. steps 10 (C or D)			Annual/hourly ratio (from table 5.0–6)		
	Distance ranges (km)			Distance ranges (km)		
	0–0.5	>0.5–2.5	>2.5–5.0	0–0.5	>0.5–2.5	>2.5–5.0
1						
2						
3						

(I) Select the highest annual/hourly ratio among all of the stacks,[14] and then estimate the maximum annual average ambient air concentrations for each pollutant by completing the following table, where:

[14] As an option, the user can identify the stack with the highest ratio for each distance range (rather than the absolute highest). In this case, extra sheets would be needed to show estimated annual average concentrations from each stack by multiplying emission rate times maximum hourly dispersion coefficient times maximum annual/hourly ratio for applicable distance range. Then sum across all stacks for each downwind distance.

C = Maximum total hourly ambient air concentration (μg/m^3) for pollutant "N" from Step 10(F),

C_a = Maximum annual average air concentration for pollutant "N" (μg/m^3).
R = Annual/hourly ratio.

TABLE 5.0–6.—95TH PERCENTILE OF ANNUAL/HOURLY RATIOS

Noncomplex Terrain			Complex Terrain		
Source	Urban	Rural	Source	Urban	Rural
1	0.019	0.014	1	0.020	0.053
2	0.033	0.019	2	0.020	0.053
3	0.031	0.018	3	0.030	0.057
4	0.029	0.017	4	0.051	0.047
5	0.028	0.017	5	0.067	0.039
6	0.028	0.017	6	0.059	0.034
7	0.031	0.015	7	0.036	0.031
8	0.030	0.013	8	0.026	0.024
9	0.029	0.011	9	0.026	0.024
10	0.029	0.008	10	0.017	0.013
11	0.018	0.015	11	0.020	0.053

Pollutant	$C_a \ (\mu g/m^3)$	$\times R = C_a \ (\mu g/m^3)$
———	—— $\times$ ——	= ——
———	—— $\times$ ——	= ——

(J) Use the maximum annual average concentrations from Step 10(I) to determine compliance with regulatory requirements.

SECTION 6.0—SIMPLIFIED LAND USE CLASSIFICATION PROCEDURE FOR COMPLIANCE WITH TIER I AND TIER II LIMITS

6.1 Introduction

This section provides a simplified procedure to classify areas in the vicinity of boilers and industrial furnace sites as urban or rural in order to set risk-based emission limits under subpart H of 40 CFR part 266. Urban/rural classification is needed because dispersion rates differ between urban and rural areas and thus, the risk per unit emission rate differs accordingly. The combination of greater surface roughness (more buildings/structures to generate turbulent mixing) and the greater amount of heat released from the surface in an urban area (generates buoyancy-induced mixing) produces greater rates of dispersion. The emission limit tables in the regulation, therefore, distinguish between urban and rural areas.

EPA guidance (EPA 1986) provides two alternative procedures to determine whether the character of an area is predominantly urban or rural. One procedure is based on land use typing and the other is based on population density. Both procedures require consideration of characteristics within a 3-km radius from a source, in this case the facility stack(s). The land use typing method is preferred because it more directly relates to the surface characteristics that affect dispersion rates. The remainder of this discussion is, therefore, focused on the land use method.

While the land use method is more direct, it can also be labor-intensive to apply. For this discussion, the land use method has been simplified so that it is consistent with EPA guidance (EPA 1986; Auer 3978), while streamlining the process for the majority of applications so that a clear-cut decision can be made without the need for detailed

analysis. Table 6.0–1 summarizes the simplified approach for classifying areas as urban or rural. As shown, the applicant always has the option of applying standard (i.e., more detailed) analyses to more accurately distinguish between urban and rural areas. However, the procedure presented here allows for simplified determinations, where appropriate, to expedite the permitting process.

TABLE 6.0–1.—CLASSIFICATION OF LAND USE TYPES

Type[1]	Description	Urban or rural designation[a]
I1	Heavy Industrial	Urban.
I2	Light/Moderate Industrial.	Urban.
C1	Commercial	Urban.
R1	Common Residential (Normal Easements).	Rural.
R2	Compact Residential (Single Family).	Urban.
R3	Compact Residential (Multi-Family).	Urban.
R4	Estate Residential (Multi-Acre Plots).	Rural.
A1	Metropolitan Natural	Rural.
A2	Agricultural	Rural.
A3	Undeveloped (Grasses/Weeds).	Rural.
A4	Undeveloped (Heavily Wooded).	Rural.
A5	Water Surfaces	Rural.

[1] EPA, Guideline on Air Quality Models (Revised), EPA–450/2–78–027, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, July, 1986.
[a] Auer, August H. Jr., "Correlation of Land Use and Cover with Meteorological Anomalies," Journal of Applied Meteorology, pp. 636–643, 1978.

6.2 Simplified Land Use Process

The land use approach considers four primary land use types: industrial (I), commercial (C), residential (R), and agricultural (A). Within These primary classes, subclasses are identified, as shown

in table 6.0–1. The goal is to estimate the percentage of the area within a 3-km radius that is urban type and the percentage that is rural type. Industrial and commercial areas are classified as urban; agricultural areas are classified as rural.

The delineation of urban and rural areas, however, can be more difficult for the residential type areas shown in table 6.0–1. The degree of resolution shown in table 6.0–1 for residential areas often cannot be identified without conducting site area inspections and/or referring to zoning maps. This process can require extensive analysis, which, for many applications, can be greatly streamlined without sacrificing confidence in selecting the appropriate urban or rural classification.

The fundamental simplifying assumption is based on the premise that many applications will have clear-cut urban/rural designations, i.e., most will be in rural settings that can be definitively characterized through a brief review of topographical maps. The color coding on USGS topographical maps provides the most effective means of simplifying the typing scheme. The suggested typing designations for the color codes found on topographical maps are as follows:

Green Wooded areas (rural).
White White areas generally will be treated as rural. This code applies to areas that are unwooded and do not have densely packed structures which would require the pink code (house omission tint). Parks, industrial areas, and unforested rural land will appear as white on the topographical maps. Of these categories, only the industrial areas could potentially be classified as urban based on EPA 1986 or Auer 1978. Industrial areas can be easily identified in most cases by the characteristics shown in Figure 6.0–1. For this simplified procedure, white areas that have an industrial classification will be treated as urban areas.

BILLING CODE 6560–50–M

Figure 6.0-1

Supplementary Publication Symbols

117 Single track
Line weight .005". Tie weight .003", length .04",
spaced .20" center to center.

118 Single track abandoned
Same as existing track with space .02", dash .18".
Label.

119 Single track under construction
Same as existing track with space .02", dash .38".
Label UNDER CONSTRUCTION.

120 Multiple main line track
Overall width .017". Line weight .003". Tie length
.052", spaced .20" center to center. If more than
two tracks label, with double cross tie at point of
change. Double cross tie .017" overall width.
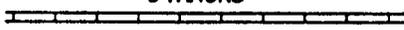
121 Multiple track abandoned
Same as existing track with space .02", dash .18".
Label ABANDONED.

122 Multiple track under construction
Same as existing track with space .02", dash .38".
Label UNDER CONSTRUCTION.
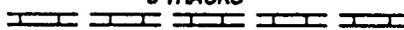
123 Juxtaposition
Alternate ties, spaced .20" center to center.
Minimum space between tracks .011". Line weight
for single tracks .005", multiple tracks .003".
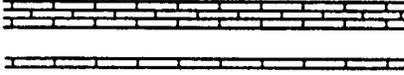
124 Railroad in street
Ties spaced .20" center to center. Label if narrow
gage. Tie weight .003".

125 Yards
Line weight .003". Space between tracks .011". Ties
spaced .20" center to center, maximum length to
touch 6 tracks.

126 Sidings
Line weight .003". Scribe to scale with minimum
space between tracks .011". Ties spaced .20"
center to center, length .04" for single track.

176 Large buildings
Outline weight .003". When width exceeds .06",
hatch at 45° angle to building in NE direction,
lines .002" spaced .02" center to center.
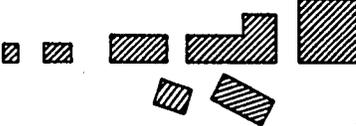
178 Sewage disposal or filtration plant
Line weight .003". See symbol 700 for blue
hatching. Label.

196 Tanks: oil, gas, water, etc.
Circle .03" minimum, 10" maximum. Label as to content.

197 Tanks: oil, gas, water, etc.
Exceeding 10" diameter. Outline weight .003".
Hatch SW-NE with .002" lines spaced .02" center
to center. Label as to content.

SECTION 7.0 STATISTICAL METHODOLOGY FOR BEVILL RESIDUE DETERMINATIONS

This section describes the statistical comparison of waste-derived residue to normal residue for use in determining eligibility for the Bevill exemption under 40 CFR 266.112.

7.1 *Comparison of Waste-derived Residue with Normal Residue*

To meet the special criteria under § 266.112(b)(1), waste-derived residue must not contain appendix VIII, Part 261, constituents (toxic constituents) at concentrations significantly higher than in residue generated without burning or processing hazardous waste. Concentrations of toxic constituents in normal residue are determined based on analysis of a minimum of 10 composite samples. (Note that "normal" residue refers to residue generated by a facility when operating without burning hazardous waste.) The 95th percent confidence interval about the mean of the normal residue concentrations must be used in the comparison of waste-derived residue with normal residue; the confidence interval is determined as described in section 7.2 below. The concentration of a toxic constituent in the waste-derived residue is not considered to be significantly higher than in the normal residue if the concentration in the waste-derived residue does not exceed the upper 95th percent confidence interval about the mean that was established for the normal residue. Concentrations of toxic constituents in waste-derived residue are determined based on analysis of samples taken over a compositing period of not more than 24 hours.

7.2. *Calculation of the 95th Percent Confidence Interval About the Mean for Toxic Constituents in Normal Residue*

The 95th percent confidence interval about the mean is calculated for a set of values using a "t" distribution. In use of the "t" distribution, it is assumed that the values are normally distributed; the "t" distribution is applicable for use with small sample sets (i.e. approximately 10–30 samples). The 95th percent confidence interval about the mean is determined using the following equation:

95th percent confidence interval $= \bar{X} \pm t_{\alpha 2} (s/\sqrt{n})$

where $\bar{X} =$ mean of the normal residue concentrations,

$$\bar{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

$\alpha =$ the level of significance $= 0.05$,
$s =$ standard deviation of the normal residue concentrations,

$$s = \left[\sum_{i=1}^{n} (X_i - \bar{X})^2 / (n-1) \right]^{1/2},$$

and
$n =$ sample size.

The values of the "t" distribution at the $\alpha 2$ level of significance and $n - 1$ degrees of freedom are given in table 7.0–1.

For example, a normal residue test results in 10 samples with the following analysis results for toxic compound A:

Sample No.	Concentration of compound A (ppm)
1	10
2	10
3	15
4	10
5	7
6	12
7	10
8	16
9	15
10	10

The mean and standard deviation of these measurements, calculated using equations above, are 11.5 and 2.9 respectively. Assuming that the values are normally distributed, the upper 95th percent confidence interval value about the mean is given by:

TABLE 7.0–1.—T DISTRIBUTION VALUES

Degrees of freedom (n-1)	Percentage point of t distribution $\alpha / 2 = 0.025$
1	12.706
2	4.303
3	3.182
4	2.776
5	2.571
6	2.447
7	2.365
8	2.306
9	2.262
10	2.228
11	2.201
12	2.179
13	2.160
14	2.145
15	2.131
16	2.120
17	2.110
18	2.101
19	2.093
20	2.086
21	2.080
22	2.074
23	2.069
24	2.064
25	2.060
26	2.056
27	2.052
28	2.048
29	2.045

95th percent confidence interval value $= 11.5 + 2.262 \times (2.9\sqrt{10}) = 13.6$ ppm.

Thus, if the concentration of compound A in the waste-derived residue is below 13.6 ppm, then the waste-derived residue is eligible for the Bevill exemption for toxic compound A.

7.3 *Normal Distribution Assumption*

As noted in section 7.2 above, this statistical approach (use of the 95th percent confidence interval about the mean) for calculation of the concentration in normal residue is based on the assumption that the concentration data are distributed normally. The Agency is aware that concentration data of this type may not be distributed normally, particularly when concentrations are near the detection limits. There are a number of procedures that can be used to test the distribution of a data set. For example, the Shapiro-Wilk test, examination of a histogram or plot of the data on normal probability paper, and examination of the coefficient of skewness are methods that may be applicable, depending on the nature of the data (Reference 1 and 2).

If the concentration data are not adequately represented by a normal distribution, the data may be transformed to attain a near normal distribution. The Agency has found that concentration data, especially when near detection levels, often exhibit a lognormal distribution. The assumption of a lognormal distribution has been used in various programs at EPA, such as in the Office of Solid Waste Land Disposal Restrictions program for determination of BDAT treatment standards. The transformed data may be tested for normality using the procedures identified above. If the transformed data are better represented by a normal distribution than the untransformed data, the transformed data should be used in determining the 95th percent confidence interval using the procedures in section 7.2 above.

In all cases where the applicant for the Bevill exemption wishes to use other than an assumption of normally distributed data, or believes that use of an alternate statistical approach is appropriate to the specific data set, the applicant must provide supporting rationale and demonstrate to the Director or permitting authority that the data treatment is based upon sound statistical practice.

7.4 *Nondetect Values*

The Agency is developing guidance regarding the treatment of nondetect values (data where the concentration of the constituent being measured is below the lowest concentration for which the analytical method is valid) in carrying out the statistical determinations described above. Until the guidance information is available, facilities may present their own approach to the handling of nondetect data points, but must provide supporting rationale in the operating record for consideration by the Director or permitting authority.

7.5 *References*

1. Shapiro, S.S. and Wilk, M.B. (1965), "An Analysis of Variance Test for Normality (complete samples)," Biometrika, 591–611.
2. Bhattacharyya, G.K. and R.A. Johnson (1977), Statistical Concepts and Methods, John Wiley and Sons, New York.

SECTION 8.0 PROCEDURES FOR DETERMINING DEFAULT VALUES FOR AIR POLLUTION CONTROL SYSTEM REMOVAL EFFICIENCIES

During interim status, owners or operators of boilers and industrial furnaces burning hazardous waste must submit documentation to EPA that certifies that emissions of HCl,

Cl_2, metals, and particulate matter (PM) are not likely to exceed allowable emission rates. See certification of precompliance under 40 CFR 266.103(b). This documentation also establishes interim status feed rate and operating limits for the facility. For the initial certification, estimates of emissions and system removal efficiencies (SREs) can be made to establish the operating limits. Subsequently, owners or operators must use emissions testing to demonstrate that emissions do not exceed allowable levels, and to establish operating limits. See 40 CFR 266.103(c). However, initial estimates of emissions for certification of precompliance can be based on estimated or established SREs.

The SRE combines the effect of partitioning of the chorine, metals, or PM and the air pollution control system removal efficiency (APCS RE) for these pollutants. The SRE is defined as:

SRE=(species input—species emitted) / species input

The SRE can be calculated from the partitioning factor (PF) and APCS RE by the following formula:

SRE=1—[(PF/100) X (1—APCS RE/100)]

where:

PF=percentage of the pollutant partitioned to the combustion gas

Estimates of the PF and/or the APCS RE can be based on either EPA's default values or engineering judgement. EPA's 'default values for the APCS RE for metals, HCl, Cl_2, and PM are described in this section. EPA's default values for partitioning of these pollutants are described in section 9.0.

Guidelines for the use of engineering judgement to estimate APCS REs or PFs are described in section 9.4.

8.1 *APCS RE Default Values for Metals*

EPA's default assumptions for APCS RE for metals are shown in Table 8.1–1. The default values in the table are conservative estimates of the removal efficiencies for metals in BIFs, depending on the volatility of the metal and the type of APCS.

The volatility of a metal depends on the temperature, the thermal input, the chlorine content of the waste, and the identity and concentration of the metal. Metals that do not vaporize at combustion zone temperatures are classified as "nonvolatile". Such metals typically enter the APCS in the form of large particles that are removed relatively easily. Metals that vaporize in the combustion zone and condense before entering the APCS are classified as "volatile". Such metals typically enter the APCS in the form of very fine, submicron particles that are rather inefficiently removed in many APCSs. Metals that vaporize in the combustion zone and do not condense before entering the APCS are classified as "very volatile". Such metals enter the APCS in the form of a vapor that is very inefficiently removed in many APCSs.

Typically, BIFs have combustion zone temperatures high enough to vaporize any hazardous metal at concentrations sufficient to exceed risk-based emission limits. For this reason, the default assumption is that there are no nonvolatile metals. Tables 8.1–2 and 8.1–3 are used to determine whether metals are classified as "volatile" or "very volatile" depending on the temperature entering the APCS, the thermal input, and whether the waste is chlorinated or nonchlorinated.

TABLE 8.1–1.—AIR POLLUTION CONTROL SYSTEMS (APCS) AND THEIR CONSERVATIVELY ESTIMATED EFFICIENCIES FOR CONTROLLING TOXIC METALS (%)

| APCS | Metal Volatility | | |
	Nonvolatile	Volatile	Very Volatile
WS..........	40	30	20
VS–20.....	80	75	20
VS–60.....	87	75	40
ESP-1.....	90	75	0
ESP-2.....	92	80	0
ESP-4.....	95	80	0
WESP.....	90	85	40
FF	90	80	0
SD/FF....	97	90	0
DS/FF....	95	90	0
IWS.........	90	87	75

WS=Wet Scrubber including: Sieve Tray Tower, Packed Tower, Bubble Cap Tower
VS–20=Venturi Scrubber, ca. 20–30 in W.G. Δp
VS.60=Venturi Scrubber, ca. >60 in W.G. Δp
ESP–1=Electrostatic Precipitator; 1 stage
ESP–2=Electrostatic Precipitator; 2 stage
ESP–4=Electrostatic Precipitator; 4 stage
IWS=Ionizing Wet Scrubber
DS=Dry Scrubber
FF=Fabric Filter (Baghouse)
SD=Spray Dryer (Wet/Dry Scrubber)
WESP=Wet Electrostatic Precipitator

TABLE 8.1–2.—TEMPERATURE (F) ENTERING APCS ABOVE WHICH METALS ARE CLASSIFIED AS VERY VOLATILE IN COMBUSTION OF NONCHLORINATED WASTES

| Metal | | Thermal Input (MMBtu/hr)[1] | | | | |
Name	Symbol	1	10	100	1000	10000
Arsenic	As	320	280	240	200	160
Cadmium	Cd	1040	940	860	780	720
Chromium	Cr	2000	1760	1580	1420	1380
Beryllium	Be	1680	1440	1240	1080	980
Antimony	Sb	680	600	540	480	420
Barium	Ba	2240	1820	1540	1360	1240
Lead	Pb	1280	1180	1080	1000	920
Mercury	Hg	340	300	260	220	180
Silver	Ag	1820	1640	1480	1340	1220
Thallium	Tl	900	800	700	620	540

[1] Interpolation of thermal input is not allowed. If a BIF fires between two ranges, the APCS temperature under the higher thermal input must be used. *Example:* For a BIF firing 10–100 MMBtu/hr, Mercury is considered very volatile at APCS temperatures above 260 F and volatile at APCS temperatures of 260 F and below.

TABLE 8.1–3.—TEMPERATURE (F) ENTERING APCS ABOVE WHICH METALS ARE CLASSIFIED AS VERY VOLATILE IN COMBUSTION OF CHLORINATED WASTES

| Metal | | Thermal Input (MMBtu/hr)[1] | | | | |
Name	Symbol	1	10	100	1000	10000
Arsenic	As	320	280	240	200	160
Cadmium	Cd	1040	940	860	780	720
Chromium	Cr	>140	>140	>140	>140	>140
Beryllium	Be	1680	1440	1240	1080	980
Antimony	Sb	680	600	540	480	420
Barium	Ba	2060	1840	1680	1540	1420
Lead	Pb	>140	>140	>140	>140	>140
Mercury	Hg	340	300	260	220	180

TABLE 8.1-3.—TEMPERATURE (F) ENTERING APCS ABOVE WHICH METALS ARE CLASSIFIED AS VERY VOLATILE IN COMBUSTION OF CHLORINATED WASTES —Continued

Metal		Thermal Input (MMBtu/hr)[1]				
Name	Symbol	1	10	100	1000	10000
Silver	Ag	1080	940	840	740	660
Thallium	Tl	900	800	700	620	540

[1] Interpolation of thermal input is not allowed. If a BIF fires between two ranges, the APCS temperature under the higher thermal input must be used. *Example:* For a BIF firing 10–100 MMBtu/hr, Mercury is considered very volatile at APCS temperatures above 260 F and volatile at APCS temperatures of 260 F and below.

A waste is considered chlorinated if chlorine is present in concentrations greater than 0.1 percent by weight. In the EPA guidance document "Guidance for Metals and Hydrogen Chloride Controls for Hazardous Waste Incinerators, Volume IV of the Hazardous Waste Incineration Guidance Series,"[1] one percent is used for the chlorinated/nonchlorinated cutoff. However, best engineering judgement, based on examination of pilot-scale data reported by Carroll et al. [2] on the effects of waste chlorine content on metals emissions, suggests that the 1 percent cutoff may not be sufficiently conservative.

Tables 8.1-2 and 8.1-3 were compiled based on equilibrium calculations. Metals are classified as very volatile at all temperatures above the temperature at which the vapor pressure of the metal is greater than 10 percent of the vapor pressure that results in emissions exceeding the most conservative risk-based emissions limits.

8.2 *APCS RE Default Values for HCl and Cl₂*

Default assumptions for APCS RE for HCl in BIFs are shown in Table 8.2-1. This table is identical to the column for other BIFs except that cement kilns have a minimum HCl removal efficiency of 83 percent. Because of the alkaline nature of the raw materials in cement kilns, most of the chlorine is converted to chloride salts. Thus, the minimum APCS RE for HCl for cement kilns is independent of the APCS train.

Removal efficiency of Cl₂ for most types of APCS is generally minimal. Therefore, the default assumption for APCS RE for Cl₂ for all APCSs is 0 percent. This is applicable to all BIFs, including cement kilns.

8.3 *APCS RE Default Values for Ash*

Default assumptions for APCS RE for PM are also shown in Table 8.1-4. These figures are conservative estimates of PM removal efficiencies for different types of APCSs. They are identical to the figures in the Nonvolatile APCS RE column for hazardous metals presented in Table 8.1-1 because the same collection mechanisms and collection efficiencies that apply to nonvolatile metals also apply to PM.

TABLE 8.2-1.—AIR POLLUTION CONTROL SYSTEMS (APCS) AND THEIR CONSERVATIVELY ESTIMATED EFFICIENCIES FOR REMOVING HYDROGEN CHLORIDE (HCL) AND PARTICULATE MATTER (PM) (%)

APCD	HCl		PM
	Cement kilns	Other BIFs	
WS	97	97	40
VS-20	97	97	80
VS-60	98	98	87
ESP-1	83	0	90
ESP-2	83	0	92
ESP-4	83	0	95
WESP	83	70	90
FF	83	0	90
SD/FF	98	98	97
DS/FF	98	98	95
WS/IWS	99	99	95
IWS	99	99	90

WS = Wet Scrubber including: Sieve Tray Tower, Packed Tower, Bubble Cap Tower
PS = Proprietary Wet Scrubber Design (A number of proprietary wet scrubbers have come on the market in recent years that are highly efficient on both particulates and corrosive gases. Two such units are offered by Calvert Environmental Equipment Co. and by Hydro-Sonic Systems, Inc.).
VS-20 = Venturi Scrubber, ca. 20–30 in W.G. Δp
VS-60 = Venturi Scrubber, ca. >60 in W.G. Δp
ESP-1 = Electrostatic Precipitator; 1 stage
ESP-2 = Electrostatic Precipitator; 2 stage
ESP-4 = Electrostatic Precipitator; 4 stage
IWS = Ionizing Wet Scrubber
DS = Dry Scrubber
FF = Fabric Filter (Baghouse)
SD = Spray Dryer (Wet/Dry Scrubber)

8.4 *References*

1. U.S. Environmental Protection Agency. "Guidance on Metals and Hydrogen Chloride Controls for Hazardous Waste Incinerators," Office of Solid Waste, Washington, D.C., August 1989.
2. Carroll, G.J., R.C. Thurnau, R.E. Maurnighan, L.R. Waterland, J.W. Lee, and D.J. Fournier. The Partitioning of Metals in Rotary Kiln Incineration. Proceedings of the Third International Conference on New Frontiers for Hazardous Waste Management. NTIS Document No. EPA/600/9–89/072, p. 555 (1989).

SECTION 9.0 PROCEDURES FOR DETERMINING DEFAULT VALUES FOR PARTITIONING OF METALS, ASH, AND TOTAL CHLORIDE/CHLORINE

Pollutant partitioning factor estimates can come from two sources: default assumptions or engineering judgement. EPA's default assumptions are discussed below for metals, HCl, Cl₂, and PM. The default assumptions are used to conservatively predict the partitioning factor for several types of BIFs. Engineering judgement-based partitioning factor estimates are discussed in section 9.4.

9.1 *Partitioning Default Value for Metals*

To be conservative, the Agency is assuming that 100 percent of each metal in each feed stream is partitioned to the combustion gas. Owners/operators may use this default value or a supportable, site-specific value developed following the general guidelines provided in section 9.4.

9.2 *Special Procedures for Chlorine, HCl, and Cl₂*

The Agency has established the special procedures presented below for chlorine because the emission limits are based on the pollutants HCl and Cl2 formed from chlorine fed to the combustor. Therefore, the owner/operator must estimate the controlled emission rate of both HCl and Cl₂ and show that they do not exceed allowable levels.

1. The default partitioning value for the fraction of chlorine in the total feed streams that is partitioned to combustion gas is 100 percent. Owners/operators may use this default value or a supportable, site-specific value developed following the general guidelines provided in section 9.4.

2. To determine the partitioning of chlorine in the combustion gas to HCl versus Cl₂, either use the default values below or use supportable site-specific values developed following the general guidelines provided in section 9.4.

• For BIFs excluding halogen acid furnaces (HAFs), with a total feed stream chlorine/hydrogen ratio ≥ 0.95, the default partitioning factor is 20 percent Cl₂, 80 percent HCl.

• For HAFs and for BIFs with a total feed stream chlorine/hydrogen ratio > 0.95, the default partitioning factor is 100 percent Cl₂.

3. To determine the uncontrolled (i.e., prior to acid gas APCS) emission rate of HCl and Cl₂, multiply the feed rate of chlorine times the partitioning factor for each pollutant. Then, for HCl, convert the chlorine emission rate to HCl by multiplying it by the ratio of the molecular weight of Cl to the molecular

weight of HCl (i.e., 35.5/36.5). No conversion is needed for Cl_2.

9.3 *Special Procedures for Ash*

This section: (1) Explains why ash feed rate limits are not applicable to cement and light-weight aggregate kilns; (2) presents the default partitioning values for ash; and (3) explains how to convert the 0.08 gr/dscf, corrected to 7% O_2, PM emission limit to a PM emission rate.

Waiver for Cement and Light-Weight Aggregate Kilns. For cement kilns and light-weight aggregate kilns, raw material feed streams contain the vast majority of the ash input, and a significant amount of the ash in the feed stream is entrained into the kiln exhaust gas. For these devices, the ash content of the hazardous waste stream is expected to have a negligible effect on total ash emissions. For this reason, there is no ash feed rate compliance limit for cement kilns or light-weight aggregate kilns. Nonetheless, cement kilns and light-weight aggregate kilns are required to initially certify that PM emissions are not likely to exceed the PM limit, and subsequently, certify through compliance testing that the PM limit is not exceeded.

Default Partitioning Value for Ash. The default assumption for partitioning of ash depends on the feed stream firing system. There are two methods by which materials may be fired into BIFs: Suspension-firing and bed-firing.

The suspension category includes atomized and lanced pumpable liquids and suspension-fired pulverized solids. The default partitioning assumption for materials fired by these systems is that 100 percent of the ash partitions to the combustion gas.

The bed-fired category consists principally of stoker boilers and raw materials (and in some cases containerized hazardous waste) fed into cement and light-weight aggregate kilns. The default partitioning assumption for materials fired on a bed is that 5 percent of the ash partitions to the combustion gas.

Converting the PM Concentration-Based Standard to a PM Mass Emission Rate. The emission limit for BIFs is 0.08 gr/dscf, corrected to 7% O_2, unless a more stringent standard applies [e.g., a New Source Performance Standard (NSPS) or a State standard implemented under the State Implementation Plan (SIP)]. To convert the 0.08 gr/dscf standard to a PM mass emission rate:

1. Determine the flue gas O_2 concentration (percent by volume, dry) and flue gas flow rate (dry standard cubic feet per minute); and

2. Calculate the allowable PM mass emission rate by multiplying the concentration-based PM emission standard times the flue gas flow rate times a dilution correction factor equal to [(21–O_2 concentration from step 1)/(21–7)].

9.4 *Use of Engineering Judgement To Estimate Partitioning and APCS RE Values*

Engineering judgement may be used in place of EPA's conservative default assumptions to estimate partitioning and APCS RE values provided that the engineering judgement is defensible and properly documented. To properly document engineering judgement, the owner/operator must keep a written record of all assumptions and calculations necessary to justify the APCS RE used. The owner/operator must provide this record to the Director upon request and must be prepared to defend the assumptions and calculations used.

If the engineering judgement is based on emissions testing, the testing will often document the emission rate of a pollutant relative to the feed rate of that pollutant rather than the partitioning factor or APCS RE.

Examples of situations where the use of engineering judgement may be supportable to estimate a partitioning factor, APCS RE, or SRE include:

• Using emissions testing data from the facility to support an SRE, even though the testing may not meet full QA/QC procedures (e.g., triplicate test runs). The closer the test results conform with full QA/QC procedures and the closer the operating conditions during the test conform with the established operating conditions for the facility, the more supportable the engineering judgement will be.

• Applying emissions testing data documenting an SRE for one metal, including nonhazardous surrogate metals to another less volatile metal.

• Applying emissions testing data documenting an SRE from one facility to a similar facility.

• Using APCS vendor guarantees of removal efficiency.

9.5 *Restrictions on Use of Test Data*

The measurement of an SRE or an APCS RE may be limited by the detection limits of the measurement technique. If the emission of a pollutant is undetectable, then the calculation of SRE or APCS RE should be based on the lower limit of detectability. An SRE or APCS RE of 100 percent is not acceptable.

Further, mass balance data of facility inputs, emissions, and products/residues may not be used to support a partitioning factor, given the inherent uncertainties of such procedures. Partitioning factors other than the default values may be supported based on engineering judgement, considering, for example, process chemistry. Emissions test data may be used to support an engineering judgement-based SRE, which includes both partitioning and APCS RE.

9.5 *References*

1. Barton, R.G., W.D. Clark, and W.R. Seeker. (1990) "Fate of Metals in Waste Combustion Systems". Combustion Science and Technology. 74, 1–6, p. 327

SECTION 10.0 ALTERNATIVE METHODOLOGY FOR IMPLEMENTING METALS CONTROLS

10.1 *Applicability*

This method for controlling metals emissions applies to cement kilns and other industrial furnaces operating under interim status that recycle emission control residue back into the furnace.

10.2 *Introduction*

Under this method, cement kilns and other industrial furnaces that recycle emission control residue back into the furnace must comply with a kiln dust concentration limit (i.e., a collected particulate matter (PM) limit) for each metal, as well as limits on the maximum feedrates of each of the metals in: (1) pumpable hazardous waste; and (2) all hazardous waste.

The following subsections describe how this method for controlling metals emissions is to be implemented:

• Subsection 10.3 discusses the basis of the method and the assumptions upon which it is founded;

• Subsection 10.4 provides an overview of the implementation of the method;

• Subsection 10.5 is a step-by-step procedure for implementation of the method;

• Subsection 10.6 describes the compliance procedures for this method; and

• Appendix A describes the statistical calculations and tests to be used in the method.

10.3 *Basis*

The viability of this method depends on three fundamental assumptions:

(1) Variations in the ratio of the metal concentration in the emitted particulate to the metal concentration in the collected kiln dust (referred to as the enrichment factor or EF) for any given metal at any given facility will fall within a normal distribution that can be experimentally determined.

(2) The metal concentrations in the collected kiln dust can be accurately and representatively measured (using procedures specified in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" (SW–846), incorporated by reference in 40 CFR 260.11).

(3) The facility will remain in compliance with the applicable particulate matter (PM) emission standard.

Given these assumptions, metal emissions can be related to the measured concentrations in the collected kiln dust by the following equation:

$$ ME \left(\frac{lb\ Emitted\ Metal}{hr} \right) = $$

$$ PME \left(\frac{lb\ PM}{hr} \right) DMC \left(\frac{lb\ Dust\ Metal}{lb\ Dust} \right) EF \left(\frac{lb\ Emitted\ Metal/lb\ PM}{lb\ Dust\ Metal/lb\ Dust} \right) \tag{1} $$

Where:

ME is the metal emitted;

PME is the particulate matter emitted;

DMC is the metal concentration in the collected kiln dust; and

EF is the enrichment factor, which is the ratio of the metal concentration in the emitted particulate matter to the metal concentration in the collected kiln dust.

This equation can be rearranged to calculate a maximum allowable dust metal

concentration limit (DMCL) by assuming worst-case conditions that: metal emissions are at the Tier III (or Tier II) limit (see 40 CFR 266.106), and that particulate emissions are at the particulate matter limit (PML):

$$ DMCL \left(\frac{lb\ Dust\ Metal}{lb\ Dust} \right) = \frac{Tier\ III\ Limit \left(\frac{lb\ Emitted\ Metal}{hr} \right)}{PML \left(\frac{lb\ PM}{hr} \right) EF \left(\frac{lb\ Emitted\ Metal/lb\ PM}{lb\ Dust\ Metal/lb\ Dust} \right)} \tag{2} $$

The enrichment factor used in the above equation must be determined experimentally from a minimum of 10 tests in which metal concentrations are measured in kiln dust and stack samples taken simultaneously. This approach provides a range of enrichment

factors that can be inserted into a statistical distribution (t-distribution) to determine $EF_{95\%}$ and $EF_{99\%}$. $EF_{95\%}$ is the value at which there is a 95% confidence level that the enrichment factor is below this value at any given time. Similarly, $EF_{99\%}$ is the value at which there is

a 99% confidence level that the enrichment factor is below this value at any given time. $EF_{95\%}$ is used to calculate the "violation" dust metal concentration limit ($DMCL_v$):

$$ DMCL_v \left(\frac{lb\ Dust\ Metal}{lb\ Dust} \right) = \frac{Tier\ III\ Limit \left(\frac{lb\ Emitted\ Metal}{hr} \right)}{PML \left(\frac{lb\ PM}{hr} \right) EF_{95\%} \left(\frac{lb\ Emitted\ Metal/lb\ PM}{lb\ Dust\ Metal/lb\ Dust} \right)} \tag{3} $$

If the kiln dust metal concentration is just above this "violation" limit, and the PM emissions are at the PM emissions limit, there is a 5% chance that the metal emissions are above the Tier III limit. In such a case, the facility would be in violation of the metals standard.

To provide a margin of safety, a second, more conservative kiln dust metal concentration limit is also used. This "conservative" dust metal concentration limit

($DMCL_c$) is calculated using a "safe" enrichment factor (SEF). If $EF_{99\%}$ is greater than two times the value of $EF_{95\%}$, the "safe" enrichment factor can be calculated using Equation 4a:

$$ SEF > 2\ EF_{95\%} \tag{4a} $$

If $EF_{99\%}$ is not greater than two times the value of $EF_{95\%}$, the "safe" enrichment factor can be calculated using Equation 4b:

$$ SEF > EF_{99\%} \tag{4b} $$

In cases where the enrichment factor cannot be determined because the kiln dust metal concentration is nondetectable, the "safe" enrichment factor is as follows:

$$ SEF = 100 \tag{4c} $$

For all cases, the "conservative" dust metal concentration limit is calculated using the following equation:

$$ DMCL_c \left(\frac{lb\ Dust\ Metal}{lb\ Dust} \right) = \frac{Tier\ III\ Limit \left(\frac{lb\ Emitted\ Metal}{hr} \right)}{PML \left(\frac{lb\ PM}{hr} \right) SEF \left(\frac{lb\ Emitted\ Metal/lb\ PM}{lb\ Dust\ Metal/lb\ Dust} \right)} \tag{5} $$

If the kiln dust metal concentration at a facility is just above the "conservative" limit based on that "safe" enrichment factor

provided in Equation 4a, and the PM emissions are at the PM emissions limit, there is a 5% chance that the metal emissions are

above one-half the Tier III limit. If the kiln dust metal concentration at the facility is just above the "conservative" limit based on the

"safe" enrichment factor provided in Equation 4b, and the PM emissions are at the PM emissions limit, there is a 1% chance that the metal emissions are above the Tier III limit. In either case, the facility would be unacceptably close to a violation. If this situation occurs more than 5% of the time, the facility would be required to rerun the series of 10 tests to determine the enrichment factor. To avoid this expense, the facility would be advised to reduce its metals feedrates or to take other appropriate measures to maintain its kiln dust metal concentrations in compliance with the "conservative" dust metal concentration limits.

In cases where the enrichment factor cannot be determined because the kiln dust metal concentration is nondetectable, and thus no $EF_{98\%}$ exists, the "violation" dust metal concentration limit is set at ten times the "conservative" limit:

$$DMCL_v = 10 \times DMCL_c \qquad (6)$$

10.4   Overview

The flowchart for implementing the method is shown in Figure 10.4–1. The general procedure is as follows:

• Follow the certification of precompliance procedures described in subsection 10.6 (to comply with 40 CFR 266.103(b)).

• For each metal of concern, perform a series of tests to establish the relationship (enrichment factor) between the concentration of emitted metal and the metal concentration in the collected kiln dust.

• Use the demonstrated enrichment factor, in combination with the Tier III (or Tier II) metal emission limit and the most stringent applicable particulate emission limit, to calculate the "violation" and "conservative" dust metal concentration limits. Include this information with the certification of compliance under 40 CFR 266.103(c).

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Figure 10.4-1

Compliance Implementation Flow Chart
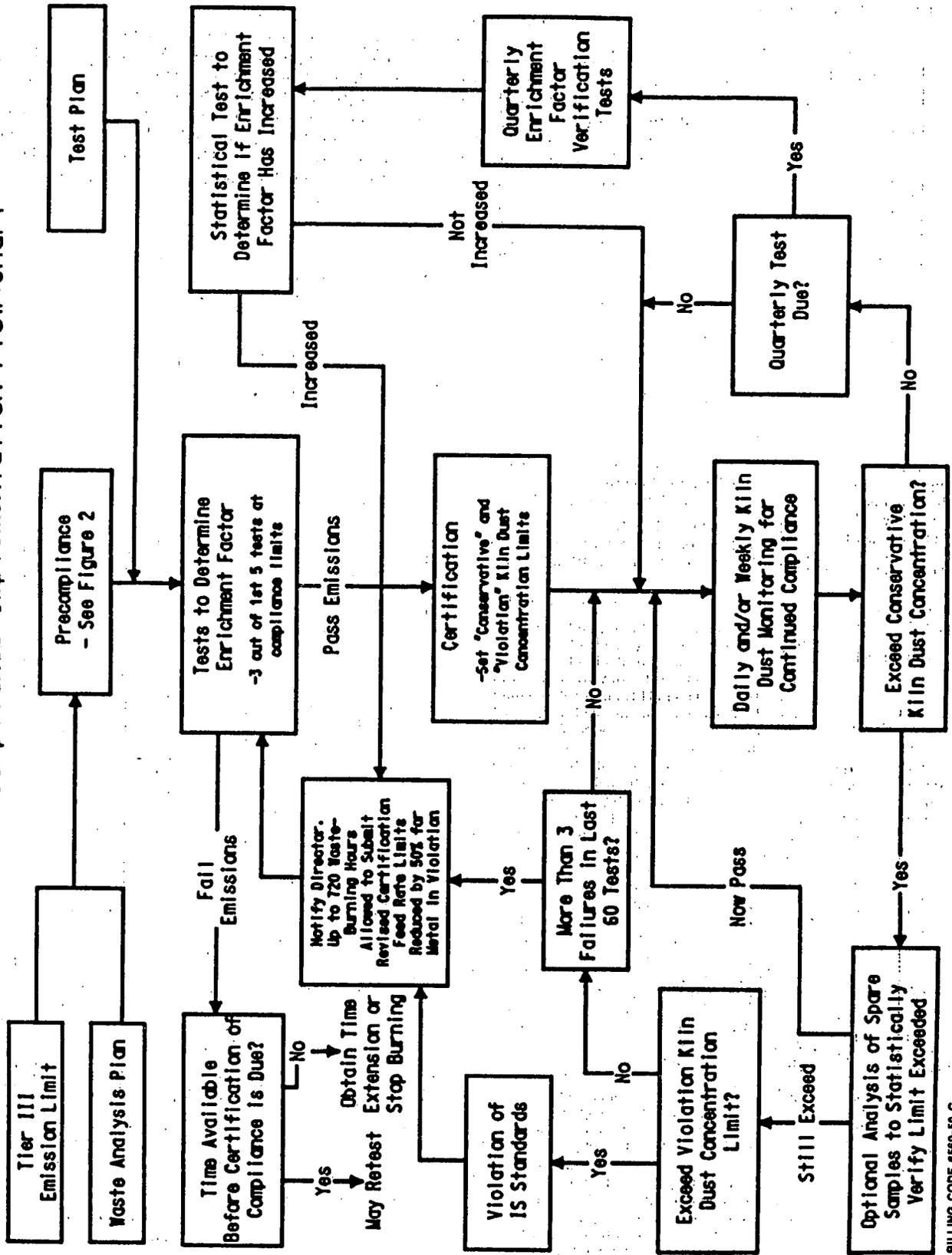
BILLING CODE 6560-50-C

• Perform daily and/or weekly monitoring of the cement kiln dust metal concentration to ensure (with appropriate QA/QC) that the metal concentration does not exceed either limit.

—If the cement kiln dust metal concentration exceeds the "conservative" limit more than 5% of the time (i.e., more than three failures in last 60 tests), the series of tests to determine the enrichment factor must be repeated.

—If the cement kiln dust metal concentration exceeds the "violation" limit, a violation has occurred.

• Perform quarterly tests to verify that the enrichment factor has not increased significantly. If the enrichment factor has increased, the series of tests to determine the enrichment factor must be repeated.

10.5 *Implementation Procedures*

A step-by-step description for implementing the method is provided below:

(1) Prepare initial limits and test plans.

• Determine the Tier III metal emission limit. The Tier II metal emission limit may also be used (see 40 CFR 266.106).

• Determine the applicable PM emission standard. This standard is the most stringent particulate emission standard that applies to the facility. A facility may elect to restrict itself to an even more stringent self-imposed PM emission standard, particularly if the facility finds that it is easier to control particulate emissions than to reduce the kiln dust concentration of a certain metal (i.e., lead).

• Determine which metals need to be monitored (i.e., all hazardous metals for which Tier III emission limits are lower than PM emission limits—assuming PM is pure metal).

• Follow the compliance procedures described in Subsection 10.6.

• Follow the guidelines described in SW-846 for preparing test plans and waste analysis plans for the following tests:

—Compliance tests to determine limits on metal feedrates in pumpable hazardous wastes and in all hazardous wastes (as well as to determine other compliance parameters);

—Initial tests to determine enrichment factors;

—Quarterly tests to verify enrichment factors;

—Analysis of hazardous waste feedstreams; and

—Daily and/or weekly monitoring of kiln dust for continuing compliance.

(2) Conduct tests to determine the enrichment factor.

• These tests must be conducted within a 14-day period. No more than two tests may be conducted in any single day. If the tests are not completed within a 14-day period, they must be repeated.

• Simultaneous stack samples and kiln dust samples must be taken.

—Stack sampling must be conducted with the multiple metals train according to procedures provided in section 10.3 of this Methods Manual.

—Kiln dust sampling must be conducted as follows:

—Follow the sampling and analytical procedures described in SW-846 and the waste analysis plan as they pertain to the condition and accessibility of the dust.

—Samples should be representative of the last ESP or Fabric Filter in the APCS series.

• The feedrates of hazardous metals in all pumpable hazardous waste streams and in all hazardous waste streams must be monitored during these tests. It is recommended (but not required) that the feedrates of hazardous metals in all feedstreams also be monitored.

• At least ten single (noncomposited) runs are required during the tests.

—The facility must follow a normal schedule of kiln dust recharging for all of the tests.

—Three of the first five tests must be compliance tests in conformance with 40 CFR 266.103(c); i.e., they must be used to determine maximum allowable feedrates of metals in pumpable hazardous wastes. and in all hazardous wastes, as well as to determine other compliance limits (see 40 CFR 266.103(c)(1)).

—The remainder of the tests need not be conducted under full compliance test conditions; however, the facility must operate at its compliance test production rate, and it must burn hazardous waste during these tests such that the feedrate of each metal for pumpable and total hazardous wastes is at least 25% of the feedrate during compliance testing. If these criteria, and those discussed below, are not met for any parameter during a test, then either the test is not valid for determining enrichment factors under this method, or the compliance limits for that parameter must be established based on these test conditions rather than on the compliance test conditions.

• Verify that compliance emission limits are not exceeded.

—Metal emissions must not exceed Tier III (or Tier II) limits.

—PM emissions must not exceed the most stringent of applicable PM standards (or an optional self-imposed particulate standard).

• The facility must generate normal, marketable product using normal raw materials and fuels under normal operating conditions (for parameters other than those specified under this method) when these tests are conducted.

• Chromium must be treated as a special case:

—The enrichment factor for total chromium is calculated in the same way as the enrichment factor for other metals (i.e., the enrichment factor is the ratio of the concentration of total chromium in the emitted particulate matter to the concentration of total chromium in the collected kiln dust).

—The enrichment factor for hexavalent chromium (if measured) is defined as the ratio of the concentration of hexavalent chromium in the emitted particulate matter to the concentration of total chromium in the collected kiln dust.

(3) Use the enrichment factors measured in Step 2 to determine $EF_{95\%}$, $EF_{99\%}$, and SEF.

• Calculate $EF_{95\%}$ and $EF_{99\%}$ according to the t-distribution as described in Appendix A

• Calculate SEF by

—Equation 4a if $EF_{95\%}$ is determinable and if $EF_{99\%}$ is greater than two times $EF_{95\%}$.

—Equation 4b if $EF_{95\%}$ is determinable and if $EF_{99\%}$ is not greater than two times $EF_{95\%}$.

—Equation 4c if $EF_{95\%}$ is not determinable.

The facility may choose to set an even more conservative SEF to give itself a larger margin of safety between the point where corrective action is necessary and the point where a violation occurs.

(4) Prepare certification of compliance.

• Calculate the "conservative" dust metal concentration limit ($DMCL_c$) using Equation 5.

—Chromium is treated as a special case. The "conservative" kiln dust chromium concentration limit is set for total chromium, not for hexavalent chromium. The limit for total chromium must be calculated using the Tier III (or Tier II) metal limit for hexavalent chromium.

—If the stack samples described in Step 2 were analyzed for hexavalent chromium, the SEF based on the hexavalent chromium enrichment factors (as defined in Step 2) must be used in this calculation.

—If the stack samples were not analyzed for hexavalent chromium, then the SEF based on the total chromium enrichment factor must be used in this calculation.

• Calculate the "violation" dust metal concentration limit ($DMCL_v$) using Equation 3 if $EF_{95\%}$ is determinable, or using Equation 6 if $EF_{95\%}$ is not determinable.

—Chromium is treated as a special case. The "violation" kiln dust chromium concentration limit is set for total chromium, not for hexavalent chromium. The limit for total chromium must be calculated using the Tier III (or Tier II) metal limit for hexavalent chromium.

—If the stack samples taken in Step 2 were analyzed for hexavalent chromium, the $EF_{95\%}$ based on the hexavalent chromium enrichment factor (as defined in Step 2) should be used in this calculation.

—If the stack samples were not analyzed for hexavalent chromium, the $EF_{95\%}$ based on the total chromium enrichment factor must be used in this calculation.

• Submit certification of compliance.

• Steps 2–4 must be repeated for recertification, which is required once every 3 years (see § 266.103(d)).

(5) Monitor metal concentrations in kiln dust for continuing compliance, and maintain compliance with all compliance limits for the duration of interim status.

• Metals to be monitored during compliance testing are classified as either "critical" or "noncritical" metals.

—All metals must initially be classified as "critical" metals and be monitored on a daily basis.

—A "critical" metal may be reclassified as a "noncritical" metal if its concentration in the kiln dust remains below 10% of its "conservative" kiln dust metal concentration limit for 30 consecutive daily samples. "Noncritical" metals must be monitored on a weekly basis.

—A "noncritical" metal must be reclassified as a "critical" metal if its concentration in the kiln dust is above 10% of its

"conservative" kiln dust metal concentration limit for any single daily or weekly sample.

• Noncompliance with the sampling and analysis schedule prescribed by this method is a violation of the metals controls under § 266.103.

• Follow the sampling, compositing, and analytical procedures described in this method and in SW-846 as they pertain to the condition and accessibility of the kiln dust.

• Follow the same procedures and sample at the same locations as were used for kiln dust samples collected to determine the enrichment factors (as discussed in Step 2).

• Samples must be collected at least once every 8 hours, and a daily composite must be prepared according to SW-846 procedures.

—At least one composite sample is required. This sample is referred to as the "required" sample.

—For QA/QC purposes, a facility may elect to collect two or more additional samples. These samples are referred to as the "spare" samples. These additional samples must be collected over the same time period and according to the same procedures as those used for the "required" sample.

—Samples for "critical" metals must be daily composites.

—Samples for "noncritical" metals must be weekly composites. These samples can be composites of the original 8-hour samples, or they can be composites of daily composite samples.

• Analyze the "required" sample to determine the concentration of each metal.

—This analysis must be completed within 48 hours of the close of the sampling period. Failure to meet this schedule is a violation of the metals standards of § 266.103.

• If the "conservative" kiln dust metal concentration limit is exceeded for any metal, refer to Step 8.

• If the "conservative" kiln dust metal concentration limit is not exceeded, continue with the daily or weekly monitoring (Step 5) for the duration of interim status.

• Conduct quarterly enrichment factor verification tests, as described in Step 6.

(6) Conduct quarterly enrichment factor verification tests.

• After certification of compliance with the metals standards, a facility must conduct quarterly enrichment factor verification tests every three months for the duration of interim status. The first quarterly test must be completed within three months of certification (or recertification). Each subsequent quarterly test must be completed within three months of the preceding quarterly test. Failure to meet this schedule is a violation.

• Simultaneous stack samples and kiln dust samples must be collected.

• Follow the same procedures and sample at the same locations as were used for kiln dust samples and stack samples collected to determine the enrichment factors (as discussed in Step 2).

• At least three single (noncomposited) runs are required. These tests need not be conducted under the operating conditions of the initial compliance test; however, the

facility must operate under the following conditions:

—It must operate at compliance test production rate.

—It must burn hazardous waste during the test, and for the 2-day period immediately preceding the test, such that the feedrate of each metal for pumpable and total hazardous wastes consist of at least 25% of the operating limits established during the compliance test.

—It must remain in compliance with all compliance parameters (see § 266.103(c)(1)).

—It must follow a normal schedule of kiln dust recharging.

—It must generate normal marketable product from normal raw materials during the tests.

(7) Conduct a statistical test to determine if the enrichment factors measured in the quarterly verification tests have increased significantly from the enrichment factors determined in the tests conducted in Step 2. The enrichment factors have increased significantly if all three of the following criteria are met:

• By applying the t-test described in appendix A, it is determined that the enrichment factors measured in the quarterly tests are not taken from the same population as the enrichment factors measured in the Step 2 tests;

• The EF_{avg} calculated for the combined data sets (i.e., the quarterly test data and the original Step 2 test data) according to the t-distribution (described in appendix A) is more than 10% higher than the EF_{avg} based on the enrichment factors previously measured in Step 2; and

• The highest measured kiln dust metal concentration recorded in the previous quarter is more than 10% of the "violation" kiln dust concentration limit that would be calculated from the combined EF_{avg}.

If the enrichment factors have increased significantly, the tests to determine the enrichment factors must be repeated (refer to Step 11). If the enrichment factors have not increased significantly, continue to use the kiln dust metal concentration limits based on the enrichment factors previously measured in Step 2, and continue with the daily and/or weekly monitoring described in Step 5.

(8) If the "conservative" kiln dust metal concentration limit was exceeded for any metal in any single analysis of the "required" kiln dust sample, the "spare" samples corresponding to the same period may be analyzed to determine if the exceedance was due to a sampling or analysis error.

• If no "spare" samples were taken, refer to Step 9.

• If the average of all the samples for a given day (or week, as applicable) (including the "required" sample and the "spare" samples) does not exceed the "conservative" kiln dust metal concentration limit, no corrective measures are necessary; continue with the daily and/or weekly monitoring as described in Step 5.

• If the average of all the samples for a given day (or week, as applicable) exceeds the "conservative" kiln dust metal concentration limit, but the average of the

"spare" samples is below the "conservative" kiln dust metal concentration limit, apply the Q-test, described in appendix A, to determine whether the "required" sample concentration can be judged as an outlier.

—If the "required" sample concentration is judged an outlier, no corrective measures are necessary; continue with the daily and/or weekly monitoring described in Step 5.

—If the "required" sample concentration is not judged an outlier, refer to Step 9.

(9) Determine if the "violation" kiln dust metal concentration has been exceeded based on either the average of all the samples collected during the 24-hour period in question, or if discarding an outlier can be statistically justified by the Q-test described in appendix A, on the average of the remaining samples.

• If the "violation" kiln dust metal concentration limit has been exceeded, a violation of the metals controls under § 266.103(c) has occurred. Notify the Director that a violation has occurred. Hazardous waste may be burned for testing purposes for up to 720 operating hours to support a revised certification of compliance. Note that the Director may grant an extension of the hours of hazardous waste burning under § 266.103(c)(7) if additional burning time is needed to support a revised certification for reasons beyond the control of the owner or operator. Until a revised certification of compliance is submitted to the Director, the feedrate of the metals in violation in total and pumpable hazardous waste feeds is limited to 50% of the previous compliance test limits.

• If the "violation" kiln dust metal concentration has not been exceeded:

—If the exceedance occurred in a daily composite sample, refer to Step 10.

—If the exceedance occurred in a weekly composite sample, refer to Step 11.

(10) Determine if the "conservative" kiln dust metal concentration limit has been exceeded more than three times in the last 60 days.

• If not, log this exceedance and continue with the daily and/or weekly monitoring (Step 5).

• If so, the tests to determine the enrichment factors must be repeated (refer to Step 11).

• This determination is made separately for each metal; For example,

—Three exceedances for each of the ten hazardous metals are allowed within any 60-day period.

—Four exceedances of any single metal in any 60-day period is not allowed.

• This determination should be made daily, beginning on the first day of daily monitoring. For example, if four exceedances of any single metal occur in the first four days of daily monitoring, do not wait until the end of the 60-day period; refer immediately to Step 11.

(11) The tests to determine the enrichment factor must be repeated if: (1) More than three exceedances of the "conservative" kiln dust metal concentration limit occur within any 60 consecutive daily samples; (2) an excursion of the "conservative" kiln dust metal concentration limit occurs in any

weekly sample; or (3) a quarterly test indicates that the enrichment factors have increased significantly.

• The facility must notify the Director if these tests must be repeated.

• The facility has up to 720 hazardous-waste-burning hours to redetermine the enrichment factors for the metal or metals in question and to recertify (beginning with a return to Step 2). During this period, the facility must reduce the feed rate of the metal in violation by 50%. If the facility has not completed the recertification process within this period, it must stop burning or obtain an extension. Hazardous waste burning may resume only when the recertification process (ending with Step 4) has been completed.

• Meanwhile, the facility must continue with daily kiln dust metals monitoring (Step 5) and must remain in compliance with the "violation" kiln dust metal concentration limits (Step 9).

10.6 Precompliance Procedures

Cement kilns and other industrial furnaces that recycle emission control residue back into the furnace must comply with the same certification schedules and procedures (with the few exceptions described below) that apply to other boilers and industrial furnaces. These schedules and procedures, as set forth

in § 266.103, require no later than the effective date of the rule, each facility submit a certification which establishes precompliance limits for a number of compliance parameters (see § 266.103(b)(3)), and that each facility immediately begin to operate under these limits.

These precompliance limits must ensure that interim status emissions limits for hazardous metals, particulate matter, HCl, and Cl_2 are not likely to be exceeded. Determination of the values of the precompliance limits must be made based on either (1) conservative default assumptions provided in this Methods Manual, or (2) engineering judgement.

The flowchart for implementing the precompliance procedures is shown in Figure 10.6-1. The step-by-step precompliance implementation procedure is described below. The precompliance implementation procedures and numbering scheme are similar to those used for the compliance procedures described in Subsection 10.5.

(1) Prepare initial limits and test plans.

• Determine the Tier III metal emission limit. The Tier II metal emission limit may also be used (see 40 CFR 266.106).

• Determine the applicable PM emission standard. This standard is the most stringent particulate emission standard that applies to

the facility. A facility may elect to restrict itself to an even more stringent self-imposed PM emission standard, particularly if the facility finds that it is easier to control particulate emissions than to reduce the kiln dust concentration of a certain metal (i.e, lead).

• Determine which metals need to be monitored (i.e., all hazardous metals for which Tier III emission limits are lower than PM emission limits, assuming PM is pure metal).

• Follow the procedures described in SW-846 for preparing waste analysis plans for the following tasks:

—Analysis of hazardous waste feedstreams.
—Daily and/or weekly monitoring of kiln dust concentrations for continuing compliance.

(2) Determine the "safe" enrichment factor for precompliance. In this context, the "safe" enrichment factor is a conservatively high estimate of the enrichment factor (the ratio of the emitted metal concentration to the metal concentration in the collected kiln dust). The "safe" enrichment factor must be calculated from either conservative default values, or engineering judgement.

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Figure 10.6-1

Precompliance Implementation Flow Chart

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• Conservative default values for the "safe" enrichment factor are as follows:

—SEF=10 for all hazardous metals except mercury. SEF=10 for antimony, arsenic, barium, beryllium, cadmium, chromium, lead, silver, and thallium.

—SEF=100 for mercury.

• Engineering judgement may be used in place of conservative default assumptions provided that the engineering judgement is defensible and properly documented. The facility must keep a written record of all assumptions and calculations necessary to justify the SEF. The facility must provide this record to EPA upon request and must be prepared to defend these assumptions and calculations.

Examples of situations where the use of engineering judgement is appropriate include:

—Use of data from precompliance tests;

—Use of data from previous compliance tests; and

—Use of data from similar facilities.

(3) This step does not apply to precompliance procedures.

(4) Prepare certification of precompliance.

• Calculate the "conservative" dust metal concentration limit (DMCL$_c$) using Equation 5.

• Submit certification of precompliance. This certification must include precompliance limits for all compliance parameters that apply to other boilers and industrial furnaces (i.e., those that do not recycle emission control residue back into the furnace) as listed in § 266.103(b)(3), except that it is not necessary to set precompliance limits on maximum feedrate of each hazardous metal in all combined feedstreams.

• Furnaces that recycle collected PM back into the furnace (and that elect to comply with this method (see § 266.103(c)(3)(ii)) are subject to a special precompliance parameter, however. They must establish precompliance limits on the maximum concentration of each hazardous metal in collected kiln dust. (which must be set according to the procedures described above).

(5) Monitor metal concentration in kiln dust for continuing compliance, and maintain compliance with all precompliance limits until certification of compliance has been submitted.

• Metals to be monitored during precompliance testing are classified as either "critical" or "noncritical" metals.

—All metals must initially be classified as "critical" metals and be monitored on a daily basis.

—A "critical" metal may be reclassified as a "noncritical" metal if its concentration in the kiln dust remains below 10% of its "conservative" kiln dust metal concentration limit for 30 consecutive daily samples. "Noncritical" metals must be monitored on a weekly basis, at a minimum.

—A "noncritical" metal must be reclassified as a "critical" metal if its concentration in the kiln dust is above 10% of its "conservative" kiln dust metal concentration limit for any single daily or weekly sample.

• It is a violation if the facility fails to analyze the kiln dust for any "critical" metal on any single day or for any "noncritical"

metal during any single week, when hazardous waste is burned.

• Follow the sampling, compositing, and analytical procedures described in this method and in SW–846 as they pertain to the condition and accessibility of the kiln dust.

• Samples must be collected at least once every 6 hours, and a daily composite prepared according to SW–846 procedures.

—At least one composite sample is required. This sample is referred to as the "required" sample.

—For QA/QC purposes, a facility may elect to collect two or more additional samples. These samples are referred to as the "spare" samples. These additional samples must be collected over the same time period and according to the same procedures as those used for the "required" sample.

—Samples for "critical" metals must be daily composites.

—Samples for "noncritical" metals must be weekly composites, at a minimum. These samples can be composites of the original 6-hour samples, or they can be composites of daily composite samples.

• Analyze the "required" sample to determine the concentration of each metal.

—This analysis must be completed within 48 hours of the close of the sampling period. Failure to meet this schedule is a violation.

• If the "conservative" kiln dust metal concentration limit is exceeded for any metal, refer to Step 8.

• If the "conservative" kiln dust metal concentration limit is not exceeded, continue with the daily and/or weekly monitoring (Step 5) for the duration of interim status.

(6) This step does not apply to precompliance procedures.

(7) This step does not apply to precompliance procedures.

(8) If the "conservative" kiln dust metal concentration limit was exceeded for any metal in any single analysis of the "required" kiln dust sample, the "spare" samples corresponding to the same period may be analyzed to determine if the exceedance is due to a sampling or analysis error.

• If no "spare" samples were taken, refer to Step 9.

• If the average of all the samples for a given day (or week, as applicable) (including the "required" sample and the "spare" samples) does not exceed the "conservative" kiln dust metal concentration limit, no corrective measures are necessary; continue with the daily and/or weekly monitoring as described in Step 5.

• If the average of all the samples for a given day (or week, as applicable) exceeds the "conservative" kiln dust metal concentration limit. but the average of the "spare" samples is below the "conservative" kiln dust metal concentration limit, apply the Q-test, described in appendix A, to determine whether the "required" sample concentration can be judged as an outlier.

—If the "required" sample concentration is judged an outlier. no corrective measures are necessary; continue with the daily and/ or weekly monitoring described in Step 5.

—If the "required" sample concentration is not judged an outlier, refer to Step 10.

(9) This step does not apply to precompliance procedures.

(10) Determine if the "conservative" kiln dust metal concentration limit has been exceeded more than three times in the last 60 days.

• If not, log this exceedance and continue with the daily and/or weekly monitoring (Step 5).

• If so, the tests to determine the enrichment factors must be repeated (refer to Step 11).

• This determination is made separately for each metal; for example

—Three exceedances for each of the ten hazardous metals are allowed within any 60-day period.

—Four exceedances of any single metal in any 60-day period is not allowed.

• This determination should be made daily, beginning on the first day of daily monitoring. For example, if four exceedances of any single metal occur in the first four days of daily monitoring, do not wait until the end of the 60-day period; refer immediately to Step 11.

(11) A revised certification of precompliance must be submitted to the Director (or certification of compliance must be submitted) if: (1) More than three exceedances of the "conservative" kiln dust metal concentration limit occur within any 60 consecutive daily samples; or (2) an exceedance of the "conservative" kiln dust metal concentration limit occurs in any weekly sample.

• The facility must notify the Director if a revised certification of precompliance must be submitted.

• The facility has up to 720 waste-burning hours to submit a certification of compliance or a revised certification of precompliance. During this period, the feed rate of the metal in violation must be reduced by 50%. In the case of a revised certification of precompliance, engineering judgement must be used to ensure that the "conservative" kiln dust metal concentration will not be exceeded. Examples of how this goal might be accomplished include:

—Changing equipment or operating procedures to reduce the kiln dust metal concentration;

—Changing equipment or operating procedures, or using more detailed engineering judgement, to decrease the estimated SEF and thus increase the "conservative" kiln dust metal concentration limit;

—Increasing the "conservative" kiln dust metal concentration limit by imposing a stricter PM emissions standard; or

—Increasing the "conservative" kiln dust metal concentration limit by performing a more detailed risk assessment to increase the metal emission limits.

• Meanwhile, the facility must continue with daily kiln dust metals monitoring (Step 5).

Appendix A to Appendix IX to Part 266—Statistics

A.1 *Determination of Enrichment Factor*

After at least 10 initial emissions tests are performed, an enrichment factor for each metal must be determined. At the 95% confidence level, the enrichment factor, $EF_{95\%}$, is based on the test results and is statistically determined so there is only a 5% chance that the enrichment factor at any given time will be larger than $EF_{95\%}$. Similarly, at the 99% confidence level, the enrichment factor, $EF_{99\%}$, is statistically determined so there is only a 1% chance that the enrichment factor at any given time will be larger than $EF_{99\%}$.

For a large number of samples (n > 30), $EF_{95\%}$ is based on a normal distribution, and is equal to:

$$EF_{95\%} = EF + z_c\,\sigma \qquad (1)$$

where:

$$EF = \frac{\sum_{i=1}^{n} EF_i}{n} \qquad (2)$$

$$\sigma = \left[\frac{\sum_{i=1}^{n}(EF_i - EF)^2}{n}\right]^{\frac{1}{2}} \qquad (3)$$

For a 95% confidence level, z_c is equal to 1.645.

For a small number of samples (n < 30), $EF_{95\%}$ is based on the t-distribution and is equal to:

$$EF_{95\%} = EF + t_c\,S \qquad (4)$$

where the standard deviation, S, is defined as:

$$S = \left[\frac{\sum_{i=1}^{n}(EF_i - EF)^2}{n-1}\right]^{\frac{1}{2}} \qquad (5)$$

t_c is a function of the number of samples and the confidence level that is desired. It increases in value as the sample size decreases and the confidence level increases. The 95% confidence level is used in this method to calculate the "violation" kiln dust metal concentration limit; and the 99% confidence level is sometimes used to calculate the "conservative" kiln dust metal concentration limit. Values of t_c are shown in table A–1 for various degrees of freedom (degrees of freedom = sample size – 1) at the 95% and 99% confidence levels. As the sample size approaches infinity, the normal distribution is approached.

A.2 *Comparison of Enrichment Factor Groups*

To determine if the enrichment factors measured in the quarterly tests are significantly different from the enrichment factors determined in the initial Step 2 tests, the t-test is used. In this test, the value t_{meas}:

$$t_{meas} = \frac{EF_1 - EF_2}{\sigma_t \left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}}} \qquad (6)$$

TABLE A–1.—T-DISTRIBUTION

n–1 or $n_1 + n_2 - 2$	$t_{.95}$	$t_{.99}$
1	6.31	31.82
2	2.92	6.96
3	2.35	4.54
4	2.13	3.75
5	2.02	3.36
6	1.94	3.14
7	1.90	3.00
8	1.86	2.90
9	1.83	2.82
10	1.81	2.78
11	1.80	2.72
12	1.78	2.68
13	1.77	2.65
14	1.76	2.62
15	1.75	2.60
16	1.75	2.58
17	1.74	2.57
18	1.73	2.55
19	1.73	2.54
20	1.72	2.53
25	1.71	2.48
30	1.70	2.46
40	1.68	2.42
60	1.67	2.39
120	1.66	2.36
∞	1.645	2.33

$$\sigma_t = \left(\frac{(n_1-1)S_1^2 + (n_2-1)S_2^2}{n_1 + n_2 - 2}\right)^{\frac{1}{2}} \qquad (7)$$

is compared to t_{crit} at the desired confidence level. The 95% confidence level is used in this method. Values of t_{crit} are shown in table A–1 for various degrees of freedom (degrees of freedom $n_1 + n_2 - 2$) at the 95% and 99% confidence levels. If t_{meas} is greater than t_{crit}, it can be concluded with 95% confidence that the two groups are not from the same population.

A.3 *Rejection of Data*

If the concentration of any hazardous metal in the "required" kiln dust sample exceeds the kiln dust metal concentration limit, the "spare" samples are analyzed. If the average of the combined "required" and "spare" values is still above the limit, a statistical test is used to decide if the upper value can be rejected.

The "Q-test" is used to determine if a data point can be rejected. The difference between the questionable result and its neighbor is divided by the spread of the entire data set. The resulting ratio, Q_{meas}, is then compared with rejection values that are critical for a particular degree of confidence, where Q_{meas} is:

$$\sigma^{meas} = \frac{DMC_{highest} - DMC_{next\ highest}}{DMC_{highest} - DMC_{lowest}} \qquad (8)$$

The 90% confidence level for data rejection is used in this method. Table A–2 provides the values of Q_{crit} at the 90% confidence level. If Q_{meas} is larger than Q_{crit}, the data point can be discarded. Only one data point from a sample group can be rejected using this method.

TABLE A–2.—CRITICAL VALUES FOR USE IN THE Q-TEST

n	Q_{crit}
3	0.94
4	0.76
5	0.64
6	0.56
7	0.51
8	0.47
9	0.44
10	0.41

Appendix X to Part 266—Guideline On Air Quality Models (Revised)

[EPA DOCUMENT NUMBER EPA–450/2–78–027R]

Preface

Industry and control agencies have long expressed a need for consistency in the application of air quality models for regulatory purposes. In the 1977 Clean Air Act, Congress mandated such consistency and encouraged the standardization of model applications. The Guideline on Air Quality Models was first published in April 1978 to satisfy these requirements by specifying models and providing guidance for their use. This guideline provides a common basis for estimating the air quality concentrations used in assessing control strategies and developing emission limits.

The continuing development of new air quality models in response to regulatory requirements and the expanded requirements for models to cover even more complex problems have emphasized the need for periodic review and update of guidance on these techniques. Four primary on-going activities provide direct input to revisions of this modeling guideline. The first is a series of annual EPA workshops conducted for the purpose of ensuring consistency and providing clarification in the application of models. The second activity, directed toward the improvement of modeling procedures, is the cooperative agreement that EPA has with the scientific community represented by the American Meteorological Society. This agreement provides scientific assessment of procedures and proposed techniques and sponsors workshops on key technical issues. The third activity is the solicitation and review of new models from the technical and user community. In the March 27, 1980 Federal Register, a procedure was outlined for the submittal to EPA of privately developed models. After extensive evaluation

and scientific review, these models, as well as those made available by EPA, are considered for recognition in this guideline. The fourth activity is the extensive on-going research efforts by EPA and others in air quality and meteorological modeling.

Based primarily on these four activities, this document embodies revisions to the "Guideline on Air Quality Models." Although the text has been revised from the 1978 guide, the present content and topics are similar. As necessary, new sections and topics are included. A new format has also been adopted in an attempt to lessen the time required to incorporate changes. The looseleaf notebook format allows future changes to be made on a page-by-page basis. Changes will not be scheduled, but announcements of proposed changes will be made in the Federal Register as needed. EPA believes that revisions to this guideline should be timely and responsive to user needs and should involve public participation to the greatest possible extent. Information on the current status of modeling guidance can always be obtained from EPA's Regional Offices.

This revised guideline was promulgated in September 1986 (51 FR 32176–32179) and, with further revisions known as supplement A, in January 1988 (53 FR 392–396).

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1.0   Introduction

This guideline recommends air quality modeling techniques that should be applied to State Implementation Plan (SIP) (1) revisions for existing sources and to new source reviews, (2) including prevention of significant deterioration (PSD). (3) It is intended for use by EPA Regional Offices in judging the adequacy of modeling analyses performed by EPA, State and local agencies and by industry. The guidance is appropriate for use by other Federal agencies and by State agencies with air quality and land management responsibilities. It serves to identify, for all interested parties, those techniques and data bases EPA considers acceptable. The guide is not intended to be a compendium of modeling techniques. Rather, it should serve as a basis by which air quality managers, supported by sound scientific judgment, have a common measure of acceptable technical analysis.

Due to limitations in the spatial and temporal coverage of air quality measurements, monitoring data normally are not sufficient as the sole basis for demonstrating the adequacy of emission limits for existing sources. Also, the impacts of new sources that do not yet exist can only be determined through modeling. Thus, models, while uniquely filling one program need, have become a primary analytical tool in most air quality assessments. Air quality measurements though can be used in a complementary manner to dispersion models, with due regard for the strengths and weaknesses of both analysis techniques. Measurements are particularly useful in assessing the accuracy of model estimates. The use of air quality measurements alone however could be preferable, as detailed in a later section of this document, when models are found to be unacceptable and monitoring data with sufficient spatial and temporal coverage are available.

It would be advantageous to categorize the various regulatory programs and to apply a designated model to each proposed source needing analysis under a given program. However, the diversity of the nation's topography and climate, and variations in source configurations and operating characteristics dictate against a strict modeling "cookbook." There is no one model capable of properly addressing all conceivable situations even within a broad category such as point sources. Meteorological phenomena associated with threats to air quality standards are rarely amenable to a single mathematical treatment; thus, case-by-case analysis and judgment are frequently required. As modeling efforts become more complex, it is increasingly important that they be directed by highly competent individuals with a broad range of experience and knowledge in air quality

meteorology. Further, they should be coordinated closely with specialists in emissions characteristics, air monitoring and data processing. The judgment of experienced meteorologists and analysts is essential.

The model that most accurately estimates concentrations in the area of interest is always sought. However, it is clear from the needs expressed by the States and EPA Regional Offices, by many industries and trade associations, and also by the deliberations of Congress, that consistency in the selection and application of models and data bases should also be sought, even in case-by-case analyses. Consistency ensures that air quality control agencies and the general public have a common basis for estimating pollutant concentrations, assessing control strategies and specifying emission limits. Such consistency is not, however, promoted at the expense of model and data base accuracy. This guide provides a consistent basis for selection of the most accurate models and data bases for use in air quality assessments.

Recommendations are made in this guide concerning air quality models, data bases, requirements for concentration estimates, the use of measured data in lieu of model estimates, and model evaluation procedures. Models are identified for some specific applications. The guidance provided here should be followed in all air quality analyses relative to State Implementation Plans and in analyses required by EPA, State and local agency air programs. The EPA may approve the use of another technique that can be demonstrated to be more appropriate than those recommended in this guide. This is discussed at greater length in section 3.0. In all cases, the model applied to a given situation should be the one that provides the most accurate representation of atmospheric transport, dispersion, and chemical transformations in the area of interest. However, to ensure consistency, deviations from this guide should be carefully documented and fully supported.

From time to time situations arise requiring clarification of the intent of the guidance on a specific topic. Periodic workshops are held with the EPA Regional Meteorologists to ensure consistency in modeling guidance and to promote the use of more accurate air quality models and data bases. The workshops serve to provide further explanations of guideline requirements to the Regional Offices and workshop reports are issued with this clarifying information. In addition, findings from on-going research programs, new model submittals, or results from model evaluations and applications are continuously evaluated. Based on this information changes in the guidance may be indicated.

All changes to this guideline must follow rulemaking requirements since the guideline has been incorporated by reference in the PSD regulations. Changes will be proposed and noticed in the Federal Register. Ample opportunity for public comment will be provided for each proposed change and public hearings scheduled if requested. Published, final changes will be made available through the National Technical Information Service (NTIS).

A wide range of topics on modeling and data bases are discussed in the remainder of this guideline. Where specific recommendations are made, the recommendations are typed in a single-spaced format. Chapter 2 gives an overview of models and their appropriate use. Chapter 3 provides specific guidance on the use of "preferred" air quality models and on the selection of alternative techniques. Chapters 4 through 7 provide recommendations on modeling techniques for application to simple-terrain stationary source problems, complex terrain problems, and mobile source problems. Specific modeling requirements for selected regulatory issues are also addressed. Chapter 8 discusses issues common to many modeling analyses, including acceptable model components. Chapter 9 makes recommendations for data inputs to models, including source, meteorological and background air quality data. Chapter 10 covers the uncertainty in model estimates and how that information can be useful to the regulatory decision-maker. The last chapter summarizes how estimates and measurements of air quality are used in assessing source impact and in evaluating control strategies.

Appendix A contains summaries of refined air quality models that are "preferred" for specific applications; both EPA models and models developed by others are included. Appendix B contains summaries of other refined models that may be considered with a case-specific justification. Appendix C contains a checklist of requirements for an air quality analysis.

2.0 Overview of Model Use

Before attempting to implement the guidance contained in this document, the reader should be aware of certain general information concerning air quality models and their use. Such information is provided in this section.

2.1 *Suitability of Models*

The extent to which a specific air quality model is suitable for the evaluation of source impact depends upon several factors. These include: (1) The meteorological and topographic complexities of the area; (2) the level of detail and accuracy needed for the analysis; (3) the technical competence of those undertaking such simulation modeling; (4) the resources available; and (5) the detail and accuracy of the data base, i.e., emissions inventory, meteorological data, and air quality data. Appropriate data should be available before any attempt is made to apply a model. A model that requires detailed, precise, input data should not be used when such data are unavailable. However, assuming the data are adequate, the greater the detail with which a model considers the spatial and temporal variations in emissions and meteorological conditions, the greater the ability to evaluate the source impact and to distinguish the effects of various control strategies.

Air quality models have been applied with the most accuracy or the least degree of uncertainty to simulations of long term averages in areas with relatively simple topography. Areas subject to major topographic influences experience

meteorological complexities that are extremely difficult to simulate. Although models are available for such circumstances, they are frequently site specific and resource intensive. In the absence of a model capable of simulating such complexities, only a preliminary approximation may be feasible until such time as better models and data bases become available.

Models are highly specialized tools. Competent and experienced personnel are an essential prerequisite to the successful application of simulation models. The need for specialists is critical when the more sophisticated models are used or the area being investigated has complicated meteorological or topographic features. A model applied improperly, or with inappropriately chosen data, can lead to serious misjudgments regarding the source impact or the effectiveness of a control strategy.

The resource demands generated by use of air quality models vary widely depending on the specific application. The resources required depend on the nature of the model and its complexity, the detail of the data base, the difficulty of the application, and the amount and level of expertise required. The costs of manpower and computational facilities may also be important factors in the selection and use of a model for a specific analysis. However, it should be recognized that under some sets of physical circumstances and accuracy requirements, no present model may be appropriate. Thus, consideration of these factors should not lead to selection of an inappropriate model.

2.2 *Classes of Models*

The air quality modeling procedures discussed in this guide can be categorized into four generic classes: Gaussian, numerical, statistical or empirical, and physical. Within these classes, especially Gaussian and numerical models, a large number of individual "computational algorithms" may exist, each with its own specific applications. While each of the algorithms may have the same generic basis, e.g., Gaussian, it is accepted practice to refer to them individually as models. For example, the CRSTER model and the RAM model are commonly referred to as individual models. In fact, they are both variations of a basic Gaussian model. In many cases the only real difference between models within the different classes is the degree of detail considered in the input or output data.

Gaussian models are the most widely used techniques for estimating the impact of nonreactive pollutants. Numerical models may be more appropriate than Gaussian models for area source urban applications that involve reactive pollutants, but they require much more extensive input data bases and resources and therefore are not as widely applied. Statistical or empirical techniques are frequently employed in situations where incomplete scientific understanding of the physical and chemical processes or lack of the required data bases make the use of a Gaussian or numerical model impractical. Various specific models in these three generic types are discussed in this guideline.

Physical modeling, the fourth generic type, involves the use of wind tunnel or other fluid modeling facilities. This class of modeling is a complex process requiring a high level of technical expertise, as well as access to the necessary facilities. Nevertheless, physical modeling may be useful for complex flow situations, such as building, terrain or stack downwash conditions, plume impact on elevated terrain, diffusion in an urban environment, or diffusion in complex terrain. It is particularly applicable to such situations for a source or group of sources in a geographic area limited to a few square kilometers. If physical modeling is available and its applicability demonstrated, it may be the best technique. A discussion of physical modeling is beyond the scope of this guide. The EPA publication "Guideline for Fluid Modeling of Atmospheric Diffusion," (4) provides information on fluid modeling applications and the limitations of that method.

2.3 Levels of Sophistication of Models

In addition to the various classes of models, there are two levels of sophistication. The first level consists of general, relatively simple estimation techniques that provide conservative estimates of the air quality impact of a specific source, or source category. These are screening techniques or screening models. The purpose of such techniques is to eliminate the need of further more detailed modeling for those sources that clearly will not cause or contribute to ambient concentrations in excess of either the National Ambient Air Quality Standards (NAAQS) (5) or the allowable prevention of significant deterioration (PSD) concentration increments. (3) If a screening technique indicates that the concentration contributed by the source exceeds the PSD increment or the increment remaining to just meet the NAAQS, then the second level of more sophisticated models should be applied.

The second level consists of those analytical techniques that provide more detailed treatment of physical and chemical atmospheric processes, require more detailed and precise input data, and provide more specialized concentration estimates. As a result they provide a more refined and, at least theoretically, a more accurate estimate of source impact and the effectiveness of control strategies. These are referred to as refined models.

The use of screening techniques followed by a more refined analysis is always desirable, however there are situations where the screening techniques are practically and technically the only viable option for estimating source impact. In such cases, an attempt should be made to acquire or improve the necessary data bases and to develop appropriate analytical techniques.

3.0 Recommended Air Quality Models

This section recommends refined modeling techniques that are preferred for use in regulatory air quality programs. The status of models developed by EPA, as well as those submitted to EPA for review and possible inclusion in this guidance, is discussed. The section also addresses the selection of models for individual cases and provides recommendations for situations where the preferred models are not applicable. Two additional sources of modeling guidance, the Model Clearinghouse (6) and periodic Regional Meteorologists' workshops, are also briefly discussed here.

In all regulatory analyses, especially if other than preferred models are selected for use, early discussions among Regional Office staff, State and local control agencies, industry representatives, and where appropriate, the Federal Land Manager, are invaluable and are encouraged. Agreement on the data base to be used, modeling techniques to be applied and the overall technical approach, prior to the actual analyses, helps avoid misunderstandings concerning the final results and may reduce the later need for additional analyses. The use of an air quality checklist, such as presented in Appendix C, and the preparation of a written protocol help to keep misunderstandings at a minimum.

It should not be construed that the preferred models identified here are to be permanently used to the exclusion of all others or that they are the only models available for relating emissions to air quality. The model that most accurately estimates concentrations in the area of interest is always sought. However, designation of specific models is needed to promote consistency in model selection and application.

The 1980 solicitation of new or different models from the technical community (7) and the program whereby these models are evaluated, established a means by which new models are identified, reviewed and made available in the guideline. There is a pressing need for the development of models for a wide range of regulatory applications. Refined models that more realistically simulate the physical and chemical process in the atmosphere and that more reliably estimate pollutant concentrations are required. Thus, the solicitation of models is considered to be continuous.

3.1 Preferred Modeling Techniques

3.1.1 Discussion

EPA has developed approximately 10 models suitable for regulatory application. More than 20 additional models were submitted by private developers for possible inclusion in the guideline. These refined models have all been organized into eight categories of use: Rural, urban industrial complex, reactive pollutants, mobile sources, complex terrain, visibility, and long range transport. They are undergoing an intensive evaluation by category. The evaluation exercises (8,9,10) include statistical measures of model performance in comparison with measured air quality data as suggested by the American Meteorological Society (11) and, where possible, peer scientific reviews. (12,13,14)

When a single model is found to perform better than others in a given category, it is recommended for application in that category as a preferred model and listed in appendix A. If no one model is found to clearly perform better through the evaluation exercise, then the preferred model listed in appendix A is selected on the basis of other factors such as past use, public familiarity, cost or resource

requirements, and availability. No further evaluation of a preferred model is required if the source follows EPA recommendations specified for the model in this guideline. The models not specifically recommended for use in a particular category are summarized in appendix B. These models should be compared with measured air quality data when they are used for regulatory applications consistent with recommendations in section 3.2.

The solicitation of new refined models which are based on sounder scientific principles and which more reliably estimate pollutant concentrations is considered by EPA to be continuous. Models that are submitted in accordance with the provisions outlined in the Federal Register notice of March 1980 (45 FR 20157) (7) will be evaluated as submitted.

These requirements are: 1. The model must be computerized and functioning in a common Fortran language suitable for use on a variety of computer systems.

2. The model must be documented in a user's guide which identifies the mathematics of the model, data requirements and program operating characteristics at a level of detail comparable to that available for currently recommended models, e.g., the Single Source [CRSTER] Model.

3. The model must be accompanied by a complete test data set including input parameters and output results. The test data must be included in the user's guide as well as provided in computer-readable form.

4. The model must be useful to typical users, e.g., State air pollution control agencies, for specific air quality control problems. Such users should be able to operate the computer program(s) from available documentation.

5. The model documentation must include a comparison with air quality data or with other well-established analytical techniques.

6. The developer must be willing to make the model available to users at reasonable cost or make it available for public access through the National Technical Information Service; the model cannot be proprietary.

The evaluation process will include a determination of technical merit, in accordance with the above six items including the practicality of the model for use in ongoing regulatory programs. Each model will also be subjected to a performance evaluation for an appropriate data base and to a peer scientific review. Models for wide use (not just an isolated case!) found to perform better, based on an evaluation for the same data bases used to evaluate models in appendix A, will be proposed for inclusion as preferred models in future guideline revisions.

3.1.2 Recommendations

Appendix A identifies refined models that are preferred for use in regulatory applications. If a model is required for a particular application, the user should select a model from that appendix. These models may be used without a formal demonstration of applicability as long as they are used as indicated in each model summary of appendix A. Further recommendations for the application of these models to specific source

problems are found in subsequent sections of this guideline.

If changes are made to a preferred model without affecting the concentration estimates, the preferred status of the model is unchanged. Examples of modifications that do not affect concentrations are those made to enable use of a different computer or those that affect only the format or averaging time of the model results. However, when any changes are made, the Regional Administrator should require a test case example to demonstrate that the concentration estimates are not affected.

A preferred model should be operated with the options listed in appendix A as "Recommendations for Regulatory Use." If other options are exercised, the model is no longer "preferred." Any other modification to a preferred model that would result in a change in the concentration estimates likewise alters its status as a preferred model. Use of the model must then be justified on a case-by-case basis.

3.2 Use of Alternative Models

3.2.1 Discussion

Selection of the best techniques for each individual air quality analysis is always encouraged, but the selection should be done in a consistent manner. A simple listing of models in this guide cannot alone achieve that consistency nor can it necessarily provide the best model for all possible situations. An EPA document, "Interim Procedures for Evaluating Air Quality Models," (15, 16) has been prepared to assist in developing a consistent approach when justifying the use of other than the preferred modeling techniques recommended in this guide. These procedures provide a general framework for objective decision-making on the acceptability of an alternative model for a given regulatory application. The document contains procedures for conducting both the technical evaluation of the model and the field test or performance evaluation. An example problem that focuses on the design and execution of the protocol for conducting a field performance evaluation is also included in that document.

This section discusses the use of alternate modeling techniques and defines three situations when alternative models may be used.

3.2.2 Recommendations

Determination of acceptability of a model is a Regional Office responsibility. Where the Regional Administrator or reviewing authority finds that an alternative model is more appropriate than a preferred model, that model may be used subject to the recommendations below. This finding will normally result from a determination that (1) a preferred air quality model is not appropriate for the particular application; or (2) a more appropriate model or analytical procedure is available and is applicable.

An alternative model should be evaluated from both a theoretical and a performance perspective before it is selected for use. There are three separate conditions under which such a model will normally be approved for use: (1) If a demonstration can be made that the model produces .

concentration estimates equivalent to the estimates obtained using a preferred model; (2) if a statistical performance evaluation has been conducted using measured air quality data and the results of that evaluation indicate the alternative model performs better for the application than a comparable model in appendix A; and (3) if there is no preferred model for the specific application but a refined model is needed to satisfy regulatory requirements. Any one of these three separate conditions may warrant use of an alternative model. Some alternative models known to be available to the public that are applicable for selected situations are contained in appendix B. However, inclusion there does not infer any unique status relative to other alternative models that are being or will be developed for the future.

Equivalency is established by demonstrating that the maximum or highest, second highest concentrations are within two percent of the estimates obtained from the preferred model. The option to show equivalency is intended as a simple demonstration of acceptability for an alternative model that is so nearly identical (or contains options that can make it identical) to a preferred model that it can be treated for practical purposes as the preferred model. Two percent was selected as the basis for equivalency since it is a rough approximation of the fraction that PSD Class I increments are of the NAAQS for SO_2, i.e., the difference in concentrations that is judged to be significant. However, this demonstration is not intended to preclude the use of models that are not equivalent. They may be used when one of two other conditions identified below are satisfied.

The procedures and techniques for determining the acceptability of a model for an individual case based on superior performance is contained in the document entitled "Interim Procedures for Evaluating Air Quality Models," (15) and should be followed, as appropriate. Preparation and implementation of an evaluation protocol which is acceptable to both control agencies and regulated industry is an important element in such an evaluation.

When no appendix A model is applicable to the modeling problem, an alternative refined model may be used provided that:

1. The model can be demonstrated to be applicable to the problem on a theoretical basis, and

2. the data bases which are necessary to perform the analysis are available and adequate, and

3a. performance evaluations of the model in similar circumstances have shown that the model is not biased toward underestimates (examples of such circumstances include long range transport and shoreline fumigation), or

3b. after consultation with the EPA Regional Office, a second model is selected as a baseline or reference point for performance and the interim procedures (15) are then used to demonstrate that the proposed model performs better than the reference model (an example of such circumstances includes complex terrain).

3.3 Availability of Supplementary Modeling Guidance

The Regional Administrator has the authority to select models that are appropriate for use in a given situation. However, there is a need for assistance and guidance in the selection process so that fairness and consistency in modeling decisions is fostered among the various Regional Offices and the States. To satisfy that need, EPA established the Model Clearinghouse and also holds periodic workshops with headquarters, Regional Office and State modeling representatives.

3.3.1 The Model Clearinghouse

3.3.1.1 Discussion.

The Model Clearinghouse is the single EPA focal point for review of air quality simulation models proposed for use in specific regulatory applications. Details concerning the Clearinghouse and its operation are found in the document, "Model Clearinghouse: Operational Plan." (6) Three primary functions of the Clearinghouse are:

(1) Review of decisions proposed by EPA Regional Offices on the use of modeling techniques and data bases.

(2) Periodic visits to Regional Offices to gather information pertinent to regulatory model usage.

(3) Preparation of an annual report summarizing activities of the Clearinghouse including specific determinations made during the course of the year.

3.3.1.2 Recommendations.

The Regional Administrator may request assistance from the Model Clearinghouse after an initial evaluation and decision has been reached concerning the application of a model, analytical technique or data base in a particular regulatory action. The Clearinghouse may also consider and evaluate the use of modeling techniques submitted in support of any regulatory action. Additional responsibilities are: (1) Review proposed action for consistency with agency policy; (2) determine technical adequacy; and (3) make recommendations concerning the technique or data base.

3.3.2 Regional Meteorologists Workshops.

3.3.2.1 Discussion.

EPA conducts an annual in-house workshop for the purpose of mutual discussion and problem resolution among Regional Office modeling specialists, EPA research modeling experts, EPA Headquarters modeling and regulatory staff and representatives from State modeling programs. A summary of the issues resolved at previous workshops was issued in 1981 as "Regional Workshops on Air Quality Modeling: A Summary Report." (17) That report clarified procedures not specifically defined in the 1978 guideline and was issued to ensure the consistent interpretation of model requirements from Region to Region. Similar workshops for the purpose of clarifying guideline procedures or providing detailed instructions for the use of those procedures are anticipated in the future.

3.3.2.2 Recommendations.

The Regional Office should always be consulted for information and guidance concerning modeling methods and

interpretations of modeling guidance, and to ensure that the air quality model user has available the latest most up-to-date policy and procedures.

4.0 SIMPLE-TERRAIN STATIONARY-SOURCE MODELS

4.1 Discussion

Simple terrain, as used here, is considered to be an area where terrain features are all lower in elevation than the top of the stack of the source(s) in question. The models recommended in this section are generally used in the air quality impact analysis of stationary sources for most criteria pollutants. The averaging time of the concentration estimates produced by these models ranges from 1 hour to an annual average.

Model evaluation exercises have been conducted to determine the "best, most appropriate point source model" for use in simple terrain. (8, 12) However, no one model has been found to be clearly superior. Thus, based on past use, public familiarity, and availability CRSTER remains the recommended model for rural, simple terrain,

single point source applications. Similar determinations were made for the other refined models that are identified in the following sections.

4.2 Recommendations.

4.2.1 Screening Techniques

The EPA document "Guidelines for Air Quality Maintenance Planning and Analysis, Volume 10R: Procedures for Evaluating Air Quality Impact of New Stationary Sources" 18 contains screening procedures that should be used if the source is in simple terrain. A computerized version of the Volume 10R screening technique for use in simple terrain (urban and rural) is available in UNAMAP" 19 as PTPLU-2.

All screening procedures should be adjusted to the site and problem at hand. Close attention should be paid to whether the area should be classified urban or rural in accordance with Section 8.2.8. The climatology of the area should be studied to help define the worst-case meteorological conditions. Agreement should be reached between the model user and the reviewing authority on the choice of the screening

model for each analysis, and on the input data as well as the ultimate use of the results.

4.2.2 Refined Analytical Techniques

Table 4–1 lists preferred models for selected applications. These preferred models should be used for the sources, land use categories and averaging times indicated in the table. A brief description of each of these models is found in appendix A. Also listed in that appendix are the model input requirements, the standard options that should be selected when running the program and output options.

When modeling for compliance with short term NAAQS and PSD increments is of primary concern, the short term models listed in Table 4–1 may also be used to provide long term concentration estimates. When modeling for sources for which long term standards alone are applicable (e.g., lead), then the long term models should be used.

The conversion from long term to short term concentration averages by any transformation technique is not acceptable in regulatory applications.

TABLE 4–1.— PREFERRED MODELS FOR SELECTED APPLICATIONS IN SIMPLE TERRAIN

	Land Use	Model[1]
Short Term (1–24 hours):		
Single Source	Rural	CRSTER
	Urban	RAM
Multiple Source	Rural	MPTR
	Urban	RAM
Complicated Sources[2]	Rural/Urban	ISCST
Buoyant Industrial Line Sources	Rural	BLP
Long Term (monthly, seasonal or annual):		
Single Source	Rural	CRSTER
	Urban	RAM
Multiple Source	Rural	MPTER
	Urban	CDM 2.0 or RAM[3]
Complicated Sources[2]	Rural/Urban	ISCLT
Buoyant Industrial Line Sources	Rural	BLP

[1] Several of these models contain options which allow them to be interchanged. For example, ISCST can be substituted for CRSTER and equivalent, if not identical, concentration estimates obtained. Similarly, for a point source application, MPTER with urban option can be substituted for RAM. Where a substitution is convenient to the user and equivalent estimates are assured, it may be made. The models as listed here reflect the applications for which they were originally intended.

[2] Complicated sources are sources with special problems such as aerodynamic downwash, particle deposition, volume and area sources, etc.

[3] If only a few sources in an urban area are to be modeled, RAM should be used.

5.0 Model Use in Complex Terrain

5.1 Discussion

For the purpose of this guideline, complex terrain is defined as terrain exceeding the height of the stack being modeled. Complex terrain dispersion models are normally applied to stationary sources of pollutants such as SO₂ and particulates.

Although the need for refined complex terrain dispersion models has been acknowledged for several years, adequate refined models have not been developed. The lack of detailed, descriptive data bases and basic knowledge concerning the behavior of atmospheric variables in the vicinity of complex terrain presents a considerable obstacle to the solution of the problem and the development of refined models.

A workshop (20) of invited complex terrain experts was held by the American Meteorological Society as a part of the AMS-

EPA Cooperative Agreement in May of 1983. Several major complex terrain problems were identified at this workshop; among them were: (1) Valley stagnation, (2) valley fumigation, (3) downwash on the leeside of terrain obstacles; and (4) the identification of conditions under which plume impaction can occur.

A first step toward the solution of two of these problems has been taken in the multi-year EPA Complex Terrain Model Development project. (21,22,23,24) One product of this project is expected to be a model suitable for regulatory application to plume impaction problems in complex terrain. In addition, insight into the leeside effects problem is also anticipated. Completion of the project is not expected before late 1987. Preliminary results have identified at least two concepts that have important implications for the regulatory application of models in complex terrain and

will require further detailed study and evaluation. First, plume impaction resulting in high concentrations was observed to occur during the field study as well as in supporting fluid modeling studies. (21) Further, the occurrence of impaction was linked to a "critical streamline" that separates flow around an obstacle from flow over an obstacle. Second, high concentrations were also observed to occur in the lee of the obstacle and were of sufficient magnitude to indicate that this phenomenon should be considered, if appropriate, in the determination of source impacts. (22)

To date most projects have been designed to identify plume behavior in complex terrain and to define the meteorological variables influencing that behavior. Until such time as it is possible to develop and evaluate a model based on the quantification of the meteorological and plume parameters identified in these studies, existing algorithms

adapted to site-specific complex terrain situations are all that are available. The methods discussed in this section should be considered screening, or "refined" screening, techniques and not refined dispersion models.

5.2 Recommendations

The following recommendations apply primarily to the situations where the impaction of plumes on terrain at elevations equal to or greater than the plume centerline during stable atmospheric conditions are determined to be the problem. The evaluation of other concentrations should be considered after consultation with the Regional Office. However, limited guidance on calculation of concentrations between stack height and plume centerline is provided.

Models developed for specific uses in complex terrain will be considered on a case-by-case basis after a suitable demonstration of their technical merits and an evaluation using measured on-site data following the procedures in "Interim Procedures for the Evaluation of Air Quality Models." (15) Since the location of plume centerline is as important a concern in complex terrain as dispersion rates, it should be noted that the dispersion models combined with a wind field analysis model should be superior to an assumption of straight-line plume travel. Such hybrid modeling techniques are also acceptable, after the appropriate demonstration and evaluation.

5.2.1 Screening Techniques

In the absence of an approved case-specific, refined, complex terrain model, four screening techniques are currently available to aid in the evaluation of concentrations due to plume impaction during stable conditions: the Valley Screening Technique as outlined in the Valley Model's User's Guide, (19, 25) COMPLEX I, (19) SHORTZ/LONGZ, (26) and the Rough Terrain Dispersion Model (RTDM) (91) in its prescribed mode described below. These methods should be used only to calculate concentrations at receptors whose elevations are greater than or equal to plume height. Receptors below stack height should be modeled using a preferred simple terrain model (see chapter 4). Receptors between stack height and plume height should be modeled with both complex terrain and simple terrain models and the highest concentration used. (For the simple terrain models, terrain may have to be "chopped-off" at stack height, since these models are frequently limited to receptors no greater than stack height.)

If a violation of any NAAQS or the controlling increment is indicated by using the Valley Screening Technique, a second- or third-level screening technique may be used. A site-specific data base of at least one full year of meteorological data is preferred for use with either the second- or third-level screening technique. If more data are available, they should be used. Meteorological data used in the analysis should be reviewed for both spatial and temporal representativeness.

Placement of receptors requires very careful attention when modeling in complex terrain. Often the highest concentrations are predicted to occur under very stable

conditions, when the plume is near, or impinges on, the terrain. The plume under such conditions may be quite narrow in the vertical, so that a change in a receptor to a location where the terrain is as little as 25 meters or so higher or lower may make a substantial change in the predicted concentration. Receptors within about a kilometer of the source may be even more sensitive to location. Thus, a very dense array of receptors may be required in some cases. In order to avoid excessively large computer runs due to such a large array of receptors, it is often desirable to model the area twice. The first model run would use a moderate number of receptors carefully located over the area of interest. The second model run would use a more dense array of receptors in areas showing potential for high concentrations, as indicated by the results of the first model run.

5.2.1.1   Initial Screening Technique.

The initial screen to determine 24-hour averages is the Valley Screening Technique. This technique uses the Valley Model with the following worst-case assumptions for rural areas: (1) P–G stability "F"; (2) wind speed of 2.5 m/s; and (3) 6 hours of occurrence. For urban areas the stability should be changed to "P–G stability E."

When using the Valley Screening Technique to obtain 24-hour average concentrations the following apply: (1) Multiple sources should be treated individually and the concentrations for each wind direction summed; (2) only one wind direction should be used (see User's Guide, (25) page 2–15) even if individual runs are made for each source; (3) for buoyant sources, the BID option may be used, and the option to use the 2.6 stable plume rise factor should be selected; (4) if plume impaction is likely on any elevated terrain closer to the source than the distance from the source to the final plume rise, then the transitional (or gradual) plume rise option for stable conditions should be selected.

The standard polar receptor grid found in the Valley Model User's Guide may not be sufficiently dense for all analyses if only one geographical scale factor is used. The user should choose an additional set of receptors at appropriate downwind distances whose elevations are equal to plume height minus 10 meters. Alternatively, the user may exercise the "VALLEY equivalent" option in COMPLEX I and note the comments above on the placement of receptors in complex terrain models.

5.2.1.2   Second-Level Screening Technique (Rural).

If the area is rural, the suggested second-level screening technique is COMPLEX I for all averaging times. COMPLEX I is a modification of the MPTER model that incorporates the plume impaction algorithm of the Valley Model. It is a multiple-source screening technique that accepts hourly meteorological data as input. The output is the same as the normal MPTER output. When using COMPLEX I the following options should be selected: (1) Set terrain adjustment IOPT(1)=1; (2) set buoyancy induced dispersion IOPT (4)=1; (3) set IOPT (25)=1; (4) set the terrain adjustment values to 0.5, 0.5, 0.5 0.5, 0.0, 0.0, (respectively for 6 stability classes); and (5) set Z MIN=10.

Gradual plume rise should be used to estimate concentrations at nearby elevated receptors, if plume impaction is likely on any elevated terrain closer to the source than the distance from the source to the final plume rise (see section 8.2.5).

5.2.1.3   Second-Level Screening Technique (Urban).

If the source is located in an urbanized (section 8.2.8) complex terrain valley, then the suggested second-level screening technique is SHORTZ for short term averages or LONGZ for long term averages. (SHORTZ and LONGZ may be used as screening techniques in these complex terrain applications without demonstration and evaluation. Application of these models in other than urbanized valley situations will require the same evaluation and demonstration procedures as are required for all appendix B models.)

Both SHORTZ and LONGZ have a number of options. When using these models as screening techniques for urbanized valley applications, the options listed in table 5–1 should be selected.

5.2.1.4   Third Level Screening Technique (Rural).

If a violation of any NAAQS or the controlling increment is indicated by using the second-level screening technique, a third-level screening technique may be used for rural applications. RTDM with the options specified in Table 5–2 may be used as a screening technique in rural complex terrain situations without demonstration and evaluation.

The RTDM [1] screening technique can provide a more refined concentration estimate if on-site wind speed and direction characteristic of plume dilution and transport are used as input to the model. In complex terrain, these winds can seldom be estimated accurately from the standard surface (10m level) measurements. Therefore, in order to increase confidence in model estimates, EPA recommends that wind data input to RTDM should be based on fixed measurements at stack top height. For stacks greater than 100m, the measurement height may be limited to 100m in height relative to stack base. However, for very tall stacks see guidance in section 9.3.3.2. This recommendation is broadened to include wind data representative of plume transport height where such data are derived from measurements taken with remote sensing devices such as SODAR. The data from both fixed and remote measurements should meet quality assurance and recovery rate requirements. The user should also be aware that RTDM in the screening mode accepts the input of measured wind speeds at only one height. The default values for the wind speed profile exponents shown in Table 5–2 are used in the model to determine the wind speed at other heights. RTDM uses wind speed at stack top to calculate the plume rise and the critical dividing streamline height, and the wind speed at plume transport level to calculate dilution. RTDM treats wind direction as constant with height.

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[1] The RTDM model is available as part of Change 3 to UNAMAP Version 6.

RTDM makes use of the "critical dividing streamline" concept and thus treats plume interactions with terrain quite differently from other models such as SHORTZ and COMPLEX I. The plume height relative to the critical dividing streamline determines whether the plume impacts the terrain, or is lifted up and over the terrain. The receptor spacing to identify maximum impact concentrations is quite critical depending on the location of the plume in the vertical. It is suggested that an analysis of the expected plume height relative to the height of the critical dividing streamline be performed for differing meteorological conditions in order to help develop an appropriate array of receptors. Then it is advisable to model the area twice according to the suggestions in section 5.2.1.

5.2.1.5 Restrictions.

For screening analyses using the Valley Screening Technique, Complex I or RTDM, a sector greater than 22½° should not be allowed. Full ground reflection should always be used in the VALLEY Screening Technique and COMPLEX I.

5.2.2 Refined Analytical Techniques

When the results of the screening analysis demonstrate a possible violation of NAAQS or the controlling PSD increments, a more refined analysis may need to be conducted.

Since there are no refined techniques currently recommended for complex terrain applications, any refined model used should be applied in accordance with section 3.2. In particular, use of the "Interim Procedures for Evaluating Air Quality Models" (15) and a second model to serve as a baseline or reference point for the comparison should be used in a demonstration of applicability. New approaches to improve the ability of models to realistically simulate atmospheric physics, for example hybrid models which incorporate an accurate wind field analysis, will ultimately provide more appropriate tools for analyses.

In the absence of an appropriate refined model, screening results may need to be used to determine air quality impact and/or emission limits.

TABLE 5–1.—PREFERRED OPTIONS FOR THE SHORTZ/LONGZ COMPUTER CODES WHEN USED IN A SCREENING MODE

Option	Selection
I Switch 9	If using NWS data, set=0. If using site-specific data, check with the Regional Office.

TABLE 5–1.—PREFERRED OPTIONS FOR THE SHORTZ/LONGZ COMPUTER CODES WHEN USED IN A SCREENING MODE—Continued

Option	Selection
I Switch 17	Set=1 (urban option).
GAMMA 1	Use default values (0.6 entrainment coefficient).
GAMMA 2	Always default to stable.
XRY	Set=0 (50 m rectilinear expansion distance).
NS, VS, FRQ (SHORTZ) (particle size, etc.).	Do not use. (Applicable only in flat terrain).
NUS, VS, FRQ (LONGZ) (particle size, etc.).	
ALPHA	Select 0.9.
SIGEPU (dispersion parameters).	Use Cramer curves (default).
SIGAPU (dispersion parameters).	If site-specific turbulence data are available, see the Regional Office for advice.
P (wind profile)......	Select default values given in table 2-2 of User's Instructions. If site-specific data are available, see the Regional Office for advice.

TABLE 5–2.—PREFERRED OPTIONS FOR THE RTDM COMPUTER CODE WHEN USED IN A SCREENING MODE

Parameter	Variable	Value	Remarks
PR001–003	SCALE		Scale factors assuming horizontal distance is in kilometers, vertical distance is in feet, and wind speed is in meters per second.
PR004	ZWIND1	Wind Measurement Height......................	See section 5.2.1.4.
	ZWIND2	Not used................................	Height of second anemometer.
	IDILUT	1..	Dilution wind speed scaled to plume height.
	ZA	0 (default).............................	Anemometer-terrain height above stack base.
PR005	EXPON	.09, .11, .12, .14, .2, .3 (default)...............	Wind profile exponents.
PR006	ICOEF	3 (default).............................	Briggs Rural/ASME (1979) dispersion parameters.
PR009	IPPP	0 (default).............................	Partial plume penetration, not used.
PR010	IBUOY	1 (default).............................	Buoyancy-enhanced dispersion is used.
	ALPHA	3.162 (default).........................	Buoyancy-enhanced dispersion coefficient.
PR011	IDMX	1 (default).............................	Unlimited mixing height for stable conditions.
PR012	ITRANS	1 (default).............................	Transitional plume rise is used.
PR013	TERCOR	6°0.5 (default).........................	Plume path correction factors.
PR014	RVPTG	0.02, 0.035 (default)...................	Vertical potential temperature gradient values for stabilities E and F.
PR015	ITIPD	1..	Stack-tip downwash is used.
PR020	ISHEAR	0 (default).............................	Wind shear, not used.
PR022	IREFL	1 (default).............................	Partial surface reflection is used.
PR023	IHORIZ	2 (default).............................	Sector averaging.
	SECTOR	6°22.5 (default).......................	Using 22.5° sectors.
PR016 to 019; 021; and 024	IY, IZ, IRVPTG, IHVPTG; IEPS; IEMIS	0..	Hourly values of turbulence, vertical potential temperature gradient, wind speed profile exponents, and stack emissions are not used.

6.0 Models for Ozone, Carbon Monoxide and Nitrogen Dioxide

6.1 *Discussion.*

Models discussed in this section are applicable to pollutants often associated with mobile sources, e.g., ozone (O_3), carbon monoxide (CO) and nitrogen dioxide (NO_2). Where stationary sources of CO and NO_2 are of concern, the reader is referred to sections 4 and 5.

A control agency whose jurisdiction contains areas with significant ozone problems and who has sufficient resources and data to use a photochemical dispersion model is encouraged to do so. Experience with and evaluations of the Urban Airshed Model show it to be an acceptable, refined approach. Better data bases are becoming available that support the more sophisticated analytical procedures. However, empirical models (e.g., EKMA) fill the gap between more sophisticated photochemical dispersion model s and proportional (rollback) modeling techniques and may be the only applicable procedure if the data bases available are insufficient for refined dispersion modeling.

Carbon monoxide is generally considered to be a problem only in specific areas with high numbers of vehicles or slow moving traffic. For that reason, frequently only "hot spots" or project level analyses are needed in SIP revisions.

Nitrogen oxides are reactive and also an important contribution to the photochemical ozone problem. They are usually of most concern in areas of high ozone concentrations. Unless suitable

photochemical dispersion models are used, assumptions regarding the conversion of NO to NO₂ are required when modeling. Site-specific conversion factors may be developed. If site-specific conversion factors are not available or photochemical models are not used, NO₂ modeling should be considered only a screening procedure.

6.2 Recommendations

6.2.1 Models for Ozone.

The Urban Airshed Model (27) is recommended for photochemical or reactive pollutant modeling applications involving entire urban areas. To ensure proper execution of this numerical model, users must satisfy the extensive input data requirements for the model as listed in appendix A and the users guide. Users are also referred to the "Guideline for Applying the Airshed Model to Urban Areas" (28) for further information on data base requirements, kinds of tasks involved in the model application, and the overall level of resources required.

The empirical model, City-specific EKMA (29,30,31,32,33) is an acceptable approach for urban ozone applications.

Appendix B contains some additional models that may be applied on a case-by-case basis for photochemical or reactive pollutant modeling. Other photochemical models, including multi-layered trajectory models, that are available may be used if shown to be appropriate. Most photochemical dispersion models require emission data on individual hydrocarbon species and may require three dimensional meteorological information on an hourly basis. Reasonably sophisticated computer facilities are also often required. Because the input data are not universally available and studies to collect such data are very resource intensive, there are only limited evaluations of those models.

Proportional (rollback/forward) modeling is no longer an acceptable procedure for evaluating ozone control strategies.

6.2.2 Models for Carbon Monoxide.

Carbon monoxide modeling for the development of SIP-required control strategies should follow the guidance provided in the "Carbon Monoxide Hot Spot Guidelines" (34) or in Volume 9 of the "Guidelines for Air Quality Maintenance Planning and Analysis." (35) These volumes provide screening techniques for locating and quantifying worst case carbon monoxide concentrations, and for establishing background values; they also provide methods for assessing carbon monoxide concentrations at multiple locations across the urban area. If results from screening techniques or measured carbon monoxide levels in an urban area are clearly well below the standards and expected to remain below the standard, or it can be demonstrated that the Federal Motor Vehicle Control Program will provide the needed CO reductions, then urban area-wide strategies may be evaluated using a modified rollback or proportional model approach.

Project analysis of mobile source emissions of carbon monoxide should first include an analysis using the screening techniques referenced above. If concentrations using these techniques exceed the NAAQS, then refined techniques are needed to determine compliance with the standards. CALINE3 (see appendix A) is the preferred model for use when refined analyses are required. For free flow sources, the latest version of mobile source emission factors are required for input to CALINE3, and for interrupted flow sources (i.e., signalyzed intersections), procedures to calculate modal emission factors as contained in Worksheet 2 of the "Guidelines for Air Quality Maintenance Planning and Analysis, Volume 9" (35) are recommended.

Situations that require the use of refined techniques on an urban-wide basis should be considered on a case-by-case basis. If a suitable model is available and the data and technical competence required for its use are available, then such a model should be considered.

Where point sources of CO are of concern, they should be modeled using the screening and preferred techniques of sections 4 or 5.

6.2.3 Models for Nitrogen Dioxide (Annual Average).

A three-tiered screening approach is recommended to obtain annual average estimates of NO₂ from point sources:

a. Initial screen: Use an appropriate Gaussian model from Appendix A to estimate the maximum annual average concentration and assume a total conversion of NO to NO₂. If the concentration exceeds the NAAQS for NO₂, proceed to the 2nd level screen.

b. 2nd level screen: Apply the Ozone Limiting Method (36) to the annual NOₓ estimate obtained in (a) above using a representative average annual ozone concentration. If the result is still greater than the NAAQS, the more refined Ozone Limiting Method in the 3rd level screen should be applied.

c. 3rd level screen: Apply the Ozone Limiting Method separately for each hour of the year or multi-year period. Use representative hourly NO₂ background and ozone levels in the calculations.

In urban areas, a proportional model may be used as a preliminary assessment to evaluate control strategies for multiple sources (mobile and area) of NOₓ; concentrations resulting from major point sources should be estimated separately as discussed above, then added to the impact of area sources. An acceptable screening technique for urban complexes is to assume that all NOₓ is emitted in the form of NO₂ and to use a model from Appendix A for nonreactive pollutants to estimate NO₂ concentrations. A more accurate estimate can be obtained by (1) calculating the annual average concentrations of NOₓ with an urban model, and (2) converting these estimates to NO₂ concentrations based on a spatially averaged NO₂/NOₓ annual ratio determined from an existing air quality monitoring network.

In situations where there are sufficient hydrocarbons available to significantly enhance the rate of NO to NO₂ conversion, the assumptions implicit in the Ozone Limiting Procedure may not be appropriate. More refined techniques should be considered on a case-by-case basis and agreement with the reviewing authority should be obtained. Such techniques should consider individual quantities of NO and NO₂ emissions, atmospheric transport and dispersion, and atmospheric transformation of NO to NO₂. Where it is available site-specific data on the conversion of NO to NO₂ may be used. Photochemical dispersion models, if used for other pollutants in the area, may also be applied to the NOₓ problem.

7.0 Other Model Requirements

7.1 Discussion

This section covers those cases where specific techniques have been developed for special regulatory programs. Most of the programs have, or will have when fully developed, separate guidance documents that cover the program and a discussion of the tools that are needed. The following paragraphs reference those guidance documents, when they are available. No attempt has been made to provide a comprehensive discussion of each topic since the reference documents were designed to do that. This section will undergo periodic revision as new programs are added and new techniques are developed.

Other Federal agencies have also developed specific modeling approaches for their own regulatory or other requirements. An example of this is the three-volume manual issued by the U.S. Department of Housing and Urban Development, "Air Quality Considerations in Residential Planning." (37) Although such regulatory requirements and manuals may have come about because of EPA rules or standards, the implementation of such regulations and the use of the modeling techniques is under the jurisdiction of the agency issuing the manual or directive.

The need to estimate impacts at distances greater than 50 km (the nominal distance to which EPA considers most Gaussian models applicable) is an important one especially when considering the effects from secondary pollutants. Unfortunately, models submitted to EPA have not as yet undergone sufficient field evaluation to be recommended for general use. Existing data bases from field studies at mesoscale and long range transport distances are limited in detail. This limitation is a result of the expense to perform the field studies required to verify and improve mesoscale and long range transport models. Particularly important and sparse are meteorological data adequate for generating three dimensional wind fields. Application of models to complicated terrain compounds the difficulty.

A current EPA agreement with Argonne National Laboratory, scheduled for completion In FY 1986, will result in the development of evaluation procedures for long range transport models. Models submitted to EPA will be tested with currently available data bases using these procedures. Similar research in this area is also being performed by others in EPA and other organizations. For the time being, however, long range and mesoscale transport models must be evaluated for regulatory use on a case-by-case basis.

7.2 Recommendations

7.2.1 Fugitive Dust/Fugitive Emissions.

Fugitive dust usually refers to the dust put into the atmosphere by the wind blowing over plowed fields, dirt roads or desert or sandy areas with little or no vegetation. Reentrained dust is that which is put into the air by reason of vehicles driving over dirt roads (or dirty roads) and dusty areas. Such sources can be characterized as line, area or volume sources. Emission rates may be based on site-specific data or values from the general literature.

Fugitive emissions are usually defined as emissions that come from an industrial source complex. They include the emissions resulting from the industrial process that are not captured and vented through a stack but may be released from various locations within the complex. Where such fugitive emissions can be properly specified, the ISC model, with consideration of gravitational settling and dry deposition, is the recommended model. In some unique cases a model developed specifically for the situation may be needed.

Due to the difficult nature of characterizing and modeling fugitive dust and fugitive emissions, it is recommended that the proposed procedure be cleared by the appropriate Regional Office for each specific situation before the modeling exercise is begun.

7.2.2   Particulate Matter.

Currently a proposed NAAQS for particulate matter includes provisions both for particles in the size range less than 10 micrometers (PM₁₀) and for Total Suspended Particulates (TSP). State Implementation Plans will be developed by States to attain and maintain this new standard when the standard is promulgated.

Screening techniques like those identified in section 4 are also applicable to PM₁₀ and to large particles (TSP). It is recommended that subjectively determined values for "half-life" or pollutant decay not be used as a surrogate for particle removal. Conservative assumptions which do not allow removal or transformation are suggested for screening. Proportional models (rollback/forward) may not be applied for screening analysis, unless such techniques are used in conjunction with receptor modeling.

Refined models such as those in section 4 are recommended for both PM₁₀ and TSP. However, where possible, particle size, gas-to-particle formation and their effect on ambient concentrations may be considered. For urban-wide refined analyses CDM 2.0 or RAM should be used. CRSTER and MPTER are recommended for point sources of small particles. For source-specific analyses of complicated sources, the ISC model is preferred. No model recommended for general use at this time accounts for secondary particulate formation or other transformations in a manner suitable for SIP control strategy demonstrations. Where possible, the use of receptor models (38, 39) in conjunction with dispersion models is encouraged to more precisely characterize the emissions inventory and to validate source specific impacts calculated by the dispersion model.

For those cases where no recommended technique is available or applicable, modeling approaches should be approved by the appropriate Regional Office on a case-by-case basis. At this time analyses involving model calculations for distances beyond 50 km should also be justified on a case-by-case basis (see section 7.2.6).

7.2.3   Lead.

The air quality analyses required for lead implementation plans are given in §§ 51.83, 51.84 and 51.85 of 40 CFR part 51. Sections 51.83 and 51.85 require the use of a modified rollback model as a minimum to demonstrate attainment of the lead air quality standard but the use of a dispersion model is the preferred approach. Section 51.83 requires the analysis of an entire urban area if the measured lead concentration in the urbanized area exceeds a quarterly (three month) average of 4.0 μg/m³. Section 51.84 requires the use of a dispersion model to demonstrate attainment of the lead air quality standard around specified lead point sources. For other areas reporting a violation of the lead standard, § 51.85 requires an analysis of the area in the vicinity of the monitor reporting the violation. The NAAQS for lead is a quarterly (three month) average, thus requiring the use of modeling techniques that can provide long-term concentration estimates.

The SIP should contain an air quality analysis to determine the maximum quarterly lead concentration resulting from major lead point sources, such as smelters, gasoline additive plants, etc. For these applications the ISC model is preferred, since the model can account for deposition of particles and the impact of fugitive emissions. If the source is located in complicated terrain or is subject to unusual climatic conditions, a case-specific review by the appropriate Regional Office may be required.

In modeling the effect of traditional line sources (such as a specific roadway or highway) on lead air quality, dispersion models applied for other pollutants can be used. Dispersion models such as CALINE3 and APRAC–3 have been widely used for modeling carbon monoxide emissions from highways. However, where deposition is of concern, the line source treatment in ISC may be used. Also, where there is a point source in the middle of a substantial road network, the lead concentrations that result from the road network should be treated as background (see section 9.2); the point source and any nearby major roadways should be modeled separately using the ISC model.

To model an entire major urban area or to model areas without significant sources of lead emissions, as a minimum a proportional (rollback) model may be used for air quality analysis. The rollback philosophy assumes that measured pollutant concentrations are proportional to emissions. However, urban or other dispersion models are encouraged in these circumstances where the use of such models is feasible.

For further information concerning the use of models in the development of lead implementation plans, the documents "Supplementary Guidelines for Lead Implementation Plans," (40) and "Updated Information on Approval and Promulgation of Lead Implementation Plans," (41) should be consulted.

7.2.4   Visibility.

The visibility regulations as promulgated in December 1980 [1] require consideration of the effect of new sources on the visibility values of Federal Class I areas. The state of scientific knowledge concerning identifying, monitoring, modeling, and controlling visibility impairment is contained in an EPA report "Protecting Visibility: An EPA Report to Congress." (42) At the present time, "although information derived from modeling and monitoring can, in some cases, aid the States in development and implementation of the visibility program," [2] the States are not currently required to establish monitoring networks or perform modeling analyses. However, a monitoring strategy is required. As additional knowledge is gained, guidance on "plume blight" and regional scale models will be provided, as appropriate.

References 43, 44, and 45 may also be useful when visibility evaluations are needed. Appendix B contains two models developed for application to visibility problems.

7.2.5   Good Engineering Practice Stack Height.

The use of stack height credit in excess of Good Engineering Practice (GEP) stack height is prohibited in the development of emission limitations by 40 CFR 51.12 and 40 CFR 51.18. The definition of GEP stack height is contained in 40 CFR 51.1. Methods and procedures for making the appropriate stack height calculations, determining stack height credits and an example of applying those techniques are found in references 46, 47, 48, and 49.

If stacks for new or existing major sources are found to be less than the height defined by EPA's refined formula for determining GEP height,[1] then air quality impacts associated with cavity or wake effects due to the nearby building structures should be determined. Detailed downwash screening procedures (17) for both the cavity and wake regions should be followed. If more refined concentration estimates are required, the Industrial Source Complex (ISC) model contains algorithms for building wake calculations and should be used. Fluid modeling can provide a great deal of additional information for evaluating and describing the cavity and wake effects.

7.2.6   Long Range Transport (beyond 50 km).

Section 165(e) of the Clean Air Act requires that suspected significant impacts on PSD Class I areas be determined. However, the useful distance to which most Gaussian models are considered accurate for setting emission limits is 50 km. Since in many cases Class I areas may be threatened at distances greater than 50 km from new sources, some procedure is needed to (1) determine if a significant impact will occur, and (2) identify the model to be used in setting an emission limit if the Class I increments are threatened (models for this purpose should be approved for use on a case-by-case basis as required in section 3.2). This procedure and the models

[1] 45 FR 80084.

[2] 40 CFR 51.3000–307

[1] The EPA refined formula height is defined as H + 1.5L (refer to reference 46).

selected for use should be determined in consultation with the EPA Regional Office and the appropriate Federal Land Manager (FLM). While the ultimate decision on whether a Class I area is adversely affected is the responsibility of the permitting authority, the FLM has an affirmative responsibility to protect air quality related values that may be affected.

LRT models for use beyond 50 km and for other than PSD purposes also should be selected on a case-by-case basis. Normally, use of these models will require an acceptable demonstration of applicability and an evaluation of model performance if possible (See section 3.2).

7.2.7 Modeling Guidance for Other Governmental Programs

When using the models recommended or discussed in this guideline in support of programmatic requirements not specifically covered by EPA regulations, the model user should consult the appropriate Federal or State agency to ensure the proper application and use of that model. For modeling associated with PSD permit applications that involve a Class I area, the appropriate Federal Land Manager should be consulted on all modeling questions.

The Offshore and Coastal Dispersion (OCD) model (92) was developed by the Minerals Management Service and is recommended for estimating air quality impact from offshore sources on onshore flat terrain areas. The OCD model is not recommended for use in air quality impact assessments for onshore sources.

8.0 General Modeling Considerations

8.1 *Discussion*

This section contains recommendations concerning a number of different issues not explicitly covered in other sections of this guide. The topics covered here are not specific to any one program or modeling area but are common to nearly all modeling analyses.

8.2 *Recommendations*

8.2.1 Design Concentrations

8.2.1.1 Design Concentrations for SO₂, Particulate Matter, Lead, and NO₂.

An air quality analysis is required to determine if the source will (1) cause a violation of the NAAQS, or (2) cause or contribute to air quality deterioration greater than the specified allowable PSD increment. For the former, background concentration (See section 9.2) should be added to the estimated impact of the source to determine the design concentration. For the latter, the design concentration includes impact from all increment consuming sources.

If the air quality analyses are conducted using the period of meteorological input data recommended in section 9.3.1.2 (e.g., 5 years of NWS data or one year of site-specific data), then the design concentration based on the highest, second-highest short term concentration or long term average, whichever is controlling, should be used to determine emission limitations to assess compliance with the NAAQS and to determine PSD increments.

When sufficient and representative data exist for less than a 5-year period from a

nearby NWS site, or when on-site data have been collected for less than a full continuous year, or when it has been determined that the on-site data may not be temporally representative, then the highest concentration estimate should be considered the design value. This is because the length of the data record may be too short to assure that the conditions producing worst-case estimates have been adequately sampled. The highest value is then a surrogate for the concentration that is not to be exceeded more than once per year (the wording of the deterministic standards). Also, the highest concentration should be used whenever selected worst-case conditions are input to a screening technique. This specifically applies to the use of techniques such as outlined in "Procedures for Evaluating Air Quality Impact of New Stationary Sources." (18)

If the controlling concentration is an annual average value and multiple years of data (on-site or NWS) are used, then the design value is the highest of the annual averages calculated for the individual years. If the controlling concentration is a quarterly average and multiple years are used, then the highest individual quarterly average should be considered the design value.

As long a period of record as possible should be used in making estimates to determine design values and PSD increments. If more than one year of site-specific data is available, it should be used.

8.2.1.2 Design Concentrations for Criteria Pollutants with Expected Exceedance Standards.

Specific instructions for the determination of design concentrations for criteria pollutants with expected exceedance standards are contained in special guidance documents for the preparation of State Implementation Plans for those pollutants. For all SIP revisions the user should check with the Regional Office to obtain the most recent guidance documents and policy memoranda concerning the pollutant in question.

8.2.2 Critical Receptor Sites

Receptor sites for refined modeling should be utilized In sufficient detail to estimate the highest concentrations and possible violations of a NAAQS or a PSD increment. In designing a receptor network, the emphasis should be placed on receptor resolution and location, not total number of receptors. The selection of receptor sites should be a case-by-case determination taking into consideration the topography, the climatology, monitor sites, and the results of the initial screening procedure. For large sources [those equivalent to a 500 MW power plant) and where violations of the NAAQS or PSD increment are likely, 360 receptors for a polar coordinate grid system and 400 receptors for a rectangular grid system, where the distance from the source to the farthest receptor is 10 km, are usually adequate to identify areas of high concentration. Additional receptors may be needed in the high concentration location if greater resolution is indicated by terrain or source factors.

8.2.3 Dispersion Coefficients

Gaussian models used in most applications should employ dispersion coefficients

consistent with those contained in the preferred models in appendix A. Factors such as averaging time, urban/rural surroundings, and type of source (point vs. line) may dictate the selection of specific coefficients. Generally, coefficients used in appendix A models are identical to, or at least based on, Pasquill-Gifford coefficients (50) in rural areas and McElroy-Pooler (51) coefficients in urban areas.

Research is continuing toward the development of methods to determine dispersion coefficients directly from measured or observed variables. (52, 53) No method to date has proved to be widely applicable. Thus, direct measurement, as well as other dispersion coefficients related to distance and stability, may be used in Gaussian modeling only if a demonstration can be made that such parameters are more applicable and accurate for the given situation than are algorithms contained in the preferred models.

Buoyancy-induced dispersion (BID), as identified by Pasquill, (54) is included in the preferred models and should be used where buoyant sources, e.g., those involving fuel combustion, are involved.

8.2.4 Stability Categories

The Pasquill approach to classifying stability is generally required in all preferred models (appendix A). The Pasquill method, as modified by Turner, (55) was developed for use with commonly observed meteorological data from the National Weather Service and is based on cloud cover, insolation and wind speed.

Procedures to determine Pasquill stability categories from other than NWS data are found in section 9.3. Any other method to determine Pasquill stability categories must be justified on a case-by-case basis.

For a given model application where stability categories are the basis for selecting dispersion coefficients, both σ_y and σ_z should be determined from the same stability category. "Split sigmas" in that instance are not recommended.

Sector averaging, which eliminates the σ_y term, is generally acceptable only to determine long term averages, such as seasonal or annual, and when the meteorological input data are statistically summarized as in the STAR summaries. Sector averaging is, however, commonly acceptable in complex terrain screening methods.

8.2.5 Plume Rise

The plume rise methods of Briggs (56, 57) are incorporated in the preferred models and are recommended for use in all modeling applications. No provisions in these models are made for fumigation or multistack plume rise enhancement or the handling of such special plumes as flares; these problems should be considered on a case-by-case basis.

Since there is insufficient information to identify and quantify dispersion during the transitional plume rise period, gradual plume rise is not generally recommended for use. There are two exceptions where the use of gradual plume rise is appropriate: (1) In complex terrain screening procedures to

determine close-in impact; (2) when calculating the effects of building wakes. The building wake algorithm in the ISC model incorporates gradual plume rise calculations. If the building wake is calculated to affect the plume for any hour, gradual plume rise is also used in downwind dispersion calculations to the distance of final plume rise, after which final plume rise is used.

Stack tip downwash generally occurs with poorly constructed stacks and when the ratio of the stack exit velocity to wind speed is small. An algorithm developed by Briggs (Hanna, et al.) (57) is the recommended technique for this situation and is found in the point source preferred models.

Where aerodynamic downwash occurs due to the adverse influence of nearby structures, the algorithms included in the ISC model (58) should be used.

8.2.6 Chemical Transformation

The chemical transformation of SO_2 emitted from point sources or single industrial plants in rural areas is generally assumed to be relatively unimportant to the estimation of maximum concentrations when travel time is limited to a few hours. However, in urban area, where synergistic effects among pollutants are of considerable consequence, chemical transformation rates may be of concern. In urban area applications, a half-life of 4 hours (55) may be applied to the analysis of SO_2 emissions. Calculations of transformation coefficients from site-specific studies can be used to define a "half-life" to be used in a Gaussian model with any travel time, or in any application, if appropriate documentation is provided. Such conversion factors for pollutant half-life should not be used with screening analyses.

Complete conversion of NO to NO_2 should be assumed for all travel time when simple screening techniques are used to model point source emissions of nitrogen oxides. If a Gaussian model is used, and data are available on seasonable variations in maximum ozone concentrations, the Ozone Limiting Method (36) is recommended. In refined analyses, case-by-case conversion rates based on technical studies appropriate to the site in question may be used. The use of more sophisticated modeling techniques should be justified for individual cases.

Use of models incorporating complex chemical mechanisms should be considered only on a case-by-case basis with proper demonstration of applicability. These are generally regional models not designed for the evaluation of individual sources but used primarily for region-wide evaluations. Visibility models also incorporate chemical transformation mechanisms which are an integral part of the visibility model itself and should be used in visibility assessments.

8.2.7 Gravitational Settling and Deposition

An "infinite half-life" should be used for estimates of total suspended particulate concentrations when Gaussian models containing only exponential decay terms for treating settling and deposition are used.

Gravitational settling and deposition may be directly included in a model if either is a significant factor. At least one preferred

model (ISC) contains settling and deposition algorithms and is recommended for use when particulate matter sources can be quantified and settling and deposition are problems.

8.2.8 Urban/Rural Classification

The selection of either rural or urban dispersion coefficients in a specific application should follow one of the procedures suggested by Irwin (59) and briefly described below. These include a land use classification procedure or a population based procedure to determine whether the character of an area is primarily urban or rural.

Land Use Procedure: (1) Classify the land use within the total area, A_o, circumscribed by a 3 km radius circle about the source using the meteorological land use typing scheme proposed by Auer (60); (2) if land use types I1, I2, C1, R2, and R3 account for 50 percent or more of A_o, use urban dispersion coefficients; otherwise, use appropriate rural dispersion coefficients.

Population Density Procedure: (1) Compute the average population density, $\bar{p}$ per square kilometer with A_o as defined above; (2) If $\bar{p}$ is greater than 750 people/km^2, use urban dispersion coefficients; otherwise use appropriate rural dispersion coefficients.

Of the two methods the land use procedure is considered more definitive. Population density should be used with caution and should not be applied to highly industrialized areas where the population density may be low and thus a rural classification would be indicated, but the area is sufficiently built-up so that the urban land use criteria would be satisfied. In this case, the classification should already be "urban" and urban dispersion parameters should be used.

Sources located in an area defined as urban should be modeled using urban dispersion parameters. Sources located in areas defined as rural should be modeled using the rural dispersion parameters. For analyses of whole urban complexes, the entire area should be modeled as an urban region if most of the sources are located in areas classified as urban.

8.2.9 Fumigation

Fumigation occurs when a plume (or multiple plumes) is emitted into a stable layer of air and that layer is subsequently mixed to the ground either through convective transfer of heat from the surface or because of advection to less stable surroundings. Fumigation may cause excessively high concentrations but is usually rather short-lived at a given receptor. There are no recommended refined techniques to model this phenomenon. There are, however, screening procedures (see "Guidelines for Air Quality Maintenance Planning and Analysis Volume 10R: Procedures for Evaluating Air Quality Impact of New Stationary Sources") (18) that may be used to approximate the concentrations. Considerable care should be exercised in the use of the results obtained from the screening techniques.

Fumigation is also an important phenomenon on and near the shoreline of bodies of water. This can affect both individual plumes and area-wide emissions. Although models have been developed to address this problem, the evaluations so far

do not permit the recommendation of any specific technique.

The Regional Office should be contacted to determine the appropriate model for applications where fumigation is of concern.

8.2.10 Stagnation

Although both short and long term periods of very light winds are important in the identification of worst-case conditions, the models identified in this guideline cannot adequately simulate such conditions. If stagnation conditions are determined to be important to the analysis, then techniques specific to the situation and location must be developed. Such techniques might include empirical models or box models. Assistance from the appropriate Regional Office should be obtained prior to embarking on the development of such a procedure.

8.2.11 Calibration of Models

Calibration of long term multi-source models has been a widely used procedure even though the limitations imposed by statistical theory on the reliability of the calibration process for long term estimates are well known. (61) In some cases, where a more accurate model is not available, calibration may be the best alternative for improving the accuracy of the estimated concentrations needed for control strategy evaluations.

Calibration of short term models is not common practice and is subject to much greater error and misunderstanding. There have been attempts by some to compare short term estimates and measurements on an event-by-event basis and then to calibrate a model with results of that comparison. This approach is severely limited by uncertainties in both source and meteorological data and therefore it is difficult to precisely estimate the concentration at an exact location for a specific increment of time. Such uncertainties make calibration of short term models of questionable benefit. Therefore, short term model calibration is unacceptable.

9.0 Model Input Data

Data bases and related procedures for estimating input parameters are an integral part of the modeling procedure. The most appropriate data available should always be selected for use in modeling analyses. Concentrations can vary widely depending on the source data or meteorological data used. Input data are a major source of inconsistencies in any modeling analysis. This section attempts to minimize the uncertainty associated with data base selection and use by identifying requirements for data used in modeling. A checklist of input data requirements for modeling analyses is included as appendix C. More specific data requirements and the format required for the individual models are described in detail in the users' guide for each model.

9.1 *Source Data*

9.1.1 Discussion

Sources of pollutants can be classified as point, line and area/volume sources. Point sources are defined in terms of size and may vary between regulatory programs. The line

sources most frequently considered are roadways and streets along which there are well-defined movements of motor vehicles, but they may be lines of roof vents or stacks such as in aluminum refineries. Area and volume sources are often collections of a multitude of minor sources with individually small emissions that are impractical to consider as separate point or line sources. Large area sources are typically treated as a grid network of square areas, with pollutant emissions distributed uniformly within each grid square.

Emission factors are compiled in an EPA publication commonly known as AP–42 (62), an indication of the quality and amount of data on which many of the factors are based is also provided. Other information concerning emissions is available in EPA publications relating to specific source categories. The Regional Office should be consulted to determine appropriate source definitions and for guidance concerning the determination of emissions from and techniques for modeling the various source types.

9.1.2 Recommendations

For point source applications the load or operating condition that causes maximum ground-level concentrations should be established. As a minimum, the source should be modeled using the design capacity (100 percent load). If a source operates at greater than design capacity for periods that could result in violations of the standards or PSD increments, this load [1] should be modeled. Where the source operates at substantially less than design capacity, and the changes in the stack parameters associated with the operating conditions could lead to higher ground level concentrations, loads such as 50 percent and 75 percent of capacity should also be modeled. A range of operating conditions should be considered in screening analyses; the load causing the highest concentration, in addition to the design load, should be included in refined modeling. The following example for a power plant is typical of the kind of data on source characteristics and operating conditions that may be needed. Generally, input data

requirements for air quality models necessitate the use of metric units; where English units are common for engineering usage, a conversion to metric is required.

a. Plant layout. The connection scheme between boilers and stacks, and the distance and direction between stacks, building parameters (length, width, height, location and orientation relative to stacks) for plant structures which house boilers, control equipment, and surrounding buildings within a distance of approximately five stack heights.

b. Stack parameters. For all stacks, the stack height and inside diameter (meters), and the temperature (K) and volume flow rate (actual cubic meters per second) or exit gas velocity (meters per second) for operation at 100 percent, 75 percent and 50 percent load.

c. Boiler size. For all boilers, the associated megawatts, 10 [6] BTU/hr, and pounds of steam per hour, and the design and/or actual fuel consumption rate for 100 percent load for coal (tons/hour), oil (barrels/hour), and natural gas (thousand cubic feet/hour).

d. Boiler parameters. For all boilers, the percent excess air used, the boiler type (e.g., wet bottom, cyclone, etc.), and the type of firing (e.g., pulverized coal, front firing, etc.).

e. Operating conditions. For all boilers, the type, amount and pollutant contents of fuel, the total hours of boiler operation and the boiler capacity factor during the year, and the percent load for peak conditions.

f. Pollution control equipment parameters. For each boiler served and each pollutant affected, the type of emission control equipment, the year of its installation, its design efficiency and mass emission rate, the date of the last test and the tested efficiency, the number of hours of operation during the latest year, and the best engineering estimate of its projected efficiency if used in conjunction with coal combustion; data for any anticipated modifications or additions.

g. Data for new boilers or stacks. For all new boilers and stacks under construction and for all planned modifications to existing boilers or stacks, the scheduled date of completion, and the data or best estimates available for items (a) through (f) above

following completion of construction or modification.

In stationary point source applications for compliance with short term ambient standards, SIP control strategies should be tested using the emission input shown on table 9–1. When using a refined model, sources should be modeled sequentially with these loads for every hour of the year. To evaluate SIP's for compliance with quarterly and annual standards, emission input data shown on table 9–1 should again be used. Emissions from area sources should generally be based on annual average conditions. The source input information in each model user's guide should be carefully consulted and the checklist in appendix C should also be consulted for other possible emission data that could be helpful.

Line source modeling of streets and highways requires data on the width of the roadway and the median strip, the types and amounts of pollutant emissions, the number of lanes, the emissions from each lane and the height of emissions. The location of the ends of the straight roadway segments should be specified by appropriate grid coordinates. Detailed information and data requirements for modeling mobile sources of pollution are provided in the user's manuals for each of the models applicable to mobile sources.

The impact of growth on emissions should be considered in all modeling analyses covering existing sources. Increases in emissions due to planned expansion or planned fuel switches should be identified. Increases in emissions at individual sources that may be associated with a general industrial/commercial/residential expansion in multi-source urban areas should also be treated. For new sources the impact of growth on emissions should generally be considered for the period prior to the start-up date for the source. Such changes in emissions should treat increased area source emissions, changes in existing point source emissions which were not subject to preconstruction review, and emissions due to sources with permits to construct that have not yet started operation.

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[1] Malfunctions which may result in excess emissions are not considered to be a normal

operating condition. They generally should not be considered in determining allowable emissions.

However, if the excess emissions are the result of poor maintenance, careless operation, or other preventable conditions, it may be necessary to consider them in determining source impact.

TABLE 9-1.—MODEL EMISSION INPUT DATA FOR POINT SOURCES [1]

	Emission limit (#/MMBtu) [2]	×	Operating level (MMBtu/hr) [2]	×	Operating factor (e.g. hr/yr, hr/day)
Stationary Point Source(s) Subject to SIP Emission Limit(s) Evaluation for Compliance with Ambient Standards (Including Areawide Demonstrations)					
Averaging time, Annual & quarterly	Maximum allowable emission limit or federally enforceable permit limit..		Actual or design capacity (whichever is greater), or federally enforceable permit condition..		Actual operating factor averaged over most recent 2 years.[3]
Short term	Maximum allowable emission limit or federally enforceable permit limit..		Actual or design capacity (whichever is greater), or federally enforceable permit condition.[4].		Continuous operation, i.e., all hours of each time period under consideration (for all hours of the meteorological data base).[5]
Nearby Background Source(s) Same input requirements as for stationary point source(s) above.					
Other Background Source(s): If modeled (see section 9.2.3), input data requirements are defined below.					
Averaging time, Annual & quarterly	Maximum allowable emission limit or federally enforceable permit limit..		Annual level when actually operating, averaged over the most recent 2 years.[3]		Actual operating factor averaged over most recent 2 years.[3]
Short term	Maximum allowable emission limit or federally enforceable permit limit..		Annual level when actually operating, averaged over the most recent 2 years.[3].		Continuous operation, i.e., all hours of each time period under consideration (for all hours of the meteorological data base).[5]

[1] The model input data requirements shown on this table apply to stationary source control strategies for STATE IMPLEMENTATION PLANS. For purposes of emissions trading, new source review, or prevention of significant deterioration, other model input criteria may apply. Refer to the policy and guidance for these programs to establish the input data.

[2] Terminology applicable to fuel burning sources; analogous terminology, e.g., #/throughput may be used for other type of sources.

[3] Unless it is determined that this period is not representative.

[4] Operating levels such as 50 percent and 75 percent of capacity should also be modeled to determine the load causing the highest concentration.

[5] If operation does not occur for all hours of the time period of consideration (e.g., 3 or 24 hours) and the source operation is constrained by a federally enforceable permit condition, an appropriate adjustment to the modeled emission rate may be made (e.g., if operation is only 8 a.m. to 4 p.m. each day, only these hours will be modeled with emissions from the source. Modeled emissions should not be averaged across nonoperating time periods.)

9.2 Background Concentrations

9.2.1 Discussion

Background concentrations are an essential part of the total air quality concentration to be considered in determining source impacts. Background air quality includes pollutant concentrations due to: (1) Natural sources; (2) nearby sources other than the one(s) currently under consideration; and (3) unidentified sources.

Typically, air quality data should be used to establish background concentrations in the vicinity of the source(s) under consideration. The monitoring network used for background determinations should conform to the same quality assurance and other requirements as those networks established for PSD purposes. (63) An appropriate data validation procedure should be applied to the data prior to use.

If the source is not isolated, it may be necessary to use a multi-source model to establish the impact of nearby sources.. Background concentrations should be determined for each critical (concentration) averaging time.

9.2.2 Recommendations (Isolated Single Source)

Two options are available to determine background near isolated sources.

Option One: Use air quality data collected in the vicinity of the source to determine the background concentration for the averaging times of concern.[1] Determine the mean background concentration at each monitor by excluding values when the source in question is impacting the monitor. The mean annual background is the average of the annual concentrations so determined at each

[1] For purposes of PSD, the location of monitors as well as data quality assurance procedures must satisfy requirements listed in the PSD Monitoring Guidelines. (63)

monitor. For shorter averaging periods, the meteorological conditions accompanying the concentrations of concern should be identified. Concentrations for meteorological conditions of concern, at monitors not impacted by the source in question, should be averaged for each separate averaging time to determine the average background value. Monitoring sites inside a 90° sector downwind of the source may be used to determine the area of impact. One hour concentrations may be added and averaged to determine longer averaging periods.

Option Two: If there are no monitors located in the vicinity of the source, a "regional site" may be used to determine background. A "regional site" is one that is located away from the area of interest but is impacted by similar natural and distant man-made sources.

9.2.3 Recommendations (Multi-Source Areas)

In multi-source areas two components of background should be determined.

Nearby Sources: All sources expected to cause a significant concentration gradient in the vicinity of the source or sources under consideration for emission limit(s) should be explicitly modeled. For evaluation for compliance with the short term and annual ambient standards, the nearby sources should be modeled using the emission input data shown in Table 9-1. The number of such sources is expected to be small except in unusual situations. The nearby source inventory should be determined in consultation with the local air pollution control agency. It is envisioned that the nearby sources and the sources under consideration will be evaluated together using an appropriate appendix A model.

The impact of the nearby sources should be examined at locations where interactions between the plume of the point source under consideration and those of nearby sources

(plus natural background) can occur. Significant locations include: (1) The area of maximum impact of the point source; (2) the area of maximum impact of nearby sources; and (3) the area where all sources combine to cause maximum impact. These locations may be identified through trial and error analyses.

Other Sources: That portion of the background attributable to all other sources (e.g., natural sources, minor sources and distant major sources) should be determined either by the procedures found in section 9.2.2 or by application of a model using Table 9-1.

9.3 Meteorological Input Data

The meteorological data used as input to a dispersion model should be selected on the basis of spatial and climatological (temporal) representativeness as well as the ability of the individual parameters selected to characterize the transport and dispersion conditions in the area of concern. The representativeness of the data is dependent on: (1) The proximity of the meteorological monitoring site to the area under consideration; (2) the complexity of the terrain; (3) the exposure of the meteorological monitoring site; and (4) the period of time during which data are collected. The spatial representativeness of the data can be adversely affected by large distances between the source and receptors of interest and the complex topographic characteristics of the area. Temporal representativeness is a function of the year-to-year variations in weather conditions.

Model input data are normally obtained either from the National Weather Service or as part of an on-site measurement program. Local universities, FAA, military stations, industry and pollution control agencies may also be sources of such data. Some recommendations for the use of each type of data are included in this section.

9.3.1 Length of Record of Meteorological Data

9.3.1.1 Discussion.

The model user should acquire enough meteorological data to ensure that worst-case meteorological conditions are adequately represented in the model results. The trend toward statistically based standards suggests a need for all meteorological conditions to be adequately represented in the data set selected for model input. The number of years of record needed to obtain a stable distribution of conditions depends on the variable being measured and has been estimated by Landsberg and Jacobs (64) for various parameters. Although that study indicates in excess of 10 years may be required to achieve stability in the frequency distributions of some meteorological variables, such long periods are not reasonable for model input data. This is due in part to the fact that hourly data in model input format are frequently not available for such periods and that hourly calculations of concentration for long periods are prohibitively expensive. A recent study (65) compared various periods from a 17-year data set to determine the minimum number of years of data needed to approximate the concentrations modeled with a 17-year period of meteorological data from one station. This study indicated that the variability of model estimates due to the meteorological data input was adequately reduced if a 5-year period of record of meteorological input was used.

9.3.1.2 Recommendations.

Five years of representative meteorological data should be used when estimating concentrations with an air quality model. Consecutive years from the most recent, readily available 5-year period are preferred. The meteorological data may be data collected either onsite or at the nearest National Weather Service (NWS) station. If the source is large, e.g., a 500 MW power plant, the use of 5 years of NWS meteorological data or at least 1 year of site-specific data is required.

If one year or more, up to five years, of site-specific data is available, these data are preferred for use in air quality analyses. Such data should have been subjected to quality assurance procedures as described in section 9.3.3.2.

For permitted sources whose emission limitations are based on a specific year of meteorological data that year should be added to any longer period being used (e.g., 5 years of NWS data) when modeling the facility at a later time.

9.3.2 National Weather Service Data

9.3.2.1 Discussion.

The National Weather Service (NWS) meteorological data are routinely available and familiar to most model users. Although the NWS does not provide direct measurements of all the needed dispersion model input variables, methods have been developed and successfully used to translate the basic NWS data to the needed model input. Direct measurements of model input parameters have been made for limited model studies and those methods and techniques are becoming more widely

applied; however, most model applications still rely heavily on the NWS data.

There are two standard formats of the NWS data for use in air quality models. The short term models use the standard hourly weather observations available from the National Climatic Data Center (NCDC). These observations are then "preprocessed" before they can be used in the models. "STAR" summaries are available from NCDC for long term model use. These are joint frequency distributions of wind speed, direction and P-G stability category. They are used as direct input to models such as the long term version of ISC. (58)

9.3.2.2 Recommendations.

The preferred short term models listed in appendix A all accept as input the NWS meteorological data preprocessed into model compatible form. Long-term (monthly seasonal or annual) preferred models use NWS "STAR" summaries. Summarized concentration estimates from the short term models may also be used to develop long-term averages; however, concentration estimates based on the two separate input data sets may not necessarily agree.

Although most NWS measurements are made at a standard height of 10 meters, the actual anemometer height should be used as input to the preferred model.

National Weather Service wind directions are reported to the nearest 10 degrees. A specific set of randomly generated numbers has been developed for use with the preferred EPA models and should be used to ensure a lack of bias in wind direction assignments within the models.

Data from universities, FAA, military stations, industry and pollution control agencies may be used if such data are equivalent in accuracy and detail to the NWS data.

9.3.3 Site-Specific Data

9.3.3.1 Discussion.

Spatial or geographical representativeness is best achieved by collection of all of the needed model input data at the actual site of the source(s). Site-specific measured data are therefore preferred as model input, provided appropriate instrumentation and quality assurance procedures are followed and that the data collected are representative (free from undue local or "micro" influences) and compatible with the input requirements of the model to be used. However, direct measurements of all the needed model input parameters may not be possible. This section discusses suggestions for the collection and use of on-site data. Since the methods outlined in this section are still being tested, comparison of the model parameters derived using these site-specific data should be compared at least on a spot-check basis, with parameters derived from more conventional observations.

9.3.3.2 Recommendations.

Site-specific Data Collection

Guidance provided in the "Ambient Montoring Guidelines for Prevention of Significant Deterioration (PSD)" (63) should be used for the establishment of special monitoring networks for PSD and other air quality modeling analyses. That guidance includes requirements and specifications for

both pollutant and meteorological monitoring. Additional information is available in the EPA quality assurance handbooks and site selection guidance documents published on a pollutant-by-pollutant basis (see the Air Programs Report and Guidelines Index EPA–450/2–82–016). Volume IV of the series of reports "Quality Assurance Handbook for Air Pollution Measurement Systems" (66) contains such information for meteorological measurements. As a minimum, site-specific measurements of ambient air temperature, transport wind speed and direction, and the parameters to determine Pasquill-Gifford stability categories should be available in meteorological data sets to be used in modeling. Care should be taken to ensure that monitors are located to represent the area of concern and that they are not influenced by very localized effects. Site-specific data for model applications should cover as long a period of measurement as is possible to ensure adequate representation of "worst-case" meteorology. The Regional Office will determine the appropriateness of the measurement locations.

All site-specific data should be reduced to hourly averages. Table 9–2 lists the wind related parameters and the averaging time requirements.

Temperature Measurements

Temperature measurements should be made at standard shelter height in accordance with the guidance referenced above.

Wind Measurements

In addition to surface wind measurements, the transport wind direction should be measured at an elevation as close as possible to the plume height. To approximate this, if a source has a stack below 100 m, select the stack top height as the transport wind measurement height. For sourcees with stacks extending above 100 m, a 100 m tower is suggested unless the stack top is significantly above 100 meters (200 m or more). In cases with stacks 200 m or above, the Regional Office should determine the appropriate measurement height on a case-by-case basis. Remote sensing may be a feasible alternative. The dilution wind speed used in determining plume rise and also used in the Gaussian dispersion equation is, by convention, defined as the wind speed at stack top.

For routine tower measurements and surface measurements the wind speed should be measured using an anemometer and the wind direction measured using a horizontal vane. Specifications for wind measuring instruments and monitoring systems are contained in the "Ambient Air Monitoring Guidelines for Prevention of Significant Deterioration (PSD)" (63) and in the quality assurance handbook on meteorological measurements (66). Irwin (67) provides additional guidance for processing wind data.

Stability Categories

The Pasquill-Gifford (P-G) stability categories, as originally defined, couple near-surface measurements of wind speed with subjectively determined insolation assessements based on hourly cloud cover

and ceiling observations. The wind speed measurements are made at or near 10 m. The insolation rate is typically assessed using the cloud cover and ceiling height criteria outlined by Turner (50). Often the cloud cover data are not available in site-specific data sets. In the absence of such observations, it is recommended that the P–G stability category be estimated using Table 9–3. This table requires σ_E, the standard deviation of the vertical wind direction fluctuations. If the surface roughness of the area surrounding the source is different from the 15 cm roughness length upon which the table is based, an adjustment may be made as indicated in the second footnote of Table 9–3. σ_E is computed from direct measurements of the elevation angle of the vertical wind directions.

If measurements of elevation angle are not available, σ_E may be determined using the transform:

$$\sigma_E = \sigma_w/u,$$

where:

σ_E = the standard deviation of the vertical wind direction fluctuations over a one-hour period.

σ_w = the standard deviation of the vertical wind speed fluctuations over a one-hour period.

u = the average horizontal wind speed for a one-hour period.

Since both σ_w and u are in meters per second, σ_{6s_E} is in radians. To use σ_E in Table 9–3, σ_E must be converted to degrees. It is recommended that a vertically mounted propeller anemometer be used to measure the vertical wind speed fluctuations. The instrument should meet the specifications given in the Ambient Monitoring Guidelines referenced above. Compute σ_w directly each hour using at least 360 values based on a recommended readout interval of up to 10 seconds. If σ_E is computed using the output of the anemometer by other than direct application of the formula for a variance, the method should be demonstrated to be equivalent to direct computation. Both the vertical wind speed fluctuations and the horizontal wind speed should be measured at the same level. Moreover, these measurements should be made at a height of 10 m for use in estimating the P–G stability category. Where trees or land use preclude measurements as low as 10 m, measurements should be made at a height above the obstructions.

If on-site measurements of either σ_E or σ_w are not available, stability categories may be determined using the horizontal wind direction flucuation, σ_A, as outlined by Irwin (68). Irwin includes the Mitchell and Timbre (69) method that uses categories of σ_A (70) listed in Table 9–3, as an initial estimate of the P–G stability category. This relationship is considered adequate for daytime use. During the nighttime (one hour prior to sunset to one hour after sunrise), the adjustments given in Table 9–4 should be applied to these categories. As with σ_E an hourly average σ_A may be adjusted for surface roughness by multiplying the table values of σ_A by a factor based on the average surface roughness length determined within 1 to 3 km of the source. The need for such adjustments should be determined on a case-by-case basis.

Wind direction meander may, at times, lead to an erroneous determination of P–G

stability category based on σ_A. To minimize wind direction meander contributions, σ_A may be determined for each of four 15-minute periods in an hour. However, 360 samples are needed during each 15-minute period. To obtain the σ_A for stability determinations in these situations, take the square root of one-quarter of the sum of the squares of the four 15-minute σ_A's, as illustrated in the footnote to Table 9–2. While this approach is acceptable for determining stability, σ_A's calculated in this manner are not likely to be suitable for input to models under development that are designed to accept on-site hourly σ's based on 60-minute periods.

There has not been a widespread use of σ_E and σ_A to determine P–G categories. As mentioned in the footnotes to Table 9–3, the techniques outlined have not been extensively tested. The criteria listed in Table 9–3, are for σ_E and σ_A values at 10 m. For best results, the σ_E and σ_A values should be for heights near the surface as close to 10 m as practicable. Obstacles and large roughness elements may preclude measurements as low as 10 m. If circumstances preclude measurements below 30 m, the Regional Meteorologist should be consulted to determine the appropriate measurements to be taken on a case-by-case basis. The criteria listed in Tables 9–3 and 9–4 result from studies conducted in relatively flat terrain in rather ideal circumstances. For routine applications where conditions are often less than ideal, it is recommended that a temporary program be initiated at each site to spot-check the stability class estimates. Irwin's method using σ_E or σ_A should be compared with P–G stability class estimates using on-site wind speed and subjective assessments of the insolation based on ceiling height and cloud cover. The Regional Meteorologist should be consulted when using the spot-check results to refine and adjust the preliminary criteria outlined in Tables 9–3 and 9–4.

In summary, when on-site data sets are being used, Pasquill-Gifford stability categories should be determined from one of the following schemes listed in the order of preference:

(1) Turner's 1964 method (54) using site-specific data which include cloud cover, ceiling height and surface (~10 m) wind speeds.

(2) σ_E from site-specific measurements and Table 9–3 (σ_E may be determined from elevation angle measurements or may be estimated from measurements of σ_w according to the transform: $\sigma_E = \sigma_w/u$ (see page 9–17)).

(3) σ_A from site-specific measurements and Tables 9–3 and 9–4.

(4) Turner's 1964 method using site-specific wind speed with cloud cover and ceiling height from a nearby NWS site.

TABLE 9–2.—Averaging Times for Site-Specific Wind and Turbulence Measurements

Parameter	Averaging time
Surface wind speed (for use in stability determinations).	1-hr
Transport direction	1-hr
Dilution wind speed	1-hr
Turbulence measurements (σ_E and σ_A) for use in stability determinations.	1-hr[1]

[1] To minimize meander effects in σ's when wind conditions are light and/or variable, determine the hourly average σ's from four 15-minute σ's according to the following formula:

$$\sigma_{1-hr} = \sqrt{\frac{\sigma_{15}^2 + \sigma_{15}^2 + \sigma_{15}^2 + \sigma_{15}^2}{4}}$$

TABLE 9–3.—Wind Fluctuation Criteria For Estimating Pasquill Stability Categories [1]

Pasquill stability category	Standard deviation of the horizontal wind direction fluctuations[2][3] (σ_A in degrees)	Standard deviation of the vertical wind direction fluctuations[2][4] (σ_E in degrees)
A	$\sigma_A \geq 22.5°$	$\sigma_E > 11.5°$
B	$17.5° < \sigma_A < 22.5°$	$10.0° < \sigma_E < 11.5°$
C	$12.5° < \sigma_A < 17.5°$	$7.8° < \sigma_E < 10.0°$
D	$7.5° < \sigma_A < 12.5°$	$5.0° < \sigma_E < 7.8°$
E	$3.8° < \sigma_A < 7.5°$	$2.4° < \sigma_E < 5.0°$
F	$\sigma_A < 3.8°$	$\sigma_E < 2.4°$

Adapted from: Irwin, J., 1980 (68).

[1] These criteria are appropriate for steady-state conditions, a measurement height of 10 m, for level terrain, and an aerodynamic surface roughness length of 15 cm. Care should be taken that the wind sensor is responsive enough for use in measuring wind direction fluctuations. (63)

[2] A surface roughness factor of $(z_o/15 \text{ cm})^{0.2}$, where z_o is the average surface roughness in centimeters within a radius of 1–3 km of the source, may be applied to the *table* values. It should be noted that this factor, while theoretically sound, has not been subjected to rigorous testing and may not improve the estimates in all circumstances. A table of z_o values that may be used as a guide to estimating surface roughness is given in Smedman-Hogstrom and Hogstrom. (71)

[3] These criteria are from a NRC proposal. (70) It would seem reasonable to restrict the possible categories to A through D during daytime hours with a restriction that for 10-m wind speeds above 6 m/s, conditions are neutral. Likewise, during the nighttime hours, some restrictions, as in Table 9–4, are needed to preclude occurrences of categories A through C.

[4] These criteria were adapted from those presented by Smith and Howard. (72) It would seem reasonable to restrict the possible categories to A through D during the daytime hours and to categories D through F during the nighttime hours. During the daytime, conditions are neutral for 10-m wind speeds equal to or greater than 6 m/s, and during the night, conditions are neutral for 10-m wind speeds equal to or greater than 5 m/s.

TABLE 9-4.—NIGHTTIME [1] P–G STABILITY CATEGORIES BASED ON σ_A FROM TABLE 9–3

If the σ_A Stability Category is	And the Wind Speed at 10 m is m/s	Then the Pasquill Stability Category is
A	<2.9	F
	2.9 to 3.6	E
	≥3.6	D
B	<2.4	F
	2.4 to 3.0	E
	≥3.0	D
C	<2.4	E
	≥2.4	D
D	wind speed not considered.	D
E	wind speed not considered.[2]	E
F	wind speed not considered.[3]	F

Adapted from Irwin, J. 1980 (68).

[1] Nighttime is considered to be from 1 hour prior to sunset to 1 hour after sunrise.

[2] The original Mitchell and Timbre (69) table had no wind speed restrictions; However, the original Pasquill criteria suggest that for wind speeds greater than 5 m/s, neutral conditions should be used.

[3] The original Mitchell and Timbre (69) table had no wind speed restrictions; however, the original Pasquill criteria suggest that for wind speeds greater than or equal to 5 m/s, the D category would be appropriate, and for wind speeds between 3 m/s and 5 m/s, the E category should be used.

9.3.4 Treatment of Calms

9.3.4.1 Discussion.

Treatment of calm or light and variable wind poses a special problem in model applications since Gaussian models assume that concentration is inversely proportional to wind speed. Furthermore, concentrations become unrealistically large when wind speeds less than 1 m/s are input to the model. A procedure has been developed for use with NWS data to prevent the occurrence of overly conservative concentration estimates during periods of calms. This procedure acknowledges that a Gaussian plume model does not apply during calm conditions and that our knowledge of plume behavior and wind patterns during these conditions does not, at present, permit the development of a better technique. Therefore, the procedure disregards hours which are identified as calm. The hour is treated as missing and a convention for handling missing hours is recommended.

Preprocessed meteorological data input to most appendix A EPA models substitute a 1.00 m/s wind speed and the previous direction for the calm hour. The new treatment of calms in those models attempts to identify the original calm cases by checking for a 1.00 m/s wind speed coincident with a wind direction equal to the previous hour's wind direction. Such cases are then treated in a prescribed manner when estimating short term concentrations.

9.3.4.2 Recommendations.

Hourly concentrations calculated with Gaussian models using calms should not be considered valid; the wind and concentration estimates for these hours should be disregarded and considered to be missing. Critical concentrations for 3, 8, and 24-hour averages should be calculated by dividing the sum of the hourly concentration for the period by the number of valid or nonmissing hours. If the total number of valid hours is less than 18 for 24-hour averages, less than 6 for 8-hour averages or less than 3 for 3-hour averages, the total concentration should be divided by 18 for the 24-hour average, 6 for the 8-hour average and 3 for the 3-hour average. For annual averages, the sum of all valid hourly concentrations is divided by the number of non-calm hours during the year. A post-processor computer program, CALMPRO (73) has been prepared following these instructions and has been hardwired in the following models: RAM, ISC, MPTER and CRSTER.

The recommendations above apply to the use of calms for short term averages and do not apply to the determination of long term averages using "STAR" data summaries. Calms should continue to be included in the preparation of "STAR" summaries. A treatment for calms and very light winds is built into the software that produces the "STAR" summaries.

Stagnant conditions, including extended periods of calms, often produce high concentrations over wide areas for relatively long averaging periods. The standard short term Gaussian models are often not applicable to such situations. When stagnation conditions are of concern, other modeling techniques should be considered on a case-by-case basis. (See also Section 8.2.10)

When used in Gaussian models, measured on-site wind speeds of less than 1 m/s but higher than the response threshold of the instrument should be input as 1 m/s; the corresponding wind direction should also be input. Observations below the response threshold of the instrument are also set to 1 m/s but the wind direction from the previous hour is used. If the wind speed or direction can not be determined, that hour should be treated as missing and short term averages should then be calculated as above.

10.0 Accuracy and Uncertainty of Models

10.1 Discussion

Increasing reliance has been placed on concentration estimates from models as the primary basis for regulatory decisions concerning source permits and emission control requirements. In many situations, such as review of a proposed source, no practical alternative exists. Therefore, there is an obvious need to know how accurate models really are and how any uncertainty in the estimates affects regulatory decisions. EPA recognizes the need for incorporating such information and has sponsored workshops (11, 74) on model accuracy, the possible ways to quantify accuracy, and on considerations in the incorporation of model accuracy and uncertainty in the regulatory process. The Second (EPA) Conference on Air Quality Modeling, August 1982, (75) was devoted to that subject.

10.1.1 Overview of Model Uncertainty

Dispersion models generally attempt to estimate concentrations at specific sites that really represent an ensemble average of numerous repetitions of the same event. The event is characterized by measured or "known" conditions that are input to the models, e.g., wind speed, mixed layer height, surface heat flux, emission characteristics, etc. However, in addition to the known conditions, there are unmeasured or unknown variations in the conditions of this event, e.g., unresolved details of the atmospheric flow such as the turbulent velocity field. These unknown conditions, may vary among repetitions of the event. As a result, deviations in observed concentrations from their ensemble average, and from the concentrations estimated by the model, are likely to occur even though the known conditions are fixed. Even with a *perfect model* that predicts the correct ensemble average, there are likely to be deviations from the observed concentrations in individual repetitions of the event, due to variations in the unknown conditions. The statistics of these concentration residuals are termed "inherent" uncertainty. Available evidence suggests that this source of uncertainty alone may be responsible for a typical range of variation in concentrations of as much as ± 50 percent. (76)

Moreover, there is "reducible" uncertainty (77) associated with the model and its input conditions; neither models nor data bases are perfect. Reducible uncertainties are caused by: (1) Uncertainties in the input values of the known condition—emission characteristics and meteorological data; (2) errors in the measured concentrations which are used to compute the concentration residuals; and (3) inadequate model physics and formulation. The "reducible" uncertainties can be minimized through better (more accurate and more representative) measurements and better model physics.

To use the terminology correctly, reference to model accuracy should be limited to that portion of reducible uncertainty which deals with the physics and the formulation of the model. The accuracy of the model is normally determined by an evaluation procedure which involves the comparison of model concentration estimates with measured air quality data. (78) The statement of accuracy is based on statistical tests or performance measures such as bias, noise, correlation, etc. (11) However, information that allows a distinction between contributions of the various elements of inherent and reducible uncertainty is only now beginning to emerge. As a result most discussions of the accuracy of models make no quantitative distinction between (1) limitations of the model versus (2) limitations of the data base and of knowledge concerning atmospheric variability. The reader should be aware that statements on model accuracy and uncertainty may imply the need for improvements in model performance that even the "perfect" model could not satisfy.

10.1.2 Studies of Model Accuracy

A number of studies (79, 80) have been conducted to examine model accuracy, particularly with respect to the reliability of short-term concentrations required for ambient standard and increment evaluations. The results of these studies are not surprising. Basically, they confirm what leading atmospheric scientists have said for some time: (1) Models are more reliable for estimating longer time-averaged

concentrations than for estimating short-term concentrations at specific locations; and (2) the models are reasonably reliable in estimating the magnitude of highest concentrations occurring sometime, somewhere within an area. For example, errors in highest estimated concentrations of ±10 to 40 percent are found to be typical, (81) i.e., certainly well within the often-quoted factor-of-two accuracy that has long been recognized for these models. However, estimates of concentrations that occur at a specific time and site, are poorly correlated with actually observed concentrations and are much less reliable.

As noted above, poor correlations between paired concentrations at fixed stations may be due to "reducible" uncertainties in knowledge of the precise plume location and to unquantified inherent uncertainties. For example, Pasquill (82) estimates that, apart from data input errors, maximum ground-level concentrations at a given hour for a point source in flat terrain could be in error by 50 percent due to these uncertainties. Uncertainty of five to 10 degrees in the measured wind direction, which transports the plume, can result in concentration errors of 20 to 70 percent for a particular time and location, depending on stability and station location. Such uncertainties do not indicate that an estimated concentration does not occur, only that the precise time and locations are in doubt.

10.1.3   Use of Uncertainty in Decision-Making

The accuracy of model estimates varies with the model used, the type of application, and site-specific characteristics. Thus, it is desirable to quantify the accuracy or uncertainty associated with concentration estimates used in decision-making. Communications between modelers and decision-makers must be fostered and further developed. Communications concerning concentration estimates currently exist in most cases, but the communications dealing with the accuracy of models and its meaning to the decision-maker are limited by the lack of a technical basis for quantifying and directly including uncertainty in decisions. Procedures for quantifying and interpreting uncertainty in the practical application of such concepts are only beginning to evolve; much study is still required. (74, 75, 77)

In all applications of models an effort is encouraged to identify the reliability of the model estimates for that particular area and to determine the magnitude and sources of error associated with the use of the model. The analyst is responsible for recognizing and quantifying limitations in the accuracy, precision and sensitivity of the procedure. Information that might be useful to the decision-maker in recognizing the seriousness of potential air quality violations includes such model accuracy estimates as accuracy of peak predictions, bias, noise, correlation, frequency distribution, spatial extent of high concentration, etc. Both space/time pairing of estimates and measurements and unpaired comparisons are recommended. Emphasis should be on the highest concentrations and the averaging times of the standards or increments of concern. Where possible, confidence intervals about the statistical values should be provided. However, while

such information can be provided by the modeler to the decision-maker, it is unclear how this information should be used to make an air pollution control decision. Given a range of possible outcomes, it is easiest and tends to ensure consistency if the decision-maker confines his judgment to use of the "best estimate" provided by the modeler (i.e., the design concentration estimated by a model recommended in this guideline or an alternate model of known accuracy). This is an indication of the practical limitations imposed by current abilities of the technical community.

To improve the basis for decision-making, EPA has developed and is continuing to study procedures for determining the accuracy of models, quantifying the uncertainty, and expressing confidence levels in decisions that are made concerning emissions controls. (83, 84) However, work in this area involves "breaking new ground" with slow and sporadic progress likely. As a result, it may be necessary to continue using the "best estimate" until sufficient technical progress has been made to meaningfully implement such concepts dealing with uncertainty.

10.1.4   Evaluation of Models

A number of actions are being taken to ensure that the best model is used correctly for each regulatory application and that a model is not arbitrarily imposed. First, this guideline clearly recommends that the most appropriate model be used in each case. Preferred models, based on a number of factors, are identified for many uses. General guidance on using alternatives to the preferred models is also provided. Second, all the models in eight categories (i.e., rural, urban, industrial complex, reactive pollutants, mobile source, complex terrain, visibility and long-range transport) that are candidates for inclusion in this guideline are being subjected to a systematic performance evaluation and a peer scientific review. (85) The same data bases are being used to evaluate all models within each of eight categories. Statistical performance measures, including measures of difference (or residuals) such as bias, variance of difference and gross variability of the difference, and measures of correlation such as time, space, and time and space combined as recommended by the AMS Woods Hole Workshop (11) are being followed. The results of the scientific review are being incorporated in this guideline and will be the basis for future revision. (12, 13) Third, more specific information has been provided for justifying the site-specific use of alternative models in the document "Interim Procedures for Evaluating Air Quality Models." (15) This document provides a method, following recommendations of the Woods Hole Workshop, that allows a judgment to be made as to what models are most appropriate for a specific application. For the present, performance and the theoretical evaluation of models are being used as an indirect means to quantify one element of uncertainty in air pollution regulatory decisions.

In addition to performance evaluation of models, sensitivity analyses are encouraged since they can provide additional information on the effect of inaccuracies in the data bases and on the uncertainty in model estimates.

Sensitivity analyses can aid in determining the effect of inaccuracies of variations or uncertainties in the data bases on the range of likely concentrations. Such information may be used to determine source impact and to evaluate control strategies. Where possible, information from such sensitivity analyses should be made available to the decisionmaker with an appropriate interpretation of the effect on the critical concentrations.

10.2   *Recommendations*

No specific guidance on the consideration of model uncertainty in decisionmaking is being given at this time. There is incomplete technical information on measures of model uncertainty that are most relevant to the decisionmaker. It is not clear how a decisionmaker could use such information, particularly given limitations of the Clean Air Act. As procedures for considering uncertainty develop and become implementable, this guidance will be changed and expanded. For the present, continued use of the "best estimate" is acceptable and is consistent with CAA requirements.

11.0   Regulatory Application of Models

11.1.   *Discussion*

Procedures with respect to the review and analysis of air quality modeling and data analyses in support of SIP revisions, PSD permitting or other regulatory requirements need a certain amount of standardization to ensure consistency in the depth and comprehensiveness of both the review and the analysis itself. This section recommends procedures that permit some degree of standardization while at the same time allowing the flexibility needed to assure the technically best analysis for each regulatory application.

Dispersion model estimates, especially with the support of measured air quality data, are the preferred basis for air quality demonstrations. Nevertheless, there are instances where the performance of recommended dispersion modeling techniques, by comparison with observed air quality data, may be shown to be less than acceptable. Also, there may be no recommended modeling procedure suitable for the situation. In these instances, emission limitations may be established solely on the basis of observed air quality data. The same care should be given to the analysis of the air quality data as would be applied to a modeling analysis.

The current NAAQS for SO_2, TSP, and CO are all stated in terms of a concentration not to be exceeded more than once a year. There is only an annual standard for NO_2. The ozone standard was revised in 1979 and that standard permits the exceedance of a concentration on an average of not more than once a year, averaged over a 3-year period. (5, 86) This represents a change from a deterministic to a more statistical form of the standard and permits some consideration to be given to unusual circumstances. The NAAQS are subjected to extensive review and possible revision every 5 years.

This section discusses general requirements for concentration estimates and

identifies the relationship to emission limits. The following recommendations apply to: (1) Revisions of State Implementation Plans; (2) the review of new sources and the prevention of significant deterioration (PSD); and (3) analyses of the emissions trades ("bubbles").

11.2   Recommendations

11.2.1   Analysis Requirements.

Every effort should be made by the Regional Office to meet with all parties involved in either a SIP revision or a PSD permit application prior to the start of any work on such a project. During this meeting, a protocol should be established between the preparing and reviewing parties to define the procedures to be followed, the data to be collected, the model to be used, and the analysis of the source and concentration data. An example of requirements for such an effort is contained in the Air Quality Analysis Checklist included here as appendix C. This checklist suggests the level of detail required to assess the air quality resulting from the proposed action. Special cases may require additional data collection or analysis and this should be determined and agreed upon at this preapplication meeting. The protocol should be written and agreed upon by the parties concerned, although a formal legal document is not intended. Changes in such a protocol are often required as the data collection and analysis progresses. However, the protocol establishes a common understanding of the requirements.

An air quality analysis should begin with a screening model to determine the potential of the proposed source or control strategy to violate the PSD increment or the NAAQS. It is recommended that the screening techniques found in "Procedures for Evaluating Air Quality Impact of New Stationary Sources" (18) be used for point source analyses. Screening procedures for area source analysis are discussed in "Applying Atmospheric Simulation Models to Air Quality Maintenance Areas." (87)

If the concentration estimates from screening techniques indicate that the PSD increment or NAAQS may be approached or exceeded, then a more refined modeling analysis is appropriate and the model user should select a model according to recommendations in sections 4, 5, 6 or 7. In some instances, no refined technique may be specified in this guide for the situation. The model user is then encouraged to submit a model developed specifically for the case at hand. If that is not possible, a screening technique may supply the needed results.

Regional Offices should require permit applicants to incorporate the pollutant contributions of all sources into their analysis. Where necessary this may include emissions associated with growth in the area of impact of the new or modified source's impact. PSD air quality assessments should consider the amount of the allowable air quality increment that has already been granted to any other sources. The most recent source applicant should be allowed the prerogative to remodel the existing or permitted sources in addition to the one currently under consideration. This would permit the use of newly acquired data or improved modeling techniques if such have become available since the last source was

permitted. When remodeling, the worst case used in the previous modeling analysis should be one set of conditions modeled in the new analysis. All sources should be modeled for each set of meteorological conditions selected and for all receptor sites used in the previous applications as well as new sites specific to the new source.

11.2.2   Use of Measured Data in Lieu of Model Estimates.

Modeling is the preferred method for determining emission limitations for both new and existing sources. When a preferred model is available, model results alone (including background) are sufficient. Monitoring will normally not be accepted as the sole basis for emission limitation determination in flat terrain areas. In some instances when the modeling technique available is only a screening technique, the addition of air quality data to the analysis may lend credence to model results.

There are circumstances where there is no applicable model, and measured data may need to be used. Examples of such situations are: (1) Complex terrain locations; (2) land/water interface areas; and (3) urban locations with a large fraction of particulate emissions from nontraditional sources. However, only in the case of an existing source should monitoring data alone be a basis for emission limits. In addition, the following items should be considered prior to the acceptance of the measured data:

a. Does a monitoring network exist for the pollutants and averaging times of concern;

b. Has the monitoring network been designed to locate points of maximum concentration;

c. Do the monitoring network and the data reduction and storage procedures meet EPA monitoring and quality assurance requirements;

d. Do the data set and the analysis allow impact of the most important individual sources to be identified if more than one source or emission point is involved;

e. Is at least one full year of valid ambient data available; and

f. Can it be demonstrated through the comparison of monitored data with model results that available models are not applicable?

The number of monitors required is a function of the problem being considered. The source configuration, terrain configuration, and meteorological variations all have an impact on number and placement of monitors. Decisions can only be made on a case-by-case basis. The Interim Procedure for Evaluating Air Quality Models (15) should be used in establishing criteria for demonstrating that a model is not applicable.

Sources should obtain approval from the Regional Office or reviewing authority for the monitoring network prior to the start of monitoring. A monitoring protocol agreed to by all concerned parties is highly desirable. The design of the network, the number, type and location of the monitors, the sampling period, averaging time as well as the need for meteorological monitoring or the use of mobile sampling or plume tracking techniques, should all be specified in the protocol and agreed upon prior to start-up of the network.

11.2.3   Emission Limits

11.2.3.1   Design Concentrations.

Emission limits should be based on concentration estimates for the averaging time that results in the most stringent control requirements. The concentration used in specifying emission limits is called the design value or design concentration and is a sum of the concentration contributed by the source and the background concentration.

To determine the averaging time for the design value, the most restrictive National Ambient Air Quality Standard (NAAQS) should be identified by calculating, for each averaging time, the ratio of the applicable NAAQS(S) minus background (B) to the predicted concentration (P) (i.e., (S–B)/P). The averaging time with the lowest ratio identifies the most restrictive standard. If the annual average is the most restrictive, the highest estimated annual average concentration from one or a number of years of data is the design value. When short term standards are most restrictive, it may be necessary to consider a broader range of concentrations than the highest value. For example, for pollutants such as SO_2, the highest, second-highest concentration is the design value. For pollutants with statistically based NAAQS, the design value is found by determining the value that is not expected to be exceeded more than once per year over the period specified in the standard.

When the highest, second-highest concentration is used in assessing potential violations of a short term NAAQS, criteria that are identified in "Guideline for Interpretation of Air Quality Standards" (88) should be followed. This guideline specifies that a violation of a short term standard occurs at a site when the standard is exceeded a second time. Thus, emission limits that protect standards for averaging times of 24 hours or less are appropriately based on the highest, second-highest estimated concentration plus a background concentration which can reasonably be assumed to occur with the concentration.

11.2.3.2   Air Quality Standards.

For new or modified sources to be located in areas where the SO_2, TSP, lead, NO_2, or CO NAAQS are being attained, the determination of whether or not the source will cause or contribute to an air quality violation should be based on (1) the highest estimated annual average concentration determined from annual averages of individual years or (2) the highest, second-highest estimated concentration for averaging times of 24-hours or less. For lead, the highest estimated concentration based on an individual calendar quarter averaging period should be used. Background concentrations should be added to the estimated impact of the source. The most restrictive standard should be used in all cases to assess the threat of an air quality violation.

11.2.3.3   PSD Air Quality Increments and Impacts.

The allowable PSD increments for criteria pollutants are established by regulation and cited in 40 CFR 51.24. These maximum allowable increases in pollutant concentrations may be exceeded once per year at each site, except for the annual

increment that may not be exceeded. The highest, second-highest increase in estimated concentrations for the short term averages as determined by a model should be less than or equal to the permitted increment. The modeled annual averages should not exceed the increment.

Screening techniques defined in sections 4 and 5 can sometimes be used to estimate short term incremental concentrations for the first new source that triggers the baseline in a given area. However, when multiple increment-consuming sources are involved in the calculation, the use of a refined model with at least one year of on-site or five years of off-site NWS data is normally required. In such cases, sequential modeling must demonstrate that the allowable increments are not exceeded temporally and spatially, i.e., for all receptors for each time period throughout the year(s) (time period means the appropriate PSD averaging time, e.g., 3-hour, 24-hour, etc.).

The PSD regulations require an estimation of the SO_2 and TSP impact on any Class I area. Normally, Gaussian models should not be applied at distances greater than can be accommodated by the steady state assumptions inherent in such models. The maximum distance for refined Gaussian model application for regulatory purposes is generally considered to be 50 km. Beyond the 50 km range, screening techniques may be used to determine if more refined modeling is needed. If refined models are needed, long range transport models should be considered in accordance with section 7.2.6. As previously noted in sections 3 and 7, the need to involve the Federal Land Manager in decisions on potential air quality impacts, particularly in relation to PSD Class I areas, cannot be overemphasized.

11.2.3.4 Emissions Trading Policy (Bubbles).

EPA's Emissions Trading Policy, commonly referred to as the "bubble policy," was proposed in the **Federal Register** on April 7, 1982. (89) Until a final policy is promulgated, principles contained in the proposal should be used to evaluate trading activities which become ripe for decision. Certain technical clarifications of the policy, including procedures for modeling bubbles, were provided to the Regional Offices in February, 1983. (90)

Emission increases and decreases within the bubble should result in ambient air quality equivalence. Two levels of analysis are defined for establishing this equivalence. In a Level I analysis the source configuration and setting must meet certain limitations (defined in the policy and clarification to the policy) that ensure ambient equivalence; no modeling is required. In a Level II analysis a modeling demonstration of ambient equivalence is required but only the sources involved in the emissions trade are modeled. The resulting ambient estimates of net increases/decreases are compared to a set of significance levels to determine if the bubble can be approved. A Level II analysis requires the use of a refined model and one year of representative meteorological data. Sequential modeling must demonstrate that the significance levels are met temporally and spatially, i.e., for all receptors for each

time period throughout the year (time period means the appropriate NAAQS averaging time, e.g., 3-hour, 24-hour, etc.)

For those bubbles that cannot meet the Level I or Level II requirements, the Emissions Trading Policy allows for a Level III analysis. A Level III analysis, from a modeling standpoint, is equivalent to the requirements for a standard SIP revision where all sources (and background) are considered and the estimates are compared to the NAAQS as in section 11.2.3.2.

The Emissions Trading Policy allows States to adopt generic regulations for processing bubbles. The modeling procedures recommended in this guideline apply to such generic regulations. However, an added requirement is that the modeling procedures contained in any generic regulation must be replicable such that there is no doubt as to how each individual bubble will be modeled. In general this means that the models, the data bases and the procedures for applying the model must be defined in the regulation. The consequences of the replicability requirement are that bubbles for sources located in complex terrain and certain industrial sources where judgments must be made on source characterization cannot be handled generically.

12.0 References [1]

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14.0 Glossary of Terms

Air Quality—Ambient pollutant concentrations and their temporal and spatial distribution.

Algorithm—A specific mathematical calculation procedure. A model may contain several algorithms.

Background—Ambient pollutant concentrations due to (1) natural sources, (2) nearby sources other than the one(s) currently under consideration; and (3) unidentified sources.

Calibrate—An objective adjustment using measured air quality data (e.g., an adjustment based on least-squares linear regression).

Calm—For purposes of air quality modeling, calm is used to define the situation when the wind is indeterminate with regard to speed or direction.

Complex Terrain—Terrain exceeding the height of the stack being modeled.

Computer Code—A set of statements that comprise a computer program.

Evaluate—To appraise the performance and accuracy of a model based on a comparison of concentration estimates with observed air quality data.

Fluid Modeling—Modeling conducted in a wind tunnel or water channel to quantitatively evaluate the influence of buildings and/or terrain on pollutant concentrations.

Fugitive Dust—Dust discharged to the atmosphere in an unconfined flow stream such as that from unpaved roads, storage piles and heavy construction operations.

Model—A quantitative or mathematical representation or simulation which attempts to describe the characteristics or relationships of physical events.

Preferred Model—A refined model that is recommended for a specific type of regulatory application.

Receptor—A location at which ambient air quality is measured or estimated.

Receptor Models—Procedures that examine an ambient monitor sample of particulate matter and the conditions of its collection to infer the types or relative mix of sources impacting on it during collection.

Refined Model—An analytical technique that provides a detailed treatment of physical and chemical atmospheric processes and requires detailed and precise input data. Specialized estimates are calculated that are useful for evaluating source impact relative to air quality standards and allowable increments. The estimates are more accurate than those obtained from conservative screening techniques.

Rollback—A simple model that assumes that if emissions from each source affecting a given receptor are decreased by the same percentage, ambient air quality concentrations decrease proportionately.

Screening Technique—A relatively simple analysis technique to determine if a given source is likely to pose a threat to air quality. Concentration estimates from screening techniques are conservative.

Simple Terrain—An area where terrain features are all lower in elevation than the top of the stack of the source.

Appendix A to Appendix X of Part 266—Summaries of Preferred Air Quality Models

Table of Contents

A.0 Introduction

This appendix summarizes key features of refined air quality models preferred for specific regulatory applications. For each model, information is provided on availability, approximate cost in 1986 [1], regulatory use, data input, output format and options, simulation of atmospheric physics, and accuracy. These models may be used without a formal demonstration of applicability provided they satisfy the recommendations for regulatory use; not all options in the models are necessarily recommended for regulatory use. The models are listed by name in alphabetical order.

Each of these models has been subjected to a performance evaluation using comparisons with observed air quality data. A summary of such comparisons for all models contained in this appendix is included in "A Survey of Statistical Measures of Model Performance and Accuracy for Several Air Quality Models," EPA-450/4-83-001. Where possible, several of the models contained herein have been subjected to evaluation exercises, including (1) statistical performance tests recommended by the American Meteorological Society and (2) peer scientific reviews. The models in this appendix have been selected on the basis of the results of the model evaluations, experience with previous use, familiarity of the model to various air quality programs, and the costs and resource requirements for use.

A.1 Buoyant Line and Point Source Dispersion Model (BLP)

Reference

Schulman, Lloyd L., and Joseph S. Scire, 1980. Buoyant Line and Point Source (BLP) Dispersion Model User's Guide. Document P-7304B. Environmental Research and Technology, Inc., Concord, MA. [NTIS PB 81-164642]

Availability

This model is available as part of UNAMAP (Version 6). The computer code is available on magnetic tape from: Computer Products, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, phone (703) 487-4650.

Abstract

BLP is a Gaussian plume dispersion model designed to handle unique modeling problems associated with aluminum reduction plants, and other industrial sources where plume rise and downwash effects from stationary line sources are important.

a. *Recommendations for Regulatory Use*

The BLP model is appropriate for the following applications:

Aluminum reduction plants which contain buoyant, elevated line sources;

Rural areas;

Transport distances less than 50 kilometers;

Simple terrain; and

---

[1] All models except the Urban Airshed Model are available on UNAMAP (Version 6) from NTIS at a price consistent with the previous version of UNAMAP.

One hour to one year averaging times.

The following options should be selected for regulatory applications:

Rural (IRU=1) mixing height option;

Default (no selection) for plume rise wind shear (LSHEAR), transitional point source plume rise (LTRANS), vertical potential temperature gradient (DTHTA), vertical wind speed power law profile exponents (PEXP), maximum variation in number of stability classes per hour (IDELS), pollutant decay (DECFAC), the constant in Briggs' stable plume rise equation (CONST2), constant in Briggs' neutral plume rise equation (CONST3), con-vergence criterion for the line source calculations (CRIT), and maximum iterations allowed for line source calculations (MAXIT); and

Terrain option (TERAN) set equal to 0., 0., 0., 0., 0., 0.

For other applications, BLP can be used if it can be demonstrated to give the same estimates as a recommended model for the same application, and will subsequently be executed in that mode.

BLP can be used on a case-by-case basis with specific options not available in a recommended model if it can be demonstrated, using the criteria in section 3.2, that the model is more appropriate for a specific application.

b. *Input Requirements*

Source data: Point sources require stack location, elevation of stack base, physical stack height, stack inside diameter, stack gas exit velocity, stack gas exit temperature, and pollutant emission rate. Line sources require coordinates of the end points of the line, release height, emission rate, average line source width, average building width, average spacing between buildings, and average line source buoyancy parameter.

Meteorological data: Hourly surface weather data from punched cards or from the preprocessor program RAMMET which provides hourly stability class, wind direction, wind speed, temperature, and mixing height.

Receptor data: Locations and elevations of receptors, or location and size of receptor grid or request automatically generated receptor grid.

c. *Output*

Printed output (from a separate post-processor program) includes:

Total concentration or, optionally, source contribution analysis; monthly and annual frequency distributions for 1-, 3-, and 24-hour average concentrations; tables of 1-, 3-, and 24-hour average concentrations at each receptor; table of the annual (or length of run) average concentrations at each receptor;

Five highest 1-, 3-, and 24-hour average concentrations at each receptor; and

Fifty highest 1-, 3-, and 24-hour concentrations over the receptor field.

d. *Type of Model*

BLP is a Gaussian plume model.

e. *Pollutant Types*

BLP may be used to model primary pollutants. This model does not treat settling and deposition.

f. *Source-Receptor Relationship*

BLP treats up to 50 point sources, 10 parallel line sources, and 100 receptors arbitrarily located.

User-input typographic elevation is applied for each stack and each receptor.

g. *Plume Behavior*

BLP uses plume rise formulas of Schulman and Scire (1980).

Vertical potential temperature gradients of .02 Kelvin per meter for E stability and .035 Kelvin per meter are used for stable plume rise calculations. An option for user input values is included.

Transitional rise is used for line sources. Option to suppress the use of transitional plume rise for point sources is included.

The building downwash algorithm of Schulman and Scire (1980) is used.

h. *Horizontal Winds*

Constant, uniform (steady-state) wind is assumed for an hour.

Straight line plume transport is assumed to all downwind distances.

Wind speeds profile exponents of .10, .15, .20, .25, .30, and .30 are used for stability classes A through F, respectively. An option for user-defined values and an option to suppress the use of the wind speed profile feature are included.

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

J. *Horizontal Dispersion*

Rural dispersion coefficients are from Turner (1969), with no adjustment made for variations in surface roughness or averaging time.

Six stability classes are used.

k. *Vertical Dispersion*

Rural dispersion coefficients are from Turner (1969), with no adjustment made for variations in surface roughness.

Six stability classes are used.

Mixing height is accounted for with multiple reflections until the vertical plume standard deviation equals 16 times the mixing height; uniform mixing is assumed beyond that point.

Perfect reflection at the ground is assumed.

1. *Chemical Transformation*

Chemical transformations are treated using linear decay. Decay rate is input by the user.

m. *Physical Removal*

Physical removal is not explicitly treated.

n. *Evaluation Studies*

Schulman, L. L., and J. S. Scire, 1980. Buoyant Line and Point Source (BLP) Dispersion Model User's Guide, P-7304B. Environmental Research and Technology, Inc., Concord, MA.

Scire, J. S., and L. L. Schulman, 1981. Evaluation of the BLP and ISC Models with SF$_6$ Tracer Data and SO$_2$ Measurements at Aluminum Reduction Plants. APCA Specialty Conference on Dispersion Modeling for Complex Sources, St. Louis, MO.

A.2   Caline3

Reference

Benson, Paul E. 1979. CALINE3—A Versatile Dispersion Model for Predicting Air Pollutant Levels Near Highways and Arterial Streets. Interim Report, Report Number FHWA/CA/TL-79/23. Federal Highway Administration, Washington, DC (NTIS PB80–220841).

Availability

The CALINE3 model computer tape is available from NTIS as PB80–220833. The model is also available from the California Department of Transportation (manual free of charge and approximately $50 for the computer tape). Requests should be directed to: Mr. Marlin Beckwith, Chief, Office of Computer Systems, California Department of Transportation, 1120 N. Street, Sacramento, California 95814.

Abstract

CALINE3 can be used to estimate the concentrations of nonreactive pollutants from highway traffic. This steady-state Gaussian model can be applied to determine air pollution concentrations at receptor locations downwind of "at-grade," "fill," "bridge," and "cut section" highways located in relatively uncomplicated terrain. The model is applicable for any wind direction, highway orientation, and receptor location. The model has adjustments for averaging time and surface roughness, and can handle up to 20 links and 20 receptors. It also contains an algorithm for deposition and settling velocity so that particulate concentrations can be predicted.

a. *Recommendations for Regulatory Use*

CALINE-3 is appropriate for the following applications:

Highway (line) sources;
Urban or rural areas;
Simple terrain;
Transport distances less than 50 kilometers; and
One hour to 24 hours averaging times.

b. *Input Requirements*

Source data: Up to 20 highway links classed as "at-grade," "fill" "bridge," or "depressed"; coordinates of link end points; traffic volume; emission factor; source height; and mixing zone width.

Meteorological data: Wind speed, wind angle (measured in degrees clockwise from the Y axis), stability class, mixing height, ambient (background to the highway) concentration of pollutant.

Receptor data: coordinates and height above ground for each receptor.

c. *Output*

Printed output includes:
Concentration at each receptor for the specified meteorological condition.

d. *Type of Model*

CALINE-3 is a Gaussian plume model.

e. *Pollutant Types*

CALINE-3 may be used to model primary pollutants.

f. *Source-Receptor Relationship*

Up to 20 highway links are treated.

CALINE-3 applies user input location and emission rate for each link.

User-input receptor locations are applied.

g. *Plume Behavior*

Plume rise is not treated.

h. *Horizontal Winds*

User-input hourly wind speed and direction are applied.

Constant, uniform (steady-state) wind is assumed for an hour.

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

j. *Horizontal Dispersion*

Six stability classes are used.

Rural dispersion coefficients from Turner (1969) are used, with adjustment for roughness length and averaging time.

Initial traffic-induced dispersion is handled implicitly by plume size parameters.

k. *Vertical Dispersion*

Six stability classes are used.

Empirical dispersion coefficients from Benson (1979) are used including an adjustment for roughness length.

Initial traffic-induced dispersion is handled implicitly by plume size parameters.

Adjustment for averaging time is included.

1. *Chemical Transformation*

Not treated.

m. *Physical Removal*

Optional deposition calculations are included.

n. *Evaluation Studies*

Bemis, G. R., et. al, 1977. Air Pollution and Roadway Location, Design, and Operation—Project Overview. FHWA-CA-TL-7080-77-25, Federal Highway Administration, Washington, DC.

Cadle, S. H., et. al, 1976. Results of the General Motors Sulfate Dispersion Experiment, GMR-2107. General Motors Research Laboratories, Warren, MI.

Dabberdt, W. F., 1975. Studies of Air Quality on and Near Highways, Project 2761. Stanford Research Institute, Menlo Park, CA.

A.3   Climatological Operation Model (CDM 2.0)

References

Irwin, J.S., T. Chico, and J. Catalano 1985. CDM 2.0—Climatological Dispersion Model—User's Guide. U. S. Environmental Protection Agency, Research Triangle Park, N.C. (NTIS PB86–136546)

Availability

This model is available as part of UNAMAP (Version 6). The computer code is available on magnetic tape from: Computer Products, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, phone (703) 487–4650.

Abstract

CDM is a climatological steady-state Gaussian plume model for determining long-term (seasonal or annual) arithmetic average pollutant concentrations at any ground-level receptor in an urban area.

a. *Recommendations for Regulatory Use*

CDM is appropriate for the following applications:
Point and area sources;
Urban areas;
Flat terrain;
Transport distances less than 50 kilometers;
Long term averages over one month to one year or longer.
The following option should be selected for regulatory applications:
Set the regulatory "default option" (NDEF=1) which automatically selects stack tip downwash, final plume rise, buoyancy-induced dispersion (BID), and the appropriate wind profile exponents.
Enter "0" for pollutant half-life for all pollutants except for SO_2 in an urban setting. This entry results in no decay (infinite half-life) being calculated. For SO_2 in an urban setting, the pollutant half-life (in hours) should be set to 4.0.

b. *Input Requirements*

Source data: Location, average emissions rates and heights of emissions for point and area sources. Point source data requirements also include stack gas temperature, stack gas exit velocity, and stack inside diameter for plume rise calculations for point sources.
Meteorological data: Stability wind rose (STAR deck day/night version), average mixing height and wind speed in each stability category, and average air temperature.
Receptor data: cartesian coordinates of each receptor.

c. *Output*

Printed output includes:
Average concentrations for the period of the stability wind rose data (arithmetic mean only) at each receptor, and
Optional point and area concentration rose for each receptor.

d. *Type of Model*

CDM is a climatological Gaussian plume model.

e. *Pollutant Types*

CDM may be used to model primary pollutants. Settling and deposition are not treated.

f. *Source-Receptor Relationship*

CDM applies user-specified locations for all point sources and receptors.
Area sources are input as multiples of a user-defined unit area source grid size.
User specified release heights are applied for individual point sources and the area source grid.
Actual separation between each source-receptor pair is used.
The user may select a single height at or above ground level that applies to all receptors.
No terrain differences between source and receptor are treated.

g. *Plume Behavior*

CDM uses Briggs (1969, 1971, 1975) plume rise equations. Optionally a plume rise-wind speed product may be input for each point source.
Stack tip downwash equation from Briggs (1974) is preferred for regulatory use. The Bjorklund and Bowers (1982) equation is also included.
No plume rise is calculated for area sources.
Does not treat fumigation or building downwash.

h. *Horizontal Winds*

Wind data are input as a stability wind rose (joint frequency distribution of 16 wind directions, 6 wind classes, and 5 stability classes).
Wind speed profile exponents for the urban case (EPA, 1980) are used, assuming the anemometer height is at 10.0 meters.

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

j. *Horizontal Dispersion*

Pollutants are assumed evenly distributed across a 22.5 or 10.0 degree sector.

k. *Vertical Dispersion*

There are seven vertical dispersion parameter schemes, but the following is recommended for regulatory applications: Briggs-urban (Gifford, 1976).
Mixing height has no effect until dispersion coefficient equals 0.8 times the mixing height; uniform vertical mixing is assumed beyond that point.
Buoyancy-induced disperion (Pasquill, 1976) is included as an option.
Perfect reflection is assumed at the ground.

l. *Chemical Transformation*

Chemical transformations are treated using exponential decay. Half-life is input by the user.

m. *Physical Removal*

Physical removal is not explicitly treated.

n. *Evaluation Studies*

Irwin, J. S., and T. M. Brown, 1985. A Sensitivity Analysis of the Treatment of Area Sources by the Climatological Dispersion Model, Journal of Air Pollution Control Association, 35:359–364.

Londergan, R., D. Minott, D. Wachter and R. Fizz, 1983. Evaluation of Urban Air Quality Simulation Models, EPA Publication No. EPA 450/4–83–020, U.S. Environmental Protection Agency, Research Triangle Park, NC

Busse, A. D. and J. R. Zimmerman, 1973. User's Guide for the Climatological Dispersion Model—Appendix E. EPA Publication No. EPA R4–73–024. Office of Research and Development Research Triangle Park, NC.

Zimmerman, J. R., 1971. Some Preliminary Results of Modeling from the Air Pollution Study of Ankara, Turkey, Proceedings of the Second Meeting of the Expert Panel on Air Pollution Modeling, NATO Committee on the Challenges of Modern Society, Paris, France.

Zimmerman, J. R., 1972. The NATO/CCMS Air Pollution Study of St. Louis, Missouri. Presented at the Third Meeting of the Expert Panel on Air Pollution Modeling, NATO Committee on the Challenges of Modern Society, Paris, France.

A.4 Gaussian-Plume Multiple Source Air Quality Algorithm (RAM)

References:

Turner, D. B., and J. H. Novak, 1978. User's Guide for RAM. Publication No. EPA–600/8–78–016 Vols a, and b. U.S. Environmental Protection Agency, Research Triangle Park, NC. (NTIS PB 294791 and PB 294792).

Reference:

Catalano, J. A., D. B. Turner, and H. Novak, 1987. User's Guide for RAM—Second Edition. U.S. Environmental Protection Agency, Research Triangle Park, NC. (Distributed as part of UNAMAP, Version 6, Documentation)

Availability:

This model is available as part of UNAMAP (Version 6). The computer code is available on magnetic tape from: Computer Products National Technical Information Service : U. S. Department of Commerce, Springfield, Virginia 22161 Phone (703) 487–4650

Abstract:

RAM is a steady-state Gaussian plume model for estimating concentrations of relatively stable pollutants, for averaging times from an hour to a day, from point and area sources in a rural or urban setting. Level terrain is assumed. Calculations are performed for each hour.

a. *Recommendations for Regulatory Use*

RAM is appropriate for the following applications:
Point and area sources;
Urban areas;
Flat terrain;
Transport distances less than 50 kilometers; and
One hour to one year averaging times.
The following options should be selected for regulatory applications:
Set the regulatory "default option" to automatically select stack tip downwash, final plume rise, buoyancy-induced dispersion (BID), a treatment for calms, the appropriate wind profile exponents, and the appropriate value for pollutant half-life.

b. *Input Requirements*

Source data: Point sources require location, emission rate, physical stack height, stack gas exit velocity, stack inside diameter and stack gas temperature. Area sources require location, size, emission rate, and height of emissions.
Meteorological data: Hourly surface weather data from the preprocessor program RAMMET which provides hourly stability class, wind direction, wind speed, temperature, and mixing height. Actual anemometer height (a single value) is also required.

Receptor data: Coordinates of each receptor. Options for automatic placement of receptors near expected concentration maxima, and a gridded receptor array are included.

c. *Output*

Printed output optionally includes:
One to 24-hour and annual average concentrations at each receptor,
Limited individual source contribution list, and
Highest through fifth highest concentrations at each receptor for period, with the highest and high, second-high values flagged.

d. *Type of Model*

RAM is a Gaussian plume model.

e. *Pollutant Types*

RAM may be used to model primary pollutants. Settling and deposition are not treated.

f. *Source-Receptor Relationship*

RAM applies user-specified locations for all point sources and receptors.
Area sources are input as multiples of a user-defined unit area source grid size.
User specified stack heights are applied for individual point sources.
Up to 3 effective release heights may be specified for the area sources. Area source release heights are assumed to be appropriate for a 5 meter per second wind and to be inversely proportional to wind speed.
Actual separation between each source-receptor pair is used.
All receptors are assumed to be at the same height at or above ground level.
No terrain differences between source and receptor are accounted for.

g. *Plume behavior*

RAM uses Briggs (1969, 1971, 1975) plume rise equations for final rise.
Stack tip downwash equation from Briggs (1974) is used.
A user supplied fraction of the area source height is treated as the physical height. The remainder is assumed to be plume rise for a 5 meter per second wind speed, and to be inversely proportional to wind speed.
Fumigation and building downwash are not treated.

h. *Horizontal Winds*

Constant, uniform (steady state) wind is assumed for an hour.
Straight line plume transport is assumed to all downwind distances.
Separate wind speed profile exponents (EPA, 1980) for urban cases are used.

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

j. *Horizontal Dispersion*

Urban dispersion coefficients from Briggs (Gifford, 1976) are used.
Buoyancy-induced dispersion (Pasquill, 1976) is included.
Six stability classes are used.

k. *Vertical Dispersion*

Urban dispersion coefficients from Briggs (Gifford, 1976) are used.

Buoyancy-induced dispersion (Pasquill, 1976) is included.
Six stability classes are used.
Mixing height is accounted for with multiple reflections until the vertical plume standard deviation equals 1.6 times the mixing height; uniform vertical sizing is assumed beyond that point.
Perfect reflection is assumed at the ground.

l. *Chemical Transformation*

Chemical transformations are treated using exponential decay. Half-life is input by the user.

m. *Physical Removal*

Physical removal is not explicitly treated.

n. *Evaluation Studies*

Ellis, H., P. Lou, and G. Dalzell, 1980. Comparison Study of Measured and Predicted Concentrations with the RAM Model at Two Power Plants Along Lake Erie, Second Joint Conference on Applications of Air Pollution Meteorology, New Orleans, LA.

Environmental Research and Technology, 1980. SO_2 Monitoring and RAM (Urban) Model Comparison Study in Summit County, Ohio. Document P-3618-152, Environmental Research & Technology. Inc.. Concord, MA, 1980.

Guldberg, P. H., and C. W. Kern, 1978. A Comparison Validation of the RAM and PTMTP Models for Short-Term Concentrations in Two Urban Areas, Journal of Air Pollution Control Association, 28:907-910.

Hodanbosi, R. R., and L. K. Peters, 1981. Evaluation of RAM Model for Cleveland, Ohio," Journal of Air Pollution Control Association, 31:253-255,

Kennedy, K. H., R. D. Siegel, and M. P. Steinberg, 1981. Case-Specific Evaluation of the RAM Atmospheric Dispersion Model in an Urban Area, 74th Annual Meeting of the American Institute of Chemical Engineers, New Orleans, LA.

Kummier, R. H.. B. Cho, G. Roginski, R. Sinha and A. Greenburg. 1979. A Comparative Validation of the RAM and Modified SAI Models for Short-Term 502 Concentrations in Detroit," Journal of Air Pollution Control Association, 29:720-723.

Londergan, R. J., N. E. Bowne, D. R. Murray, H. Borenstein, and J. Mangano, 1980. An Evaluation of Short-Term Air Quality Models Using Tracer Study Data, Report No. 4333, American Petroleum Institute, Washington, DC.

Morgenstern, P., M. J. Geraghty, and A. McKnight, 1979. A Comparative Study of the RAM (Urban) and RAMR (Rural) Models for Short-term SO_2 Concentrations in Metropolitan Indianapolis. 72nd Annual Meeting of the Air Pollution Control Association, Cincinnati, OH.

Ruff, R. E, 1980. Evaluation of the RAM Using the RAPS Data Base, Contract 68-02-2770, SRI International, Menlo Park, CA.

Londergan, R., D. Minott, D. Wackter, and R. Fizz, 1983. Evaluation of Urban Air Quality Simulation Models. EPA Publication No. EPA 450/4-83-020, U.S. Environmental Protection Agency, Research Triangle Park, NC.

A.5 Industrial Source Complex Model (ISC)

Reference

Environmental Protection Agency, 1986. Industrial Source Complex (ISC) Dispersion Model User's Guide, Second Edition, Volumes 1 and 2. Publication Nos. EPA-450/4-86-005a, and -005b. U.S. Environmental Protection Agency, Research Triangle Park, NC. (NTIS PB86 234259 and PB86 234267).

Environmental Protection Agency, 1987. Industrial Source Complex (ISC) Dispersion Model. Addendum to the User's Guide. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Availability

This model is available as part of UNAMAP (Version 6). The computer code is available on magnetic tape from: Computer Products, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, Phone (703) 487-4650.

Abstract

The ISC model is a steady-state Gaussian plume model which can be used to assess pollutant concentrations from a wide variety of sources associated with an industrial source complex. This model can account for the following: settling and dry deposition of particulates; downwash; area, line and volume sources; plume rise as a function of downwind distance; separation of point sources; and limited terrain adjustment. It operates in both long-term and short-term modes.

a. *Recommendations for Regulatory Use*

ISC is appropriate for the following applications:
Industrial source complexes;
Rural or urban areas;
Flat or rolling terrain;
Transport distances less than 50 kilometers; and
One hour to annual averaging times.
The following options should be selected for regulatory applications:
For short term modeling, set the regulatory "default option" (ISW(28)=1), which automatically selects stack tip downwash, final plume rise, buoyancy induced dispersion (BID), the vertical potential temperature gradient, a treatment for calms, the appropriate wind profile exponents, the appropriate value for pollutant half-life, and a revised building wake effects algorithm; set rural option (ISW(20)=0) or urban option (ISW(20)=3); and set the concentration option (ISW(1)=1).
For long term modeling, set the regulatory "default option" (ISW(22)=0), which automatically selects stack tip downwash, final plume rise, buoyancy-induced dispersion (BID), the vertical potential temperature gradient, the appropriate wind profile exponents, and the appropriate value for pollutant half-life, and a revised building wake effects algorithm; set rural option (ISW(9)=3) or urban option (ISW(9)=4); and set the concentration option (ISW(1)=1).
b. *Input Requirements*

Source data: Location, emission rate, physical stack height, stack gas exit velocity, stack inside diameter, and stack gas temperature. Optional inputs include source elevation, building dimensions, particle size distribution with corresponding settling velocities, and surface reflection coefficients.

Meteorological data: ISCST requires hourly surface weather data from the preprocessor program RAMMET, which provides hourly stability class, wind direction, wind speed, temperature, and mixing height. For ISCLT, input includes stability wind rose (STAR deck), average afternoon mixing height, average morning mixing height, and average air temperature.

Receptor data: coordinates and optional ground elevation for each receptor.

c. *Output*

Printed output options include:

Program control parameters, source data and receptor data;

Tables of hourly meteorological data for each specified day;

"N"-day average concentration or total deposition calculated at each receptor for any desired combinations of sources;

Concentration or deposition values calculated for any desired combinations of sources at all receptors for any specified day or time period within the day;

Tables of highest and second-highest concentration or deposition values calculated at each receptor for each specified time period during an "N"-day period for any desired combinations of sources; and tables of the maximum 50 concentration or deposition values;

Calculated for any desired combinations of sources for each specified time period.

d. *Type of Model*

ISC is a Gaussian plume model.

e. *Pollutant Types*

ISC may be used to model primary pollutants. Settling and deposition are treated.

f. *Source-Receptor Relationships*

ISC applies user-specified locations for point, line, area and volume sources, and user-specified receptor locations or receptor rings.

User input topographic elevation for each receptor is used. Elevations above stack top are reduced to the stack top elevation, i.e., "terrain chopping".

User input height above ground level may be used when necessary to simulate impact at elevated or "flag pole" receptors, e.g., on buildings.

Actual separation between each source-receptor pair is used.

g. *Plume Behavior*

ISC uses Briggs (1969, 1971, 1975) plume rise equations for final rise.

Stack tip downwash equation from Briggs (1974) is used.

Revised building wake effects algorithm is used. For stacks higher than building height plus one-half the lesser of the building height or building width, the building wake algorithm of Huber and Snyder (1976) is used. For lower stacks, the building wake algorithm of Schulman and Scire (Schulman and

Hanna, 1966) is used, but stack tip downwash and BID are not used.

For rolling terrain (terrain not above stack height), plume centerline is horizontal at height of final rise above source.

Fumigation is not treated.

h. *Horizontal Winds*

Constant, uniform (steady-state) wind is assumed for each hour.

Straight line plume transport is assumed to all downwind distances.

Separate wind speed profile exponents (EPA, 1980) for both rural and urban cases are used.

An optional treatment for calm winds is included for short term modeling.

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

j. *Horizontal Dispersion*

Rural dispersion coefficients from Turner (1969) are used, with no adjustments for surface roughness or averaging time.

Urban dispersion coefficients from Briggs (Gifford, 1976) are used.

Buoyancy-induced dispersion (Pasquill, 1976) is included.

Six stability classes are used.

k. *Vertical Dispersion*

Rural dispersion coefficients from Turner (1969) are used, with no adjustments for surface roughness.

Urban dispersion coefficients from Briggs (Gifford, 1976) are used.

Buoyancy-induced dispersion (Pasquill, 1976) is included.

Six stability classes are used.

Mixing height is accounted for with multiple reflections until the vertical plume standard deviation equals 1.6 times the mixing height; uniform vertical mixing is assumed beyond that point.

Perfect reflection is assumed at the ground.

l. *Chemical Transformation*

Chemical transformations are treated using exponential decay. Time constant is input by the user.

m. *Physical Removal*

Settling and dry deposition of particulates are treated.

n. *Evaluation Studies*

Bowers, J. F., and A. J. Anderson, 1981. An Evaluation Study for the Industrial Source Complex (ISC) Dispersion Model, EPA Publication No. EPA–450/4–81–002. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Bowers, J. F., A. J. Anderson, and W. R. Hargraves, 1982. Tests of the Industrial Source Complex (ISC) Dispersion Model at the Armco Middletown, Ohio Steel Mill, EPA Publication No. EPA–450/4–82–006. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Scire, J. S., and L. L. Schulman, 1981. Evaluation of the BLP and ISC Models with SF6 Tracer Data and S02 Measurements at Aluminum Reduction Plants. Air Pollution Control Association Specialty Conference on Dispersion Modeling for Complex Sources, St. Louis, MO.

Schulman, L. L., and S. R. Hanna, 1986. Evaluation of Downwash Modifications to the Industrial Source Complex Model. Journal of the Air Pollution Control Association, 36:258–264.

A.6 Multiple Point Gaussian Dispersion Algorithm with Terrain Adjustment (MPTER)

Reference

Pierce, Thomas D. and D. Bruce Turner, 1980. User's Guide for MPTER. EPA Publication No. EPA–600/8–80–016. U.S. Environmental Protection Agency, Research Triangle Park, NC. (NTIS No. PB–80–197361).

Chico, T. and J.A. Catalano, 1986. Addendum to the User's Guide for MPTER. U.S. Environmental Protection Agency, Research Triangle Park, NC 27711. (Distributed as part of UNAMAP, Version 6, Documentation)

Availability

This model is available as part of UNAMAP (Version 6). The computer code is available on magnetic tape from: Computer Products, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, Phone (703) 487–4650.

Abstract

MPTER is a Multiple Point Source Algorithm. This algorithm is useful for estimating air quality concentrations of relatively non-reactive pollutants. Hourly estimates are made using the Gaussian steady state model.

a. *Recommendations for Regulatory Use*

MPTER is appropriate for the following applications:

Point sources;

Rural or urban areas;

Flat or rolling terrain (no terrain above stack height);

Transport distances less than 50 kilometers; and

One hour to one year averaging times.

The following options should be selected for regulatory applications:

Set the regulatory "default option" (IOPT(25)=1) to automatically select stack tip downwash, final plume rise, buoyancy-induced dispersion (BID), a treatment for calms, the appropriate wind profile exponents, and the appropriate value for pollutant half-life.

b. *Input Requirements*

Source data: location, emission rate, physical stack height, stack gas exit velocity, stack inside diameter, stack gas temperature, and optional ground level elevation.

Meteorological data: hourly surface weather data from the preprocessor program RAMMET which provides hourly stability class, wind direction, wind speed, temperature, and mixing height. Actual anemometer height (a single value) is also required.

Receptor data: coordinates and optional ground elevation for each receptor.

c. *Output*

Printed output includes:

One to 24-hour and annual average concentrations at each receptor;

Highest through fifth highest concentrations at each receptor for period, with the highest and high, second-high values flagged; and

Limited source contribution table.

d. Type of Model

MPTER is a Gaussian plume model.

e. Pollutant Types

MPTER may be used to model primary pollutants. Settling and deposition are not treated.

f. Source-Receptor Relationship

MPTER applies user-specified locations of point sources and receptors.

User input stack height and source characteristics for each source are used.

User input topographic elevation for each receptor is used.

g. Plume Behavior

MPTER uses Briggs (1969, 1971, 1975) plume rise equations for final rise.

Stack tip downwash equation from Briggs (1974) is used.

For rolling terrain (terrain not above stack height), plume centerline is horizontal at height of final rise above the source.

Fumigation and building downwash are not treated.

h. Horizontal Winds

Constant, uniform (steady-state) wind is assumed for an hour.

Straight line plume transport is assumed to all downwind distances.

Separate wind speed profile exponents (EPA, 1980) for both rural and urban cases are used.

i. Vertical Wind Speed

Vertical speed is assumed equal to zero.

j. Horizontal Dispersion

Rural dispersion coefficients from Turner (1969) are used with no adjustments made for variations in surface roughness or averaging times.

Urban dispersion coefficients from Briggs (Gifford, 1976) are used.

Buoyancy-induced dispersion (Pasquill, 1976), is included.

Six stability classes are used.

k. Vertical Dispersion

Rural dispersion coefficients from Turner (1969) are used, with no adjustments made for variations in surface roughness.

Urban dispersion coefficients from Briggs (Gifford, 1976) are used.

Buoyancy-induced dispersion (Pasquill, 1976), is included.

Six stability classes are used.

Mixing height is accounted for with multiple reflections until the vertical plume standard deviation equals 1.6 times the mixing height; uniform vertical mixing is assumed beyond that point.

Perfect reflection is assumed at the ground.

l. Chemical Transformation

Chemical transformations are treated using exponential decay. Half-life is input by the user.

m. Physical Removal

Physical removal is not explicitly treated.

n. Evaluation Studies

No specific studies for MPTER because regulatory editions of CRSTER and MPTER are equivalent. Studies for CRSTER are relevant to MPTER as well (See page A-32).

A.7 Single Source (CRSTER) Model

Reference

Environmental Protection Agency, 1977. User's Manual for Single Source (CRSTER) Model. EPA Publication No. EPA-450/2-77-013. U.S. Environmental Protection Agency, Research Triangle Park, NC. (NTIS No. PB 271360).

Catalano, J.A., 1986. Single Source (CRSTER) Model. Addendum to the User's Manual. U.S. Environmental Protection Agency, Research Triangle Park, NC 27711. (Distributed as part of UNAMAP, Version 6, Documentation)

Availability

This model is available as part of UNAMAP (Version 6). The computer code is available on magnetic tape from: Computer Products, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, phone (703) 487-4650.

Abstract

CRSTER is a steady state, Gaussian dispersion model designed to calculate concentrations from point sources at a single location in either a rural or urban setting. Highest and high-second high concentrations are calculated at each receptor for 1-hour, 3-hour, 24-hour, and annual averaging time.

a. Recommendations for Regulatory Use

CRSTER is appropriate for the following applications:

Single point sources;

Rural or urban areas;

Transport distances less than 50 kilometers; and

Flat or rolling terrain (no terrain above stack height).

The following options should be selected for regulatory applications:

Set the regulatory "default option" which automatically selects stack tip downwash, final plume rise, buoyancy-induced dispersion (BID), a treatment for calms, the appropriate wind profile exponents, and the appropriate value for pollutant half-life.

b. Input Requirements

Source data: Emission rate, physical stack height, stack gas exit velocity, stack inside diameter, and stack gas temperature.

Meteorological data: Hourly surface weather data from the preprocessor program RAMMET. Preprocessor output includes hourly stability class wind direction, wind speed, temperature, and mixing height. Actual anemometer height (a single value) is also required.

Receptor data: require distance of each of the five receptor rings.

c. Output

Printed output includes:

Highest and second highest concentrations for the year at each receptor for averaging times of 1, 3, and 24-hours, plus a user-selected averaging time which may be 2, 4, 6, 8, or 12 hours;

Annual arithmetic average at each receptor;

For each day, the highest 1-hour and 24-hour concentrations over the receptor field; and

Option for source contributions to concentrations at selected receptors.

d. Type of Model

CRSTER is a Gaussian plume model.

e. Pollutant Types

CRSTER may be used to model primary pollutants. Settling and deposition are not treated.

f. Source-Receptor Relationship

CRSTER treats up to 19 point sources, no area sources.

All point sources are assumed collocated.

User input stack height is used for each source.

User input topographic elevation is used for each receptor, but must be below top of stack or program will terminate execution.

Receptors are assumed at ground level.

g. Plume Behavior

CRSTER uses Briggs (1969, 1971, 1975) plume rise equations for final rise.

Stack tip downwash equation from Briggs (1974) is used.

For rolling terrain (terrain not above stack height), plume centerline is horizontal at height of final rise above the source.

Fumigation and building downwash are not treated.

h. Horizontal Winds

Constant, uniform (steady-state) wind is assumed for an hour.

Straight line plume transport is assumed to all downwind distances.

Separate set of wind speed profile exponents (EPA, 1980) for both rural and urban cases are used.

i. Vertical Wind Speed

Vertical wind speed is assumed equal to zero.

j. Horizontal Dispersion

Rural dispersion coefficients from Turner (1969) are used in CRSTER with no adjustments made for variations in surface roughness or averaging times.

Urban dispersion coefficients from Briggs (Gifford, 1976) are used.

Buoyancy-induced dispersion (Pasquill, 1976) is included.

Six stability classes are used.

k. Vertical Dispersion

Rural dispersion coefficients from Turner (1969) are used with no adjustments made for surface roughness.

Urban dispersion coefficients from Briggs (Gifford, 1975) are used.

Buoyancy-induced dispersion (Pasquill, 1976) is included.

Six stability classes are used.

Mixing height is accounted for with multiple reflections until the vertical plume standard deviation equals 1.6 times the mixing height; uniform mixing is assumed beyond that point.

Perfect reflection is assumed at the ground.

l. *Chemical Transformation*

Chemical transformations are treated using exponential decay. Half-life is input by the user.

m. *Physical Removal*

Physical removal is not explicitly treated.

n. *Evaluation Studies*

Klug, W., 1974. Dispersion from Tall Stacks. Fifth NATO/CCMS International Technical Meeting on Air Pollution Modeling, Denmark.

Londergan, R.J., N.E. Bowne, D.R. Murray, H. Borenstein, and J. Mangano, 1980. An Evaluation of Short-Term Air Quality Models Using Tracer Study Data, Report No. 3. American Petroleum Institute, Washington, DC.

Mills, M.T., R. Caiazza, D.D. Hergert, and D.A. Lynn, 1981. Evaluation of Point Source Dispersion Models. EPA Publication No. EPA–450/4–81–032. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Mills, M.T., and F.A. Record, 1975. Comprehensive Analysis of Time-Concentration Relationships and the Validation of a Single Source Dispersion Model. EPA Publication No. EPA–450/3–75–083. U.S. Environmental Protection Agency, Research Triangle Park, NC.

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Londergan, R., D. Minott, D. Wackter, T. Kincaid, and B. Bonitata, 1983. Evaluation of Rural Air Quality Simulation Models. EPA Publication No. EPA–450/4–83–033. U.S. Environmental Protection Agency, Research Triangle Park, NC.

TRC-Environmental Consultants, Inc., 1983. Overview, Results, and Conclusions for the EPRI Plume Model Validation and Development Project: Plains Site, EPRI EA–3074. Electric Power Research Institute, Palo Alto, CA.

A.8　Urban Airshed Model (UAM)

References

Ames, J., T. C. Myers, L. E. Reid, D. C. Whitney, S. H. Golding, S.R. Hayes, and S. D. Reynolds, 1985. SAI Airshed Model Operations Manuals-Volume I—User's Manual. EPA Publication No. EPA–600/8–85–007a. U. S. Environmental Protection Agency, Research Triangle Park, NC. (NTIS No. PB 85–191567).

Ames, J. S., R. Hayes, T. C. Myers, and D. C. Whitney, 1985. SAI Airshed Model Operations Manuals-Volume II—Systems Manual. EPA Publication No. EPA–600/8–85–007b. U.-S. Environmental Protection Agency, Research Triangle Park, NC. (NTIS No. PB 85–191575).

Environmental Protection Agency, 1980. Guideline for Applying the Airshed Model to Urban Areas. Publication No. EPA 450/4–80–020. U. S. Environmental Protection Agency, Research Triangle Park, NC. (NTIS No. PB 81–200529).

Availability

The computer code is available on magnetic tape from: Computer Products, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, phone (703) 487–4650.

Abstract

UAM is an urban scale, three dimensional, grid type, numerical simulation model. The model incorporates a condensed photochemical kinetics mechanism for urban atmospheres. The UAM is designed for computing ozone (O_3) concentrations under short-term, episodic conditions lasting one or two days resulting from emissions of oxides of nitrogen (NO_x) and volatile organic compounds (VOC). The model treats urban VOC emissions as their carbon-bond surrogates.

a. *Recommendations for Regulatory Use*

UAM is appropriate for the following applications: Single urban areas having significant ozone attainment problems in the absence of interurban emission transport; and one hour averaging times.

UAM has many options but no specific recommendations can be made at this time on all options. The reviewing agency should be consulted on selection of options to be used in regulatory applications. At the present time, the following options should be selected for regulatory applications:

Omit SO_2 and AEROSOLS from the SPECIES packet for the CHEMPARAM file;

Set ROADWAY flag to FALSE in the SIMULATION packet for the SIM–CONTROL file; and

Set surface layer height to zero in the REGION packet for the AIRQUALITY, BOUNDARY, DIFFBREAK, METSCALARS, PTSOURCE, REGIONTOP, TEMPERATUR, TERRAIN, TOPCONC, and WIND files.

b. *Input Requirements*

Source data: Gridded, hourly emissions of PAR, OLE, ETH, ARO, CARB, NO, and NO_2 for low-level sources. CO is optional. For major elevated point sources, hourly emissions, stack height, stack diameter, exit velocity, and exit temperature.

Meteorological data: Hourly, gridded, divergence free, u and v wind components for each vertical level; hourly gridded mixing heights; hourly gridded surface temperatures; hourly exposure class; hourly vertical potential temperature gradient above and below the mixing height; hourly surface atmospheric pressure; hourly water mixing ratio; and gridded surface roughness lengths.

Air quality data: Concentration of O_3, NO, NO_2, PAR, OLE, ETH, ARO, CARB, PAN, and CO at the beginning of the simulation for each grid cell; and hourly concentrations of each pollutant at each level along the inflow boundaries and top boundary of the modeling region.

Other data requirements are: Hourly mixed layer average, NO_2 photolysis rates; and

ozone surface uptake resistance along with associated gridded vegetation (scaling) factors.

c. *Output*

Printed output includes: Gridded instantaneous concentration fields at user-specified time intervals for user-specified pollutants and grid levels; Gridded time average concentration fields for user-specified time intervals, pollutants, and grid levels.

d. *Type of Model*

UAM is a-three dimensional, numerical photochemical grid model.

e. *Pollutant Types*

UAM may be used to model ozone (O_3) formation from oxides of nitrogen (NOx) and volatile organic compound (VOC) emissions.

f. *Source-Receptor Relationship*

Low-level area and point source emissions are specified within each surface grid cell.

Up to 500 major point sources are allowed.

Hourly average concentrations of each pollutant are calculated for all grid cells at each vertical level.

g. *Plume Behavior*

Plume rise is calculated for major point sources using relationships recommended by Briggs (1971).

h. *Horizontal Winds*

See Input Requirements.

i. *Vertical Wind Speed*

Calculated at each vertical grid cell interface from the mass continuity relationship using the input gridded horizontal wind field.

j. *Horizontal Dispersion*

Horizontal eddy diffusivity is set to a user specified constant value (nominally 50 m^2/s).

k. *Vertical Dispersion*

Vertical eddy diffusivities for unstable and neutral conditions calculated using relationships of Lamb et al. (1977); for stable conditions, the relationship of Businger and Arya (1974) is employed. Stability class, friction velocity, and Monin-Obukhov length determined using procedure of Liu et al. (1976).

l. *Chemical Transformation*

UAM employs a simplified version of the Carbon-Bond II Mechanism (CBM–II) developed by Whitten, Killus, and Hogo (1980) employing various steady-state approximations. CBM–II is further simplified during nighttime hours to improve computational efficiency. CBM–II utilizes five carbon-bond species (PAR-single bonded carbon atoms; OLE-terminal double bonded carbon atoms; ETH-ethylene; ARO-alkylated aromatic rings; and CARB-aldehydes, ketones, and surrogate carbonyls) which serve as surrogates for the large variety of emitted organic compounds in the urban atmosphere.

m. *Physical Removal*

Dry deposition of ozone and other pollutant species are calculated. Vegetation (scaling) factors are applied to the reference surface

uptake resistance of each species depending on land use type.

n. *Evaluation Studies*

Builtjes, P.J.H., K.D. van der Hurt, and S.D. Reynolds, 1982. Evaluation of the Performance of a Photochemical Dispersion Model in Practical Applications, 13th International Technical Meeting on Air Pollution Modeling and Its Application, Ile des Embiez, France.

Cole, H.S., D.E. Layland, G.K. Moss, and C.F. Newberry, 1983. The St. Louis Ozone Modeling Project. EPA Publication No. EPA 450/4–83–019. U. S. Environmental Protection Agency, Research Triangle Park, NC.

Dennis, R.L., M.W. Downton, and R.S. Keil, 1983. Evaluation of Performance Measures for an Urban Photochemical Model. EPA Publication No. EPA 450/4–83–021. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Haney, J.L. and T.N. Braverman, 1985. Evaluation and Application of the Urban Airshed Model in the Philadelphia Air Quality Control Region. EPA Publication No. EPA 450/4–85–003. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Layland, D.E. and H.S. Cole, 1983. A Review of Recent Applications of the SAI Urban Airshed Model. EPA Publication No. EPA 450/4–84–004. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Layland, D.E., S.D. Reynolds, H. Hogo and W.R. Oliver, 1983. Demonstration of Photochemical Grid Model Usage for Ozone Control Assessment. 76th Annual Meeting of the Air Pollution Control Association, Atlanta, GA.

Reynolds, S.D., H. Hogo, W.R. Oliver, L.E. Reid, 1982. Application of the SAI Airshed Model to the Tulsa Metropolitan Area, SAI No. 82004. Systems Applications, Inc., San Rafael, CA.

Schere, K.L. and J.H. Shreffler, 1982. Final Evaluation of Urban-Scale Photochemical Air Quality Simulation Models. EPA Publication No. EPA 600/3–82–094. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Seigneur, C., T.W. Tesche, C.E. Reid, P.M. Roth, W.R. Oliver, and J.C. Cassmassi, 1981. The Sensitivity of Complex Photochemical Model Estimates to Detail In Input Information, Appendix A—A Compilation of Simulation Results. EPA Publication No. EPA 450/4–81–031b. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Stern, R. and B. Scherer, 1982. Simulation of a Photochemical Smog Episode in the Rhine-Ruhr Area with a Three Dimensional Grid Model. 13th International Technical Meeting on Air Pollution Modeling and Its Application, Ile des Embiez, France.

Tesche, T.W., C. Seigneur, L.E. Reid, P.M. Roth, W.R. Oliver, and J.C. Cassmassi, 1981. The Sensitivity of Complex Photochemical Model Estimates to Detail In Input Information. EPA Publication No. EPA 450/4–81–031a. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Tesche, T.W., W.R. Oliver, H. Hogo, P. Saxeena and J.L. Haney, 1983. Volume IV—Assessment of NO_x Emission Control Requirements in the South Coast Air Basin—Appendix A. Performance Evaluation of the Systems Applications Airshed Model for the 26–27 June 1974 O_3 Episode in the South Coast Air Basin, SYSAPP 83/037. Systems Applications, Inc., San Rafael, CA.

Tesche, T.W., W.R. Oliver, H. Hogo, P. Saxeena and J.L. Haney, 1983. Volume IV—Assessment of NO_x Emission Control Requirements in the South Coast Air Basin—Appendix B. Performance Evaluation of the Systems Applications Airshed Model for the 7–8 November 1978 NO_2 Episode in the South Coast Air Basin, SYSAPP 83/038. Systems Applications, Inc., San Rafael, CA.

A.9 Offshore and Coastal Dispersion Model (OCD)

Reference

Hanna, S.R., L.L. Schulman, R.J. Paine and J.E. Pleim, 1984. The Offshore and Coastal Dispersion (OCD) Model User's Guide, Revised. OCS Study, MMS 84–0069. Environmental Research and Technology, Inc., Concord, MA. (NTIS PB 86–159803)

Availability

The above user's guide is available for $40.95 from NTIS. The computer tape is available from NTIS as number PB85–246106 at a cost of $800.

Technical Contact

Minerals Management Service, 12203 Sunrise Valley Drive, Mail Stop 644, Reston, VA 22091, ATTN: Mitchell Baer.

Abstract

OCD is a straight-line Gaussian model developed to determine the impact of offshore emissions from point sources on the air quality of coastal regions. OCD incorporates overwater plume transport and dispersion as well as changes that occur as the plume crosses the shoreline. Hourly meteorological data are needed from both offshore and onshore locations. These include water surface temperature and overwater air temperature and relative humidity.

Some of the key features include platform building downwash, partial plume penetration into elevated inversions, direct use of turbulence intensities for plume dispersion, interaction with the overland internal boundary layer, and continuous shoreline fumigation.

a. *Recommendations for Regulatory Use*

OCD has been recommended for use by the Minerals Management Service for emissions located on the Outer Continental Shelf (Federal Register 50, 12248, 28 March 1985). OCD is applicable for overwater sources where onshore receptors are below the lowest source height. Where onshore receptors are above the lowest source height, offshore plume transport and dispersion may be modeled on a case-by-case basis in consultation with the EPA Regional Office.

b. *Input Requirements*

Source data: Point source location, pollutant emission rate, building height, stack height, stack gas temperature, stack inside diameter, stack gas exit velocity, stack angle from vertical, elevation of stack base above water surface and gridded specification of the land/water surfaces. As an option, emission rate, stack gas exit velocity and temperature can be varied hourly.

Meteorological data (overwater): Wind direction, wind speed, mixing height, relative humidity, air temperature, water surface temperature, vertical wind direction shear (optional), vertical temperature gradient (optional), turbulence intensities (optional). For all meteorological input variables, hourly data are preferred to climatological values.

Meteorological data (overland): Wind direction, wind speed, temperature, stability class, mixing height.

Receptor data: Location, height above local ground-level, ground-level elevation above the water surface.

c. *Output*

All input options, specification of sources, receptors and land/water map including locations of sources and receptors.

Summary tables of five highest concentrations at each receptor for each averaging period, and average concentration for entire run period at each receptor.

Optional case study printout with hourly plume and receptor characteristics.

Concentration files written to disk or tape can be used by ANALYSIS postprocessor to produce the highest concentrations for each receptor, the cumulative frequency distributions for each receptor, the tabulation of all concentrations exceeding a given threshold, and the manipulation of hourly concentration files.

d. *Type of Model*

OCD is a Gaussian plume model constructed on the framework of the MPTER model.

e. *Pollutant Types*

OCD may be used to model primary pollutants. Settling and deposition are not treated.

f. *Source-Receptor Relationship*

Up to 250 point sources and 180 receptors may be used.

Receptors and sources are allowed at any location.

The coastal configuration is determined by a grid of up to 3600 rectangles. Each element of the grid is designated as either land or water to identify the coastline.

g. *Plume Behavior*

As in MPTER, the basic plume rise algorithms are based on Briggs' recommendations.

Momentum rise includes consideration of the stack angle from the vertical.

The effect of drilling platforms, ships, or any overwater obstructions near the source are used to decrease plume rise following the approach of the BLP model.

Partial plume penetration of elevated inversions is included using the suggestions of Briggs (1975) and Weil and Brower (1984).

If overwater conditions are stable and overland conditions unstable, the Deardorff-Willis (1982) fumigation model is used to simulate the entrainment of the plume in the rising thermal internal boundary layer. The fumigation calculations are used only if the concentrations are lower than those resulting from the change to overland dispersion coefficients at the water/land interface.

h. Horizontal Winds

Constant, uniform wind is assumed for each hour.

Overwater wind speed can be estimated from overland wind speed using relationship of Hsu (1981).

Wind speed profiles are estimated using similarity theory (Businger 1973). Surface layer fluxes for these formulas are calculated from bulk aerodynamic methods.

i. Vertical Wind Speed

Vertical wind speed is assumed equal to zero.

j. Horizontal Dispersion

Lateral turbulence intensity is recommended as a direct estimate of horizontal dispersion. If lateral turbulence intensity is not available, it is estimated from boundary layer theory. For wind speeds less than 10 m/s, lateral turbulence intensity is assumed inversely proportional to wind speed.

Horizontal dispersion may be enhanced because of obstructions near the source. A virtual source technique, as in the BLP model, is used to simulate the initial plume dilution due to downwash.

Formulas recommended by Pasquill (1976) are used to calculate buoyant plume enhancement and wind direction shear enhancement.

At the water/land interface, the change to overland dispersion rates is modeled using a virtual source. The overland dispersion rates can be calculated from either lateral turbulence intensity or the Turner (1969) coefficients. The change is implemented where the plume intercepts the rising internal boundary layer.

k. Vertical Dispersion

Vertical turbulence intensity is recommended as a direct estimate of vertical dispersion. If not available, turbulence intensity is estimated from boundary layer theory. For very stable conditions, vertical dispersion is also a function of lapse rate.

Vertical dispersion may be enhanced because of obstructions near the source. A virtual source technique, as in the BLP model, is used to simulate the initial plume dilution due to downwash.

Formulas recommended by Pasquill (1976) are used to calculate buoyant plume enhancement.

At the water/land interface, the change to overland dispersion rates is modeled using a virtual source. The overland dispersion rates can be calculated from either vertical turbulence intensity or the Turner (1969) coefficients. The change is implemented where the plume intercepts the rising internal boundary layer.

l. Chemical Transformation

Chemical transformations are treated using exponential decay. Different rates can be specified by month and by day or night.

m. Physical Removal

Physical removal is also treated using exponential decay.

n. Evaluation Studies

Hanna, S.R., L.L. Schulman, R.J. Paine and J.E. Pleim, 1984. The Offshore and Coastal Dispersion (OCD) Model User's Guide, Revised. OCS Study, MMS 84–0069. Environmental Research & Technology, Inc., Concord, MA. (NTIS No. PB 86–159803)

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Lamb, R.G., et al., 1977. Continued Research in Mesoscale Air Pollution Simulation Modeling—Vol. VI: Further Studies in the Modeling of Microscale Phenomena, Report Number EF77–143. Systems Applications, Inc., San Rafael, CA.

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McElroy, J.L. and F. Pooler, Jr., 1968. St. Louis Dispersion Study Volume II-Analysis. NAPCA Publication No. AP–53. U.S. Environmental Protection Agency, Research Triangle Park, NC.

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Pasquill, F., 1976. Atmospheric Dispersion Parameters in Gaussian Plume Modeling Part II. Possible Requirements for Change in the Turner Workbook Values. EPA Publication No. EPA 600/4–76–030b. U.S. Environmental Protection Agency, Research Triangle Park, NC.

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Appendix B to appendix X to Part 266—Summaries of Alternative Air Quality Models

Table of Contents

B.0 Introduction

This appendix summarizes key features of refined air quality models that may be considered on a case-by-case basis for individual regulatory applications. For each model, information is provided on availability, approximate cost in 1986*, regulatory use, data input, output format and options, simulation of atmospheric physics and accuracy. These summaries are based directly on information supplied by the model developers and have been included without change. The Models are listed by name in alphabetical order.

There are three separate conditions under which these models will normally be approved for use: first, if a demonstration can be made that the model produces concentration estimates equivalent to the estimates obtained using a preferred model (e.g. the maximum or high, second-high concentration is within 2% of the estimate using the comparable preferred model); second, if a statistical performance evaluation has been conducted using measured air quality data and the results of that evaluation indicate the model in appendix B performs better for the application than a comparable model in appendix A; and third, if there is no preferred model for the specific application but a refined model is needed to satisfy regulatory requirements. Any one of these three separate conditions may warrant use of these models. See section 3.2, Use of Alternative Models, for additional details.

Many of these models have been subjected to a performance evaluation by comparison with observed air quality data. A summary of such comparisons for models contained in this appendix is included in "A Survey of Statistical Measures of Model Performance and Accuracy for Several Air Quality Models," EPA–450/4–83–001. Where possible, several of the models contained herein have been subjected to rigorous evaluation exercises, including (1) statistical performance measures recommended by the American Meteorological Society and (2) peer scientific reviews.

B.1 Air Quality Display Model (AQDM)

Reference

TRW Systems Group, 1969. Air Quality Display Model. Prepared for National Air Pollution Control Administration, DHEW, U.S. Public Health Service, Washington, DC. (NTIS No. PB 189194).

Availability

The above User's Guide is available from NTIS at a cost of $16.95. This model is available at no cost in the form of a punched card deck from: Library Services, MD–35, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, Attn: Ann Ingram.

Abstract

AQDM is a climatological steady state Gaussian plume model that estimates annual arithmetic average sulfur dioxide and particulate concentrations at ground level in urban areas. A statistical model based on Larsen (1971) is used to transform the average concentration data from a limited

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*All models on UNAMAP (Version 6) are available from NTIS at a price consistent with the previous version of UNAMAP.

number of receptors into expected geometric mean and maximum concentration values for several different averaging times.

a. *Recommendations for Regulatory Use*

AQDM can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. AQDM must be executed in the equivalent mode.

AQDM can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that AQDM is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. *Input Requirements*

Source data requirements are: Average emissions rates and heights of emissions for point and area sources; stack gas temperature, stack gas exit velocity, and stack inside diameter for plume rise calculations for point sources.

Meteorological data requirements are: Stability wind rose (STAR deck), average afternoon mixing height, average morning mixing height, and average air temperature.

Receptor data requirements are: Number and locations of receptors. If the Larsen transform option is to be used to estimate short averaging time concentrations, measured standard geometric deviation of concentrations is required.

c. *Output*

Printed output includes:

One month to one year average concentrations (arithmetic mean only) at each receptor;

Optional arbitrary averaging time by Larsen (1971) procedure (typically 1–24 hr); and

Optional individual point, area source culpability list for each receptor.

d. *Type of Model*

AQDM is a Gaussian plume model.

e. *Pollutant Types*

AQDM may be used to model non-reactive pollutants. Settling and deposition are not treated.

f. *Source Receptor Relationship*

AQDM applies user-specified locations and stack height for each point source.

AQDM uses any location and size for each area source.

Up to 225 receptors may be located on uniform rectangular grid.

Up to 12 user-specified receptor locations are permitted.

Unique release height is used for each point and area source.

Receptors are assumed to be at ground level.

No terrain differences between source and receptor are treated.

g. *Plume Behavior*

AQDM uses Briggs (1969) plume rise formulas.

No plume rise is calculated for area sources.

Fumigation and downwash are not treated.

Zero concentration is assumed when plume height is greater than mixing height.

h. *Horizontal Winds*

Wind data are input as stability wind rose (joint frequency distribution) of 16 wind directions, six wind speed classes, and five stability classes.

No variation in wind speed with height is assumed.

Constant, uniform (steady-state) wind is assumed.

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

j. *Horizontal Dispersion*

Pollutants are assumed evenly distributed across a 22.5 degree sector.

Frequency of occurrence of a meteorological state is interpolated between sector center lines.

Averaging times from 1 month to 1 year or longer are treated.

k. *Vertical Dispersion*

Rural dispersion coefficients from Turner (1969) are used.

Five stability classes are as defined by Turner (1964). Stability classes E and F are combined, and assigned dispersion values equivalent to stability class D.

Neutral stability is split internally into 60% day, 40% night, with the two differing only in the treatment of mixing height.

Mixing height is a function of a single input afternoon mixing height a single input morning mixing height, modified by the stability class.

l. *Chemical Transformations*

Not treated.

m. *Physical Removal*

Not treated.

n. *Evaluation Studies*

NcNidar, R.R., 1977. Variability Analysis of Long-term Dispersion Models. Joint Conference on Applications of Air Pollution Meteorology, American Meteorology Society, 29 Nov.–2 Dec., 1977, Salt Lake City, UT.

Turner, D.B., J.R. Zimmerman, and A.D. Busse, 1973. An Evaluation of Some Climatological Dispersion Models. In Appendix E, User's Guide to the Climatological Dispersion Model, EPA Publication No. EPA–R4–73–024, Environmental Protection Agency, Research Triangle Park, NC.

Londergan, R.J., D.H. Minott, D.J. Wachter and R.R. Fizz, 1983. Evaluation of Urban Air Quality Simulation Models, EPA Publication No. EPA–450/4–83–020, U.S, Environmental Protection Agency, Research Triangle Park, NC.

B.2 Air Resources Regional Pollution Assessment (ARRPA) Model

Reference

Mueller, S.F., R.J. Valente, T.L. Crawford, A.L. Sparks, and L.L. Gautney, Jr., 1983. Description of the Air Resources Regional Pollution Assessment (ARRPA) Model. TVA/ONR/AQB–83/14. Tennessee Valley Authority, Muscle Shoals, AL.

Availability

The computer code and sample input for this model on magnetic tape and a copy of the User's Guide are available from: Computer Services Development Branch, Office of Natural Resources and Economic Development, Tennessee Valley Authority, OSWHA, Muscle Shoals, Alabama 35660, phone (205) 386–2985. A hard copy of the model output corresponding with the sample input is also available. The cost of copying model information to a buyer-supplied 2400-ft., high density tape is estimated to be about $100. The User's Guide is free of charge.

Abstract

The ARRPA model is a medium/long-range segmented-plume model. It is designed to compute air concentrations and surface dry mass deposition of sulfur dioxide and sulfate. A unique feature of the model is its use of prognostic meteorological output from the National Weather Service Boundary Layer Model (BLM). Boundary layer conditions are computed by the BLM on a grid with a spatial resolution of 80 km, and are archived in intervals of 3 hours. BLM output used by this model includes three dimensional wind field components and potential temperature at 10 height levels from the surface through 2000 m above the surface.

a. *Recommendations for Regulatory Use*

Use of the model for transport distances of less than 10 km is not recommended. For 10 km to beyond 50 km, there is no specific recommendation at the present time. The model may be used on a case-by-case basis.

b. *Input Requirements*

Source data requirements: Location (latitude and longitude), stack height, stack diameter, stack gas exit velocity, stack gas temperature, SO_2 emission rate, SO_4 emission rate, stack base elevation.

Meteorological data requirements: Hourly wind field components (u,v,w), potential temperature (θ), Pasquill-Gifford stability class and mixing height. These data are obtained as output from the BLM output preprocessing program called MDPP (S.F. Mueller and R.J. Valente, 1983). Required input to MDPP is BLM output (in three-hour intervals) of u, v, w, and θ, surface layer friction velocity (u*) and surface layer values of the inverse Monin-Obukhov length (L^{-1}).

Receptor data requirements: Gridded receptor array coordinates (x and y) and receptor heights (z) from a receptor preprocessing program called HEIGHT. HEIGHT produces a user-designed array of points which may be skewed up to ±90 degrees relative to the model x axis. The elevation of each receptor is adjusted to give height above smoothed model terrain. Non-

gridded receptors can be specified using latitude/longitude coordinates.

c. *Output*

Printed output includes:

Listings of input parameters (except for meteorological data);

Listing of hours processed and flags for missing data periods.

Disk output: Parameters for controlling analysis and printout options in the postprocessing program called ANALYSIS; hourly SO_2 and SO_4 air concentrations and dry deposition amounts at each receptor.

Optional printed output: Two programs are available for displaying model output— DISPLAY and ANALYSIS; DISPLAY prints out hourly gridded concentration and/or deposition fields for user-specified time periods; ANALYSIS prints out (1) the five highest concentrations of SO_2 and/or SO_4 at each receptor for 1-hour, 3-hour (optional) and 24-hour (optional) averaging periods, (2) average SO_2 and/or SO_4 concentrations at each receptor for the entire analysis period and (3) gridded SO_2 and/or SO_4 dry deposition amounts for the day having the greatest dry deposition and for the entire analysis period.

d. *Type of Model*

The ARRPA model is a Gaussian segmented-plume model.

e. *Pollutant Types*

SO_2 and SO_4 are treated.

f. *Source-Receptor Relationship*

One source is treated per model run, though results from several sources may be superimposed.

Either constant or variable emission rates may be used.

Receptors (up to 100) in gridded network may have different elevations.

Height of receptors above ground is variable.

g. *Plume Behavior*

Plume rise is computed in a piecewise-continuous manner through discrete model layers (Mueller, et al., 1983).

Plume can be isolated from the ground (lofting).

Plume height varies in time and space.

h. *Horizontal Winds*

Hourly horizontal wind components, specified at 80-km intervals across the model grid, are spatially interpolated and vertically averaged through the plume depth to get plume transport vectors. A model option is available that uses the wind vector near the vertical plume center instead of computing a vertically-averaged vector.

i. *Vertical Wind Speed*

The mass-conserving BLM wind field used in this model provides vertical wind components that vary horizontally and vertically, and are used to adjust plume height.

j. *Horizontal Dispersion*

Plume half-width (σ_y) growth goes through four stages:

(1) Growth follows Turner curves for $\sigma_y < 1000$ m;

(2) A transition in growth behavior from Turner curves to dynamical-statistical (Langevin) theory occurs for $1000 \text{ m} < \sigma_y < 6000 \text{ m}$;

(3) Growth is based on dynamical-statistical theory for $\sigma_y > 6000 \text{ m}$; eddy diffusivity computed from Pasquill-Gifford stability class;

(4) Growth approaches that described by Taylor's statistical theory (limit of dynamical-statistical theory for time much larger than the Lagrangian time correlation) for $\sigma_y > 10000 \text{ m}$.

k. Vertical Dispersion

Plume half-depth (σ_z) growth is based on combination of Brookhaven curves for elevated plumes and Turner curves for near-ground plumes.

Vertical plume structure is Gaussian, with superimposed reflection terms, until σ_z becomes sufficiently large that a vertically uniform plume assumption is appropriate.

Maximum depth of a plume is 2000 m.

l. Chemical Transformation

SO_2 oxidation to SO_4 is treated using a first-order chemical reaction rate constant which is parameterized to vary hourly following diurnal and seasonal cycles.

m. Physical Removal

Dry deposition is computed using the source depletion equation. Dry deposition velocities vary according to the stability of the surface layer.

n. Evaluation Studies

Muller, S.F. and L.W. Reisinger, 1986. Evaluation of the Air Resources Regional Pollution Assessment (ARRPA) Model. (Report in Progress).

B.3 APRAC-3

Reference

Simmon, P. B., R. M. Patterson, F. L. Ludwig, and L. B. Jones, 1981. The APRAC-3/ Mobile 1 Emissions and Diffusion Modeling Package. EPA Publication No. EPA 909-9-81-002. U.S. Environmental Protection Agency, Region IX, San Francisco, CA. (NTIS No. PB82-103763).

Availability

This model is available as part of UNAMAP (Version 6). The computer code is available on magnetic tape from: Computer Products, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, phone (703) 487-4650.

Abstract

APRAC-3 is a model which computes hourly average carbon monoxide concentrations for any urban location. The model calculates contributions from dispersion on various scales: Extraurban, mainly from sources upwind of the city of interest; intraurban, from freeway, arterial, and feeder street sources; and local, from dispersion within a street canyon. APRAC-3 requires an extensive traffic inventory for the city of interest. APRAC-3, as it exists on UNAMAP (Version 6), has been updated with Mobile 2 emission factors.

a. Recommendations for Regulatory Use

APRAC-3 can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. APRAC-3 must be executed in the equivalent mode.

APRAC-3 can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated using the criteria in section 3.2, that APRAC-3 is more appropriate for the specific application. In this case the model options/mode which are most appropriate for the application should be used.

Although the user's manual for APRAC-3 contains Mobile 1 emission factors, it is recommended that those emission factors be updated with the latest version of Mobile (Mobile Source Emissions Model) for use in regulatory applications.

b. Input Requirements

Source data requirements are: line source (traffic link) end points, road type and daily traffic volume.

Meteorological data requirements are: hourly wind direction (nearest 10 degrees), hourly wind speed, and hourly cloud cover for stability calculations.

Receptor data requirements are: coordinates for up to 10 receptors for any single day and up to 8 receptors for the intersection submodel.

c. Output

Printed ouput includes:

Hourly calculations at each receptor.

d. Type of Model

APRAC-3 is a Gaussian plume model.

e. Pollutant Types

APRAC-3 may be used to model primary pollutants.

f. Source-Receptor Relationship

Traffic links may have arbitrary length and orientation. Off-link traffic is allocated to two-mile square grids. Link traffic emissions are aggregated into a receptor oriented area source array.

The boundaries of the area sources actually treated are (1) arcs at radial distances from the receptor which increase in geometric progression, (2) the sides of a 22.5° sector oriented upwind for distances greater than 1000 m, and (3) the sides of a 45° sector oriented upwind for distances less than 1000 m.

A similar area source array is established for each receptor.

Sources are assumed to be at ground level.

Up to 10 receptors are accepted for any single day.

Up to 625 receptors are accepted for a single-hour.

Up to 8 receptors are accepted for the intersection submodel.

Receptors are at ground level.

Receptor locations are arbitrary.

Four internally defined receptor locations on each user-designated street are used in a special street canyon sub-model.

A box model is used to estimate contribution from upwind sources beyond 32 km based on wind speed, mixing height, annual fuel consumption.

In street canyon sub-model, contribution from other streets is included in background.

g. Plume Behavior

Plume rise is not treated.

Fumigation and downwash are not treated except in street canyon sub-model.

In street canyon sub-model, a helical circulation pattern is assumed.

h. Horizontal Winds

User input hourly wind speed and direction in tens of degrees are used.

No variation of wind speed or direction with height is assumed.

Constant, uniform (steady-state) wind is assumed within each hour.

The model can interpolate winds at receptors if more than one wind is provided.

i. Vertical Wind Speed

Vertical wind speed is assumed equal to zero except in street canyon sub-model.

Helical circulation assumed by street canyon sub-model.

j. Horizontal Dispersion

Sector averaging is used with uniform distribution within sectors. Sector size is 22.5 degrees beyond 1 km and 45.0 degrees within 1 km.

k. Vertical Dispersion

Six stability classes are used. Stability class is determined internally from user-supplied meteorological data modified from Turner (1964).

Dispersion coefficients are adapted from McElroy and Pooler (1968).

No adjustments are made for variations in surface roughness.

Downwind distance variation of σ_z is assumed to be ax^b for purposes of doing analytical integration.

In street canyon sub-model, an empirical function of wind speed and street width and direction is used.

Perfect reflection at the surface is assumed.

Mixing height is ignored until concentration equals that calculated using box model. A box model (uniform vertical distribution) is used beyond that distance.

l. Chemical Transformation

Not treated.

m. Physical Removal

Not treated.

n. Evaluation Studies

Ludwig, F. L. and W. F. Dabberdt, 1972. Evaluation of the APRAC-1A Urban Dispersion Model for Carbon Dioxide, SRI Project 8563. Stanford Research Institute, Menlo Park, CA.

B.4 COMPTER

Reference

State of Alabama, 1980. COMPTER Model Users Guide. Alabama Department of Environmental Management, Air Division, Montgomery, AL.

Availability

This model is available to users for tape and reproduction charges. If a tape is sent, the reproduction is free. Send tape and desired format and specifications to: Mr. Richard E. Grusnick, Chief, Air Division, Alabama Department of Environmental

Management, 1751 Federal Drive, Montgomery, Alabama 36109.

Abstract

COMPTER is based on the Gaussian steady-state technique applicable to both urban and rural areas. The model contains the following attributes: (a) Determines maximum 24-hour, 3-hour, 1-hour and variable hour concentrations for both block and running averages; (b) elevated terrain considered with the standard plume-chopping technique or stability dependent plume path trajectory; (c) uses annual hourly meteorological data in the CRSTER preprocessor format; (d) uses Pasquill-Gifford stability curves; (e) allows for stability class substitution in the stable categories. Typical model use is in rural areas with moderate to low terrain features.

a. *Recommendations for Regulatory Use*

COMPTER can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. COMPTER must be executed in the equivalent mode.

COMPTER can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that COMPTER is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. *Input Requirements*

Source data requirements are: annual or hourly values of emission rate, exit velocity, stack gas temperature, stack height, and stack diameter.

Meteorological data requirements are: Hourly surface weather data from the EPA meteorological preprocessor program. Preprocessor output includes hourly stability class wind direction, wind speed, temperature, and mixing height. Actual anemometer height (a single value) is optional.

Receptor data requirements are: individual receptor coordinates; or a location and distance from the center of five rings of receptors; or a combination of individual receptors and either the rectangular grid or the rings of receptors. Elevations of all receptors may be input.

c. *Output*

Printed output includes:

Highest and second highest concentrations for the year at each receptor for averaging times of 1, 3 and 24-hours, a user-selected averaging time which may be 2–12 hours (variable hourly), and a 50 high table for 1, 3, variable hourly, and 24-hours;

Annual arithmetic average at each receptor; and the highest 1-hour and 24-hour concentrations over the receptor field for each day considered.

Computer readable output includes: Hourly, 3-hourly, variable hourly, and 24-hourly concentrations for each receptor on magnetic storage device.

d. *Type of Model*

COMPTER is a Gaussian plume model.

e. *Pollutant Types*

COMPTER may be use to model primary pollutants. Settling and deposition are not treated.

f. *Source-Receptor Relationship*

A maximum 50 sources and 200 receptors are treated.

COMPTER applies user-specified locations of sources and receptors.

User input stack height and source characteristics for each source are applied.

User input topographic elevation for each receptor is applied.

Receptors are assumed to be at ground level.

g. *Plume Behavior*

Briggs' (1969, 1971, 1972) plume rise equations with limited mixing are used.

Plume height is adjustable according to stability with use of plume path coefficient.

h. *Horizontal Winds*

Constant, uniform (steady-state) wind is assumed for an hour.

Straight line plume transport is assumed to all downwind distances.

Power law wind profile exponents used are .10, .15, .20, .25, .30, .30, for stability classes A through F, respectively. Anemometer height is assumed to be 10 meters.

i. *Vertical Wind Speed*

Vertical wind speeds are assumed equal to zero.

j. *Horizontal Dispersion*

Dispersion coefficients are from Turner (1969), with no further adjustments made for variations in surface roughness or averaging time.

Optionally, stability class 7 may be treated as Class 6.

Other options for stable class substitution include changing stabilities F and G to E, and reducing E, F, and G to D, E, and F, respectively.

k. *Vertical Dispersion*

Dispersion coefficients are from Turner (1969), with no further adjustments made for variations in surface roughness.

Optionally, by source, buoyancy induced dispersion ($\Delta H^2/10$) is included.

Optionally, stability class 7 may be treated as class 6.

Other options for stable class substitution include changing stabilities F and G to E; and reducing E, F, and G to D, E, and F, respectively.

l. *Chemical Transformation*

Not treated.

m. *Physical Removal*

Not treated.

n. *Evaluation Studies*

Londergan, R., D. Minott, D. Wackter, T. Kincaid and D. Bonitata, 1983. Evaluation of Rural Air Quality Simulation Models. EPA Publication No. EPA-450/4-83-003. U.S. Environmental Protection Agency, Research Triangle Park, NC.

B.5 ERT Air Quality Model (ERTAQ)

Reference

Environmental Research & Technology, Inc., 1980. ERTAQ User's Guide. ERT Document No. M-0186-001E. Environmental Research & Technology, Inc., Concord, MA.

Availability

The above report and a computer tape are available from: Computer Products, National Technical Information Service, U.S. Department of Commerce, 5825 Port Royal Road, Springfield, Virginia 22161, phone (703) 487-4650.

Abstract

ERTAQ is a multiple point, line and area source dispersion model which utilizes the univariate Gaussian formula with multiple reflections. With the fugitive dust option, entrainment of particulates from ground-level sources and subsequent deposition are accountable. The model offers an urban/rural option, and calculates long-term or worst-case concentrations due to arbitrarily located sources for arbitrarily located receptors above or at ground level. Background concentrations and calibration factors at each receptor can be user specified. Unique flexibility is afforded by postprocessing storage and manipulation capability.

a. *Recommendations for Regulatory Use*

ERTAQ can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. ERTAQ must be executed in the equivalent mode.

ERTAQ can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that ERTAQ is more appropriate for the specific application in this case the model options/modes which are most appropriate for the application should be used.

b. *Input Requirements*

Source data requirements are: Up to six pollutants may be specified, citing quantity and calibration factor for each (and particle size, if appropriate); heat rate and height of emissions per source for determining plume height.

Meteorological data requirements are: Stability wind rose, plus annual average ambient air temperature and mixing height.

Receptor data requirements are: Cartesian coordinates for each receptor.

c. *Output*

Printed output includes: Mean concentrations at designated receptors for long-term mode. In worst-case mode, concentrations for user-specified meteorological conditions.

d. *Type of Model*

ERTAQ is a climatological Gaussian plume model.

e. *Pollutant Types*

ERTAQ treats primary pollutants with or without significant settling velocities.

f. Source-Receptor Relationship

Up to 501 user-specified locations for point, area, and line sources, and up to 128 arbitrarily located receptors are permitted.

User-specified release heights are applied for all sources.

Simple terrain relief is treated.

Receptors may be at or above ground level.

g. Plume Behavior

Briggs (1975) final plume rise only is used.

Briggs calm formula is used when wind speed is less than 1.37 meters per second.

Plume rise may be calculated for point and area sources.

Top or mixed layer is perfect reflector (full or no plume penetration).

Fumigation and downwash are not treated.

Buoyancy-induced dispersion is not treated.

h. Horizontal Winds

Steady state and homogeneous winds are assumed.

Sixteen wind directions and six speed classes are treated.

Exponential vertical profile extrapolates observed wind to release height for plume rise and to plume height for downwind dilution.

The exponents used are .10, .15, .20, .25, and .30 for stability classes A through E, respectively.

i. Vertical Wind Speed

Vertical wind speed is assumed to be zero.

j. Horizontal Dispersion

Uniform distribution in 22.5 degree sector, or triangular distribution in 45-degree sector (user specified).

k. Vertical Dispersion

Gaussian plume with initial mixing specification is assumed.

Five stability categories are treated (converts all stability class F to class E).

Rural dispersion coefficients from Turner (1969) are used with no adjustments made for surface roughness.

Urban case is treated by shifting each stability category (except class A) one class toward unstable.

Top of mixed layer is perfect reflector (full or no plume penetration).

Ground surface is total reflector.

Surface deposition reduces entire plume concentration using a source depletion factor.

l. Chemical Transformation

Chemical transformations are treated using exponential decay. Half-life is input by the user.

m. Physical Removal

Particle deposition for ground-level sources is treated.

n. Evaluation Studies

Londergan, R.J., D.H. Minott, D.J. Wackter and R.R. Fizz, 1983. Evaluation of Urban Air Quality Simulation Models. EPA Publication No. EPA-450/4-83-020. U.S. Environmental Protection Agency, Research Triangle Park, NC.

B.6 ERT Visibility Model

Reference

Drivas, P.J., Savithri M., and D.W. Heinold, 1980. ERT Visibility Model: Version 3; Technical Description and User's Guide. Document M2020-001. Environmental Research & Technology, Inc., Concord, MA.

Availability

The above report and a computer tape are available from: Computer Products, National Technical Information Service, U. S. Department of Commerce, 5825 Port Royal Road, Springfield, Virginia 22161, phone (703) 487-4650.

Abstract

The ERT Visibility model is a Gaussian dispersion model designed to estimate visibility impairment for arbitrary lines of sight due to isolated point source emissions by simulating gas-to-particle conversion, dry deposition, NO to NO_2 conversion and linear radiative transfer.

a. Recommendations for Regulatory Use

There is no specific recommendation at the present time. The ERT Visibility model may be used on a case-by-case basis.

b. Input Requirements

Source data requirements are: stack height, stack temperature, emissions of SO_2, NO_x, TSP, fraction of NO_x as NO_2, fraction of TSP which are carbonaceous, exit velocity, and exit radius.

Meteorological data requirements are: Hourly ambient temperature, mixing depth, wind speed at stack height, stability class, potential temperature gradient, and wind direction.

Receptor data rquirements are: Observer coordinates with respect to source, latitude, longitude, time zone, date, time of day, elevation, relative humidity, background visual range, line-of-sight azimuth and elevation angle, inclination angle of the observed object, distance from observer to object, object reflectivity, surface reflectivity, number and spacing of integral receptor points along line-of-sight.

Other data requirements are: Ambient concentrations of O_3 and NO_x, deposition velocity of TSP, sulfate, nitrate, SO_2 and NO_x, first-order transformation rate for sulfate and nitrate.

c. Output

Printed output includes both summary and detailed results as follows: Summary output: Page 1—site, observer and object parameters; page 2—optical pollutants and associated extinction coefficients; page 3—plume model input parameters; page 4—total calculated visual range reduction, and each pollutant's contribution; page 5—calculated plume contrast, object contrast and object contrast degradation at the 550 nm wavelength; page 6—calculated blue/red ratio and $_\Delta E$ (U^*V^*W) value for both sky and object discoloration.

Detailed output: Phase functions for each pollutant in four wavelengths (400, 450, 550, 650 nm), concentrations for each pollutant along sight path, solar geometry, contrast parameters at all wavelengths, intensities, tristimulus values and chromaticity

coordinates for views of the object, sun, background sky and plume.

d. Type of Model

ERT Visibility model is a Gaussian plume model for estimating visibility impairment.

e. Pollutant Types

Optical activity of sulfate, nitrate (derived from SO_2 and NO_x emissions), primary TSP and NO_2 is simulated.

f. Source Receptor Relationship

Single source and hour is simulated. Unlimited number of lines-of-sight (receptors) is permitted per model run.

g. Plume Behavior

Briggs (1971) plume rise equations for final rise are used.

h. Horizontal Wind Field

A single wind speed and direction is specified for each case study. The wind is assumed to be spatially uniform.

i. Vertical Wind Speed

Vertical wind speed is assumed equal to zero.

j. Horizontal Dispersion

Rural dispersion coefficients from Turner (1969) are used.

k. Vertical Dispersion

Rural dispersion coefficients from Turner (1969) are used. Mixing height is accounted for with multiple reflection handled by summation of series near the source, and Fourier representation farther downwind.

l. Chemical Transformation

First order transformations of sulfates and nitrates are used.

m. Physical Removal

Dry deposition is treated by the source depletion method.

n. Evaluation Studies

Seigneur, C., R.W. Bergstrom, and A.B. Hudischewskyj, 1982. Evaluation of the EPA PLUVUE Model and the ERT Visibility Model Based on the 1979 VISTTA Data Base, EPA Publication No. EPA-450/4-82-008, U. S. Environmental Protection Agency, Research Triangle Park, NC.

White, W.H., C. Seigneur, D.W. Heinold, M.W. Eltgroth, L.W. Richards, P.T. Roberts, P.S. Bhardwaja, W.D. Conner and W.E. Wilson, Jr., 1985. Predicting the Visibility of Chimney Plumes: An Intercomparison of Four Models with Observations at a Well-Controlled Power Plant. Atmospheric Environment, 19:515-528.

B.7 HIWAY-2

Reference

Petersen, W.B., 1980. User's Guide for HIWAY-2. EPA Publication No. EPA-600/8-80-018. U.S. Environmental Protection Agency, ESRL, Research Triangle Park, NC (NTIS PB 80-227-556).

Availability

This model is available as part of UNAMAP (Version 6). The computer code is available on magnetic tape from: Computer

Products, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, phone (703) 487-4650.

Abstract

HIWAY-2 can be used to estimate the concentrations of non-reactive pollutants from highway traffic. This steady-state Gaussian model can be applied to determine air pollution concentrations at receptor locations downwind of "at-grade" and "cut section" highways located in relatively uncomplicated terrain. The model is applicable for any wind direction, highway orientation, and receptor location. The model was developed for situations where horizontal wind flow dominates. The model cannot consider complex terrain or large obstructions to the flow such as buildings or large trees.

a. *Recommendations for Regulatory Use*

HIWAY-2 can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. HIWAY-2 must be executed in the equivalent mode.

HIWAY-2 can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in Section 3.2, that HIWAY-2 is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. *Input Requirements*

Source data requirements are: A uniform emission rate by lane, roadway end points; height of emission; length, width, and number of lanes; and width of center strip.

Meteorological data requirements are: One set at a time of hourly averages of wind speed, wind direction, and mixing height and the Pasquill-Gifford stability class. Wind speed and direction are preferred to be at 2 meters above ground.

Receptor data requirements are: Coordinates of each receptor.

c. *Output*

Printed output includes: One hourly average concentration at each specified receptor location.

d. *Type of Model*

HIWAY-2 is a Gaussian plume model.

e. *Pollutant Types*

HIWAY-2 may be used to model primary pollutants. Settling and deposition are not treated.

f. *Source-Receptor Relationship*

HIWAY-2 applies user-specified end points for a single roadway segment, and user-specified receptor locations.

Plume impact on receptor is calculated by finite difference integration of a point source along each lane of the roadway.

g. *Plume Behavior*

HIWAY-2 does not treat plume rise.

h. *Horizontal Winds*

Constant, uniform (steady-state) wind is assumed for an hour.

Straight line plume transport is assumed to all downwind distances.

An aerodynamic drag factor is applied when winds are parallel to the roadway and speeds are less than 2 m/sec.

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

j. *Horizontal Dispersion*

The total horizontal dispersion is that due to ambient turbulence plus the turbulence generated by the vehicles on the roadway.

Beyond 300 m downwind total turbulence is considered to be dominated by atmospheric turbulence, with plume dispersion as described by Turner (1969).

Three stability classes are considered: Unstable, neutral and stable.

k. *Vertical Dispersion*

The total horizontal dispersion is that due to ambient turbulence plus the turbulence generated by the vehicles on the roadway.

Beyond 300 m downwind total turbulence is considered to be dominated by atmospheric turbulence, with plume dispersion as described by Turner (1969).

Mixing height is accounted for with multiple reflections until the vertical plume size equals 1.6 times the mixing height; uniform vertical mixing is assumed beyond that point.

Three stability classes are considered: Unstable, neutral and stable.

l. *Chemical Transformation*

Not treated.

m. *Physical Removal*

Not treated.

n. *Evaluation Studies*

Rao, S.T., and J.A. Visalli, 1981. On the Comparative Assessment of the Performance of Air Quality Models, Journal of Air Pollution Control Association, 31:851-860.

B.8 Integrated Model for Plumes and Atmospheric Chemistry in Complex Terrain (IMPACT)

Reference

Fabrick, Allan J. and Peter J. Haas, 1980. User Guide to IMPACT: An Integrated Model for Plumes and Atmospheric Chemistry in Complex Terrain. DCN 80-241-403-01. Radian Corporation, 8501 Mo-Pac Blvd., Austin, TX.

Availability

A magnetic tape containing the IMPACT model, a set of test data and a copy of the IMPACT User's Guide are available for a cost of $500 from: Howard Balentine, Senior Meteorologist, Radian Corporation, Post Office Box 9948, Austin, Texas 78766.

Abstract

IMPACT is an Eulerian, three-dimensional, finite difference grid model designed to calculate the impact of pollutants, either inert or reactive, in simple or complex terrain, emitted from either point or area sources. It automatically treats single or multiple point or area sources, the effects of vertical temperature stratifications on the wind and diffusion fields, shear flows caused by the atmospheric boundary layer or by terrain effects, and chemical transformations.

a. *Recommendations for Regulatory Use*

IMPACT can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. IMPACT must be executed in the equivalent mode.

IMPACT can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that IMPACT is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

There is no specific recommendation concerning the use of IMPACT for photochemical applications. IMPACT may be used on a case-by-case basis.

b. *Input Requirements*

Source data requirements are: for point sources—location (I, J), stack height, exit temperature, volume flow rate or stack diameter and exit velocity, hourly emission rates for all pollutants; for area sources location of corners, and hourly emission rates for each pollutant.

Meterological data requirements are: Hourly wind speed and direction, surface and elevated, from meteorological stations within and surrounding the modeling area, temperature, pressure, humidity and insolation (the three last variables are optional).

Receptor data requirements are: None since concentrations are output for cells in the computational grid.

Air quality data (optional): One or more vertical concentration profiles for each pollutant.

Other data: 2-D array of terrain heights, 2-D array of surface roughness values (optional).

c. *Output*

Printed output options include: Surface and elevated horizontal cross sections of pollutant concentrations (instantaneous, or averages over N hours where N=1, 2, 3, . . .); Horizontal cross sections of diffusivities and wind velocities; and Arbitrary vertical and horizontal cross sections of pollutant concentrations and diffusivities, and CALCOMP wind field vector plots are generated by the POST post-processor program.

Computer readable output includes: Concentration, wind field and diffusivity data for each hour.

d. *Type of Model*

IMPACT is an Eulerian finite difference model.

e. *Pollutant Types*

IMPACT may be used to model any inert pollutant.

IMPACT may be used to model SO_2, $SO_4^=$, NO_x, NO_2, O_3, hydrocarbons (depends upon chemistry mechanism selected).

f. *Source-Receptor Relationship*

Up to 20 point sources and 20 area sources may be treated (greater number of sources may be treated by increasing common block storage allocation).

Concentrations are calculated at the center of each cell in the grid.

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g. *Plume Behavior*

Briggs (1975) formulation for plume rise is used.

Elevated inversions are considered.

h. *Horizontal Winds*

A three dimensional stability and terrain dependent nondivergent wind field is interpolated from single or multiple wind data measurements using a Poisson technique.

i. *Vertical Wind Speed*

Vertical wind speed is treated at each wind site, user specified or extrapolated from surface data. Interpolated is accomplished as part of the three dimensional wind field interpolation.

j. *Horizontal Dispersion*

A three dimensional diffusivity field is calculated using either the technique of Myrup/Ranzieri or the DEPICT method (see User Guide, Fabrick and Haas, 1980).

k. *Vertical Dispersion*

A three dimensional diffusivity field is calculated using either the technique of Myrup/Ranzieri or the DEPICT method (see User Guide, Fabrick and Haas, 1980).

l. *Chemical Transformation*

Either 3, 6, 8 or 15-species mechanisms are currently available (see User Guide). Calculations are also performed for inert pollutants.

m. *Physical Removal*

Physical removal is treated using exponential decay. Half-life is input by the user.

n. *Evaluation Studies*

Fabrick, A.J., R. Sklarew, and J. Wilson, 1977. Point Source Model Evaluation and Development Study. Report prepared for the California Air Resources Board.

Fabrick, A.J., and P.J. Haas, 1980. Analysis of Dispersion Models used for Complex Terrain Simulation. Presented at the Sumposium on Intermediate Range Transport Processes and Technology Assessment, Gatlinburg, TN.

Sklarew, R., and V. Mirabella, 1979. Experience in IMPACT Modeling of Complex Terrain Fourth Symposium on Turbulence, Diffusion and Air Pollution, Reno, NV.

Sklarew, R., J. Wilson, A.J. Fabrick and V. Mirabella, 1976. "Rough Terrain Modeling." Presented at Geothermal Environmental Seminar '76, Clear Lake, CA.

Sklarew, R., and K. Tran, 1978. "The NEWEST Wind Field Model with Applications to Thermally Driven Drainage Wind in Mountainous Terrain." Presented at the AMS Meeting, Lake Tahoe, NV.

Wackter, D., and R. Londergan, 1984. Evaluation of Complex Terrain Air Quality Simulation Models. EPA Publication No. EPA–450/4–84–017. U.S. Environmental Protection Agency, Research Triangle Park, NC.

B.9   LONGZ

Reference

Bjorklund, J.R., and J.F. Bowers, 1982. User's Instructions for the SHORTZ and LONGZ Computer Programs, Volumes I and II, EPA Publication No. EPA 903/9–82–004. U.S. Environmental Protection Agency, Region III, Philadelphia, PA.

Availability

The model is available as part of UNAMAP (Version 6). The computer code is available on magnetic tape from: Computer Products, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, phone (703) 487–4650.

Abstract

LONGZ utilizes the steady-state univariate Gaussian plume formulation for both urban and rural areas in flat or complex terrain to calculate long-term (seasonal and/or annual) ground-level ambient air concentrations attributable to emissions from up to 14,000 arbitrarily placed sources (stacks, buildings and area sources). The output consists of the total concentration at each receptor due to emissions from each user-specified source or group of sources, including all sources. An option which considers losses due to deposition (see the description of SHORTZ) is deemed inappropriate by the authors for complex terrain, and is not discussed here.

a. *Recommendations for Regulatory Use*

LONGZ can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. LONGZ must be executed in the equivalent mode.

LONGZ can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that LONGZ is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. *Input Requirements*

Source data requirements are: For point, building or area sources, location, elevation, total emission rate (optionally classified by gravitational settling velocity) and decay coefficient; for stack sources, stack height, effluent temperature, effluent exit velocity, stack radius (inner), emission rate, and ground elevation (optional); for building sources, height, length and width, and orientation; for area sources, characteristic vertical dimension, and length, width and orientation.

Meteorological data requirements are: Wind speed and measurement height, wind profile exponents, wind direction standard deviations (turbulent intensities), mixing height, air temperature, vertical potential temperature gradient.

Receptor data requirements are: Coordinates, ground elevation.

c. *Output*

Printed output includes: Total concentration due to emissions from user-specified source groups, including the combined emissions from all sources (with optional allowance for depletion by deposition).

d. *Type of Model*

LONGZ is a climatological Gaussian plume model.

e. *Pollutant Types*

LONGZ may be used to model primary pollutants. Settling and deposition are treated.

f. *Source-Receptor Relationships*

LONGZ applies user specified locations for sources and receptors.

Receptors are assumed to be at ground level.

g. *Plume Behavior*

Plume rise equations of Bjorklund and Bowers (1982) are used.

Stack tip downwash (Bjorklund and Bowers, 1982) is included.

All plumes move horizontally and will fully intercept elevated terrain.

Plumes above mixing height are ignored.

Perfect reflection at mixing height is assumed for plumes below the mixing height.

Plume rise is limited when the mean wind at stack height approaches or exceeds stack exit velocity.

Perfect reflection at ground is assumed for pollutants with no settling velocity.

Zero reflection at ground is assumed for pollutants with finite settling velocity.

LONGZ does not simulate fumigation.

Tilted plume is used for pollutants with settling velocity specified.

Buoyancy-induced dispersion is treated (Briggs, 1972).

h. *Horizontal Winds*

Wind field is homogeneous and steady-state.

Wind speed profile exponents are functions of both stability class and wind speed. Default values are specified in Bjorklund and Bowers (1982).

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

j. *Horizontal Dispersion*

Pollutants are initially uniformly distributed within each wind direction sector. A smoothing function is then used to remove discontinuities at sector boundaries.

k. *Vertical Dispersion*

Vertical dispersion is derived from input vertical turbulent intensities using adjustments to plume height and rate of plume growth with downwind distance specified in Bjorklund and Bowers (1982).

l. *Chemical Transformation*

Chemical transformations are treated using exponential decay. Time constant is input by the user.

m. *Physical Removal*

Gravitational settling and dry deposition of particulates are treated.

n. *Evaluation Studies*

Bjorklund, J.R., and J.F. Bowers, 1982. User's Instructions for the SHORTZ and LONGZ Computer Programs, Volume I and II. EPA Publication No. EPA–903/9–82–004, U.S. Environmental Protection Agency, Region III, Philadelphia, PA.

B.10 Maryland Power Plant Siting Program (PPSP) Model

References

Brower, R., 1982. The Maryland Power Plant Siting Program (PPSP) Air Quality Model User's Guide. Ref. No. PPSP–MP–38. Prepared for Maryland Department of Natural Resources, by Environmental Center, Martin Marietta Corporation, Baltimore, MD. (NTIS No. PB82–238387).

Weil, J.C. and R.P. Brower, 1982. The Maryland PPSP Dispersion Model for Tall Stacks. Ref. No. PPSP–MP–36. Prepared for Maryland Department of Natural Resources, by Environmental Center, Martin Marietta Corporation, Baltimore, MD. (NTIS No. PB82–219155).

Availability

Two reports referenced above are available from NTIS. The model code and test data are available on magnetic tape for a cost of $210 from: Power Plant Siting Program, Department of Natural Resources, Tawes State Office Building, Annapolis, Maryland 21401, attn: Dr. Michael Hirshfield.

Abstract

PPSP is a Gaussian dispersion model applicable to tall stacks in either rural areas, but in terrain that is essentially flat (on a scale large compared to the ground roughness elements). The PPSP model follows the same general formulation and computer coding as CRSTER, also a Guassian model, but it differs in four major ways. The differences are in the scientific formulation of specific ingredients or "sub-models" to the Gaussian model, and are based on recent theoretical improvements as well as supporting experimental data. The differences are: (1) Stability during daytime is based on convective scaling instead of the Turner criteria; (2) Briggs' dispersion curves for elevated sources are used; (3) Briggs plume rise formulas for convective conditions are included; and (4) plume penetration of elevated stable layers is given by Briggs' (1984) model.

a. *Recommendations for Regulatory Use*

PPSP can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. PPSP must be executed in the equivalent mode.

PPSP can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that PPSP is more appropriate for the scientific application. In this case the model options/modes which are most appropriate for the application should be used.

b. *Input Requirements*

Source data requirements are: Emission rate (monthly rates optional), physical stack height, stack gas exit velocity, stack inside diameter, stack gas temperature.

Meteorological data requirements are: Hourly surface weather data from the EPA meteorological preprocessor program. Preprocessor output includes hourly stability class, wind direction, wind speed, temperature, and mixing height. Actual anemometer height (a single value) is also required. Wind speed profile exponents (one for each stability class) are required if on-site data are input.

Receptor data requirements are: distance of each of the five receptor rings.

c. *Output*

Printed output includes: Highest and second highest concentrations for the year at each receptor for averaging times of 1, 3, and 24 hours, plus a user-selected averaging time which may be 2, 4, 6, 8, or 12 hours;

Annual arithmetic average at each receptor; and

For each day, the highest 1-hour and 24-hour concentrations over the receptor field.

d. *Type of Model*

PPSP is a Gaussian plume model.

e. *Pollutant Types*

PPSP may be used to model primary pollutants. Setting and deposition are not treated.

f. *Source-Receptor Relationship*

Up to 19 point sources are treated.

All point sources are assumed at the same location.

Unique stack height and stack exit conditions are applied for each source.

Receptor locations are restricted to 36 azimuths (every 10 degrees) and five user-specified radial distances.

g. *Plume Behavior*

Briggs (1975) final rise formulas for buoyant plumes are used. Momentum rise is not considered.

Transitional or distance-dependent plume rise is not modeled.

Penetration (complete, partial, or zero) of elevated inversions is treated with Briggs (1984) model; ground-level concentrations are dependent on degree of plume penetration.

h. *Horizontal Winds*

Wind speeds are corrected for release height based on power law variation, with different exponents for different stability classes and variable reference height (7 meters is default). Wind speed power law exponents are .10, .15, .20, .25, .30, and .30 for stability classes A through F, respectively.

Constant, uniform (steady-state) wind assumed within each hour.

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

j. *Horizontal Dispersion*

Rural dispersion parameters are Briggs (Gifford, 1975), with stability class defined by u/w^* during daytime, and by the method of Turner (1964) at night.

Urban dispersion is treated by changing all stable cases to stability class D.

Buoyancy-induced dispersion (Pasquill, 1976) is included (using $\Delta H / 3.5$).

k. *Vertical Dispersion*

Rural dispersion parameters are Briggs (Gifford, 1975), with stability class defined by u/w^* during daytime, and by the method of Turner (1964).

Urban dispersion is treated by changing all stable cases to stability class D.

Buoyancy-induced dispersion (Pasquill, 1976) is included (using $\Delta H / 3.5$).

l. *Chemical Transformation*

Not treated.

m. *Physical Removal*

Not treated.

n. *Evaluation Studies*

Weil, J.C. and R.P. Brower, 1982. The Maryland PPSP dispersion model for tall stacks. Ref. No. PPSP MP–36. Prepared for Maryland Department of Natural Resources. Prepared by Environmental Center, Martin Marietta Corporation, Baltimore, Maryland (NTIS No. PB 82–2199155).

Londergan, R., D. Minott, D. Wackter, T. Kincaid, and D. Bonitata, 1983. Evaluation of Rural Air Quality Simulation Models, Appendix G: Statistical Tables for PPSP. EPA Publication No. EPA 450/4–83–003, Environmental Protection Agency, Research Triangle Park, NC.

B11 MESOSCALE PUFF MODEL (MESOPUFF II)

Reference

Scire, J.S., F.W. Lurmann, A. Bass, S.R. Hanna, 1984. User's Guide to the Mesopuff II Model and Related Processor Programs. EPA Publication No. EPA 600/8–84–013. U.S. Environmental Protection Agency, Research Triangle Park, NC NTIS PB 84–181775).

Availability

This model is available as part of UNAMAP (Version 6). The computer code is available on magnetic tape from: Computer Products, National Technical Information Service, U.S. Department of Commerce, Springfield, VA 22161, phone (703) 487–4650.

Abstract

MESOPUFF II is a short term, regional scale puff model designed to calculate concentrations of up to 5 pollutant species (SO_2, SO_4, NO_x, HNO_3, NO_3). Transport, puff growth, chemical transformation, and wet and dry deposition are accounted for in the model.

a. *Recommendations for Regulatory Use*

There is no specific recommendation at the present time. The model may be used on a case-by-case basis.

b. *Input Requirements*

Required input data include four types: (1) Input control parameters and selected technical options, (2) hourly surface meteorological data and twice daily upper air measurements. hourly precipitation data are optional, (3) surface land use classification information, (4) source and emissions data.

Data from up to 25 surface National Weather Service stations and up to 10 upper air stations may be considered. Spatially variable fields at hour intervals of winds, mixing height, stability class, and relevant turbulence parameters are derived by MESOPAC II, the meteorological preprocessor program described in the User Guide.

Source and emission data for up to 25 point sources and/or up to 5 area sources can be included. Required information are: Location is grid coordinates, stack height, exit velocity and temperature, and emission rates for the pollutant to be modeled.

Receptor data requirements: Up to a 40 x 40 grid may be used and non-gridded receptor locations may be considered.

c. *Output*

Line printer output includes: All input parameters, optionally selected arrays of ground-level concentrations of pollutant species at specified time intervals.

Liner printer contour plots output from MESOFILE II post-processor program.

Computer readable output of concentration array to disk/tape for each hour.

d. *Type of Model*

MESOPUFF II is a Gaussian puff superposition model.

e. *Pollutant types modeled*

Up to five pollutant species may be modeled simultaneously and include: SO_2, SO_4, NO_x, HNO_3, NO_3.

f. *Source-Receptor Relationship*

Up to 25 point sources and/or up to 5 area sources are permitted.

g. *Plume behavior*

Briggs (1975) plume rise equations are used, including plume penetration with bouyancy flux computed in the model.

Fumigation of puffs is considered and may produce immediate mixing or multiple reflection calculations at user option.

h. *Horizontal Winds*

Gridded wind fields are computed for 2 layers; boundary layer and above the mixed layer. Upper air rawinsonde data and hourly surface winds are used to obtain spatially variable u,v component fields at hourly intervals. The gridded fields are computed by interpolation between stations in the MESOPAC II preprocessor.

i. *Vertical Wind Speed*

Vertical winds are assumed to be zero.

j. *Horizontal Dispersion*

Incremental puff growth is computed over discrete time steps with horizontal growth parameters determined from power law equations fit to sigma y curves of Turner out to 100 km. At distances greater than 100 km, puff growth is determined by the rate given by Heffter (1965).

Puff growth is a function of stability class and changes in stability are treated. Optionally, user input plume growth coefficients may be considered.

k. *Vertical Dispersion*

For puffs emitted at an effective stack height which is less than the mixing height,

uniform mixing of the pollutant within the mixed layer is performed. For puffs centered above the mixing height, no effect at the ground occurs.

l. *Chemical Transformation*

Hourly chemical rate constants are computed from empirical expressions derived from photochemical model simulations.

m. *Physical Removal*

Dry deposition is treated with a resistance method.

Wet removal may be considered if hourly precipitation data are input.

n. *Evaluation Studies*

Results of tests for some model parameters are discussed in: Scire, J.S., F.W. Lurmann, A. Bass, S.R. Hanna, 1984. Development of the MESOPUFF II Dispersion Model. EPA Publication No. EPA 600/3–84–057, U.S. Environmental Protection Agency, Research Triangle Park, NC.

B.12 MESOSCALE TRANSPORT DIFFUSION AND DEPOSITION MODEL FOR INDUSTRIAL SOURCES (MTDDIS)

Reference

Wang, I.T. and T.L. Waldron, 1980. User's Guide for MTDDIS Mesoscale Transport, Diffusion, and Deposition Model for Industrial Sources. EMSC6062.1UR(R2). Combustion Engineering, Newbury Park, CA.

Availability

A magnetic tape copy of the FORTRAN coding and the user's guide are available for a cost of $100 from: Dr. I.T. Wang, Combustion Engineering, Environmental Monitoring and Services, Inc., 2421 West Hillcrest Drive, Newbury Park, California 19320.

Abstract

MTDDIS is a variable-trajectory Gaussian puff model applicable to long-range transport of point source emissions over level or rolling terrain. It can be used to determine 3-hour maximum and 24-hour average concentrations of relatively nonreactive pollutants from up to 10 separate stacks.

a. *Recommendations for Regulatory Use*

There is no specific recommendation at the present time. The MTDDIS Model may be used on a case-by-case basis.

b. *Input Requirements*

Source data requirements are: emission rate, physical stack height, stack gas exit velocity, stack inside diameter, stack gas temperature, and location.

Meterological data requirements are: Hourly surface weather data, from up to 10 stations, including cloud ceiling, wind direction, wind speed, temperature, opaque cloud cover and precipitation. For long-range applications, user-analyzed daily mixing heights are recommended. If these are not available, the NWS daily mixing heights will be used by the program. A single upper air sounding station for the region is assumed. For each model run, air trajectories are generated for a 48-hour period, and therefore, the afternoon mixing height of the day before

and the mixing heights of the day after are also required by the model as input, in order to generate hourly mixing heights for the modeled period.

Receptor data requirements are: Up to three user-specified rectangular grids.

c. *Output*

Printed output includes:

Tabulations of hourly meteorological parameters include both input surface observations and calculated hourly stability classes and mixing heights for each station;

Printed air trajectories for the two consecutive 24-hour periods for air parcels generated 4 hours apart starting at 0000 LST; and

3-hour maximum and 24-hour average grid concentrations over user-specified rectangular grids are output for the second 24-hour period.

d. *Type of Model*

MTDDIS is a Gaussian puff model.

e. *Pollutant Types*

MTDDIS can be used to model primary pollutants. Dry deposition is treated.

Exponential decay can account for some reactions.

f. *Source-Receptor Relationship*

MTDDIS treats up to 10 point sources.

Up to three rectangular receptor grids may be specified by the user.

g. *Plume Behavior*

Briggs (19 , 1972) plume rise formulas are used.

If plume height exceeds mixing height, ground level concentration is assumed zero.

Fumigation and downwash are not treated.

h. *Horizontal Winds*

Wind speeds and wind directions at each station are first corrected for release height. Speed conversions are based on power law variation and direction conversions are based on linear height dependence as recommended by Irwin (1979).

Converted wind speeds and wind directions are then weighted according to the algorithms of Heffter (1980) to calculate the effective transport wind speed and direction.

i. *Vertical Wind Field*

Vertical wind speed is assumed equal to zero.

j. *Horizontal Dispersion*

Transport-time-dependent dispersion coefficients from Heffter (1980) are used.

k. *Vertical Dispersion*

Transport-time-dependent dispersion coefficients from Heffter (1980) are used.

l. *Chemical Transformation*

Chemical transformations are treated using exponential decay. Half-life is input by the user.

m. *Physical Removal*

Dry deposition is treated. User input deposition velocity is required.

Wet deposition is treated. User input hourly precipitation rate and precipitation layer depth or cloud ceiling height are required.

n. Evaluation Studies

None cited.

B.13   Models 3141 and 4141

Reference

Enviroplan, Inc, 1981. User's Manual for Enviroplan's Model 3141 and Model 4141. Enviroplan, Inc., West Orange, NJ.

Availability

A magnetic tape copy of the FORTRAN coding and the user's guide are available for a cost of $1,900 from: Environplan, Inc., 59 Main Street, West Orange, New Jersey 07052.

Abstract

Models 3141 and 4141 are modifications of CRSTER (UNAMAP VERSION 3) and are applicable to complex terrain particularly where receptor elevation approximately equals or exceeds the stack top elevation. The model utilizes intermediate ground displacement procedures and dispersion enhancements developed from an aerial tracer study and ground level concentrations measured for a power plant located in complex terrain.

a. Recommendations for Regulatory Use

3141 or 4141 can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. 3141 or 4141 must be executed in the equivalent mode.

3141 or 4141 can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that 3141 or 4141 is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. Input Requirements

Source data requirements are: emission rate, physical stack height, stack gas exit velocity, stack inside diameter, stack gas exit temperature.

Meteorological data requirements are: Hourly surface weather data from the EPA meteorological preprocessor program. Preprocessor output includes hourly stability class, wind direction, wind speed, temperature, and mixing height. Actual anemometer height (a single value) is also required. Wind speed profile exponents (one for each stability class) are required if on-site data are input.

Receptor data requirements are: Distance of each of five receptor rings, and receptor elevation.

c. Output

Printed output includes: Highest and second highest concentrations for the year at each receptor for averaging times of 1, 3, and 24-hours, plus a user-selected averaging time which may be 2, 4, 6, 8, or 12 hours.

Annual arithmetic average at each receptor.

For each day, the highest 1-hour and 24-hour concentrations over the receptor field.

d. Type of Model

3141 and 4141 are Gaussian plume models.

e. Pollutant Types

3141 and 4141 may be used to model non-reactive pollutants. Settling and deposition are not treated.

f. Source-Receptor Relationship

Up to 19 point sources are treated.

No area sources are treated.

All point sources are assumed to be collocated.

Unique stack height is used for each source.

Receptor locations are restricted to 36 azimuths (every 10 degrees) and 5 user-specified radial distances.

Unique topographic elevation is used for each receptor.

g. Plume Behavior

Briggs (1969, 1971, 1972) final plume rise formulas are used.

If plume height exceeds mixing height at a receptor location after terrain adjustment, concentration is assumed equal to zero.

h. Horizontal Winds

Wind speeds are corrected for release height based on power law variation exponents from DeMarrais (1959), different exponents for different stability classes, reference height=7 meters. Exponents used are .10, .15, .20, .25, .30, and .30 for stability classes A through F, respectively.

Constant, uniform (steady-state) wind is assumed within each hour.

i. Vertical Wind Speed

Vertical wind speed is assumed equal to zero.

j. Horizontal Dispersion

Dispersion coefficients are Pasquill-Gifford coefficients from Turner (1969).

Dispersion is adjusted to 60 minutes averaging time by one-fifth power rule (Gifford, 1975).

Buoyancy-induced dispersion (Briggs, 1975) is included.

k. Vertical Dispersion

Dispersion coefficients are Pasquill-Gifford coefficients from Turner (1969).

Buoyancy-induced dispersion (Brigg, 1975) is included.

l. Chemical Transformation

Not treated.

m. Physical Removal

Not treated.

n. Evaluation Studies

Ellis, H.M., P.C. Liu, and C. Runyon, 1979. "Comparison of Predicted and Measured Concentrations for 54 Alternate Models of Plume Transport in Complex Terrain." Presented in APCA Annual Conference, Cincinnati, OH.

Ellis, H.M., P.C. Liu and C. Runyon, 1980. Comparison of Predicted and Measured Concentrations for 58 Alternative Models of Plume Transport in Complex Terrain. Journal of the Air Pollution Control Association, 30(6).

Londergan, R., D. Minott, D. Wachter, T. Kincaid and D. Bonitata. Evaluation of Rural Air Quality Simulation Models. EPA Publication No. EPA-450/4-83-003, Environmental Protection Agency, Research Triangle Park, NC.

Wackter, D., and R. Longergan, 1984. Evaluation of Complex Terrain Air Quality Simulation Models. EPA Publication No. EPA-450/4-84-017. U.S. Environmental Protection Agency, Research Triangle Park, NC.

B.14   Multimax

Reference

Moser, J.H., 1979. MULTIMAX: An Air Dispersion Modeling Program for Multiple Sources, Receptors, and Concentration Averages. Shell Development Company, Westhollow Research Center, P.O. Box 1380, Houston, TX. (NTIS PB 80-170178).

Availability

The above report is available from NTIS ($16.95 for paper copy; $5.95 on microfiche). The accession number for the computer tape for MULTIMAX is PB 80-170160, and the cost is $370.00. Requests should be sent to: Computer Products, National Technical Information Service, U.S. Department of Commerce, 5825 Port Royal Road, Springfield, Virginia 22161, phone (703) 487-4650.

Abstract

MULTIMAX is a Gaussian plume model applicable to both urban and rural areas. It can be used to calculate highest and second-highest concentrations, for each of several averaging times due to up to 100 sources arbitrarily located.

a. Recommendations for Regulatory Use

MULTIMAX can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. MULTIMAX must be executed in the equivlent mode.

MULTIMAX can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in Section 3.2, that MULTIMAX is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. Input Requirements

Source data requirements are: Emission rate, physical stack height, stack gas exit velocity, stack inside diameter, and stack gas temperature.

Meteorological data requirements are: Hourly surface weather data from the EPA meteorological preprocessor program. Preprocessor output includes hourly stability class, wind direction, wind speed, temperature, and mixing height. Actual anemometer height (a single value) is also required. Wind speed profile exponents (one for each stability class) are required if on-site data are input.

Receptor requirements are: Individual receptor points, arcs and circles of receptors, or lines of receptors may be input, with receptor point locations, receptor line end

points, and receptor circle center and radius defined in either cartesian or polar coordinates.

c. *Output*

Printed output includes: Highest and second-highest concentrations for the year at each receptor for averaging time of 1, 3, and 24 hours. Annual arithmetic average at each receptor.

Computer readable output includes: Input data and results.

d. *Type of Model*

MULTIMAX is a Gaussian plume model.

e. *Pollutant Types*

MULTIMAX may be used to model primary pollutants. Settling and deposition are not treated.

f. *Source-Receptor Relationship*

Up to 100 point sources at any location may be input.

Area sources are not treated.

Point sources may be at any location.

Unique stack height is used for each source.

Unique topographic elevation is used for each receptor; must be below top of stack.

Receptors can be defined individually, or along lines or arcs.

g. *Plume Behavior*

MULTIMAX uses Briggs (1969, 1971, 1972) final plume rise formulas.

If plume height exceeds mixing height, concentrations downwind are assumed equal to zero.

h. *Horizontal Winds*

Wind speeds are corrected for release height based on power law variation exponents from DeMarrais (1959), different exponents for different stability classes, reference height = 10 meters. The exponents are .10, .15, .20, .25, .30, and .30 for stability classes A through F, respectively.

Constant, uniform (steady-state) wind is assumed within each hour.

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

j. *Horizontal Dispersion*

Rural dispersion coefficients from Turner (1969) are used in MULTIMAX with no adjustments made for variations in surface roughness.

Six stability classes are used, with Turner class 7 treated as Class 6.

Averaging time adjustment is optional.

k. *Vertical Dispersion*

Rural dispersion coefficients from Turner (1969) are used in MULTIMAX with no adjustments made for variations in surface roughness.

Six stability classes are used, with Turner class 7 treated as Class 6.

Perfect reflection at the ground is assumed.

Mixing height is accounted for with multiple reflections until the vertical plume size equals 1.6 times the mixing height; uniform mixing is assumed beyond that point.

l. *Chemical Transformation*

Not treated.

m. *Physical Removal*

Not treated.

n. *Evaluation Studies*

Londergan, R., D. Minott, D. Wackter, T. Kincaid, and D. Bonitata. 1983. Evaluation of Rural Air Quality Simulation Models. EPA Publication No. EPA–450/4–83–003, U.S. Environmental Protection Agency, Research Triangle Park, NC.

B.15 Multiple Point Source Diffusion Model (MPSDM)

Reference

Environmental Research & Technology, Inc., 1984. User's Guide to MPSDM. ERT Document No. PB–881585. Environmental Research & Technology, Inc., Concord, MA.

Availability

The above report and a computer tape are available from: Computer Products, National Technical Information Service, U.S. Department of Commerce, 5825 Port Royal Road, Springfield, Virginia 22161, phone (703) 487–4650.

Abstract

MPSDM is a steady-state Gaussian dispersion model designed to calculate, in sequential mode or in "case-by-case" mode, concentrations of nonreactive pollutants resulting from single or multiple source emissions. The MPSDM model may be used for sources located in flat or complex terrain, in a univariate (σ_z) or bivariate (σ_y, σ_z) mode. Sufficient flexibility is allowed in the specification of model parameters to enable the MPSDM user to duplicate results that would be obtained from many other Gaussian point-source models. A number of features are incorporated to facilitate site-specific model validation studies.

a. *Recommendations for Regulatory Use*

MPSDM can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. MPSDM must be executed in the equivalent mode.

MPSDM can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that MPSDM is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. *Input Requirements*

Source data requirements are: Hourly or constant emission rate, stack gas temperature, exit velocity, and stack inside diameter.

Meteorological data requirements are: Hourly wind speed, wind direction, air temperature and mixing height; and vertical temperature difference or stability class. Optional meteorological parameters include solar intensity and wind speed standard deviation.

Receptor data requirements are: Northing, easting, and ground level elevation of each receptor.

Air quality data requirements are: Observed concentrations at any monitor for any or all hours ("case-by-case" mode only)

will be compared with estimates, or (sequential mode only) will be used to determine background levels. Background is calculated as the average of those monitors more than ± i radians from the plume centerline defined in the model. Default for i is the equivalent of 60°. User input for i is optional.

c. *Output*

Printed output includes:

"Case-by-case" mode: Printed output includes hourly centerline, off centerline, sector averaged and observed concentrations at all monitors; downwind profiles of centerline concentrations; and a statistical summary of all cases addressed.

Sequential mode: Printed output limited to ratio of predicted maximum concentration to maximum concentration measured at each monitor. Primary output is a file output containing hourly averaged concentrations.

A post-processing program, ANALYSIS, is used to produce averages for longer periods. For a user-specified average period a ranked order of peak concentrations, the cumulative frequency of occurrence of user-specified concentration levels or a summary of hourly meteorological characteristics and concentrations contributing to levels above a user-specified value can also be obtained with the ANALYSIS post-processor.

d. *Type of Model*

MPSDM is a Gaussian plume model.

e. *Pollutant Types*

MPSDM may be used to model primary pollutants. Settling and deposition are not treated.

f. *Source-Receptor Relationship*

Arbitrary locations for sources and receptors are used.

Actual terrain elevations may be specified and accounted for by plume-height adjustments.

Actual separation between each source receptor pair is used.

Receptors are assumed to be at ground level.

Unique stack height is used for each source.

g. *Plume Behavior*

Briggs (1969, 1974, 1975) plume rise equations are used.

Partial (or total) penetration of plume into elevated inversions (Briggs, 1975) is included.

Stack tip downwash (Briggs, 1975) is treated.

Fumigation (Turner, 1969) is treated.

Convective dispersion using a probability density function model is optional (Venkatram, 1980).

h. *Horizontal Winds*

User-supplied hourly wind speed and direction are assumed to specify horizontally homogeneous, steady-state conditions.

Wind speeds vary with height according to user-designated profiles for each stability.

Wind direction is specifiable in whole degrees from 1° to 360°.

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

j. Horizontal Dispersion

ASME (Brookhaven) diffusion coefficients (ASME, 1968) are used.

Options are Pasquill-Gifford coefficients or user input horizontal plume with coefficients of the form ax^b, or sector average with user-input sector width.

Hourly stability (six classes—very unstable through moderately stable) is determined internally from input vertical temperature gradient and mean wind speed or stability classes.

A buoyancy-induced dispersion algorithm (Pasquill, 1976) is optional.

k. Vertical Dispersion

ASME (Brookhaven) diffusion coefficients (ASME, 1966) are used. Options are Pasquill-Gifford coefficients or user input horizontal plume with coefficients of the form ax^b. One model option employs a convective dispersion algorithm developed by Venkatram (1980).

Hourly stability (six classes—very unstable through moderately stable) are determined internally from input vertical temperature gradient and mean wind speed or stability classes.

A buoyancy-induced dispersion algorithm (Pasquill, 1976) is optional.

Perfect reflection at ground is assumed.

Perfect reflection is assumed at the mixing height of pollutant above or below top of mixing layer (except for partial plume penetration).

l. Chemical Transformation

Not treated.

m. Physical

Not treated.

n. Evaluation Studies

Lavery, T.F., and L.L. Schulman, 1977. The Validity of a Gaussian Plume Point Source Diffusion Model for Predicting Short-Term SO2 Levels in the Vicinity of Electric Generating Plants in New York State. Joint conference on Applications of Air Pollution Meteorology, AMS/APCA, Salt Lake City, UT.

Londergan R., D. Minott, D. Wackter, T. Kincaid and D. Bonitata, 1983. Evaluation of Rural Air Quality Simulation Models. EPA Publication No. EPA–45014–83–003, U.S. Environmental Protection Agency, Research Triangle Park, NC.

B.16   Multi-Source (SCSTER) Model

Reference

Malik, M.H. and B. Baldwin, 1980. Program Documentation for Multi-Source (SCSTER) Model. Program Documentation EN7408SS. Southern Company Services, Inc., Technical Engineering Systems, 64 Perimeter Center East, Atlanta, GA.

Availability

The SCSTER model and user's manual are available at no charge to a limited number of persons through Southern Company Services. A magnetic tape must be provided by those desiring the model. Requests should be directed to: Mr. Bryan Baldwin, Research Program Supervisor, Air Quality Program, Southern Company Services, Post Office Box 2625, Birmingham, Alabama 35202.

Abstract

SCSTER is a modified version of the EPA CRSTER model. The primary distinctions of SCSTER are its capability to consider multiple sources that are not necessarily collocated, its enhanced receptor specifications, its variable plume height terrain adjustment procedures and plume distortion from directional wind shear.

a. Recommendations for Regulatory Use

SCSTER can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. SCSTER must be executed in the equivalent mode.

SCSTER can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that SCSTER is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. Input Requirements

Source data requirements are: Emission rate, stack gas exit velocity, stack gas temperature, stack exit diameter, physical stack height, elevation of stack base, and coordinates of stack location. The variable emission data can be monthly or annual averages.

Meteorological data requirements are: Hourly surface weather data from the EPA meteorological preprocessor program. Preprocessor output includes hourly stability class wind direction, wind speed, temperature, and mixing height. Actual anemometer height (a single value) is optional. Wind speed profile exponents (one for each stability class) are optional.

Receptor data requirements are: Cartesian coordinates and elevations of individual receptors; distances of receptor rings, with elevation of each receptor; receptor grid networks, with elevation of each receptor. Any combination of the three receptor input types may be used to consider up to 600 receptor locations.

c. Output

Printed output includes:

Highest and second highest concentrations for the year at each receptor for averaging times of 1-, 3-, and 24-hours, a user-selected averaging time which may be 2–12 hours, and a 50 high table for 1-, 3-, and 24-hours;

Annual arithmetic average at each receptor; and the highest 1-hour and 24-hour concentrations over the receptor field for each day considered.

Optional tables of source contributions of individual point sources at up to 20 receptor locations for each averaging period;

Optional magnetic tape output in either binary or fixed block format includes:

All 1-hour concentrations.

Optional card/disk output includes for each receptor:

Receptor coordinates; receptor elevation; highest and highest, second-highest, 1-, 3-, and 24-hour concentrations; and annual average concentration.

d. Type of Model

SCSTER is a Gaussian plume model.

e. Pollutant Types

SCSTER may be used to model primary pollutants. Settling and deposition are not treated.

f. Source-Receptor Relationship

SCSTER can handle up to 60 separate stacks at varying locations and up to 600 receptors, including up to 15 receptor rings.

User input topographic elevation for each receptor is used.

g. Plume Behavior

SCSTER uses Briggs (1969, 1971, 1972) final plume rise formulas.

Transitional plume rise is optional.

SCSTER contains options to incorporate wind directional shear with a plume distortion method described in appendix A of the User's Guide.

SCSTER provides four terrain adjustments including the CRSTER full terrain height adjustment and a user-input, stability-dependent plume path coefficient adjustment for receptors above stack height.

h. Horizontal Winds

Wind speeds are corrected for release height based on power law exponents from DeMarrais (1959), different exponents for different stability classes; default reference height of 7 m. Default exponents are .10, .15, .20, .25, .30, and .30 for stability classes A through F, respectively.

Steady-state wind is assumed within a given hour.

Optional consideration of plume distortion due to user-input, stability-dependent wind-direction shear gradients.

i. Vertical Wind Speed

Vertical wind speed is assumed equal to zero.

j. Horizontal Dispersion

Rural dispersion coefficients from Turner (1969) are used.

Six stability classes are used.

k. Vertical Dispersion

Rural dispersion coefficients from Turner (1969) are used.

Six stability classes are used.

An optional test for plume height above mixing height before terrain adjustment is included.

l. Chemical Transformation

Chemical transformations are treated using exponential decay. Half-life is input by the user.

m. Physical Removal

Physical removal is treated using exponential decay. Half-life is input by the user.

n. Evaluation Studies

Londergan, R., D. Minott, D. Wackter, T. Kincaid and D. Bonitata, 1983. Evaluation of Rural Air Quality Simulation Models. EPA Publication No. EPA 450/4–83–003, U.S. Environmental Protection Agency, Research Triangle Park, NC.

B.17 Pacific Gas and Electric Plume5 Model

Reference

User's Manual for Pacific Gas and Electric Plume5 Model, 1981. Pacific Gas and Electric, San Francisco, CA.

Availability

The User's Manual will be supplied for cost of reproduction. An IBM version of the model can be obtained on a user supplied tape free of charge from: Mr. Robert N. Swanson, Pacific Gas and Electric Company, 245 Market Street, RM 451, San Francisco, California 94106.

Abstract

PLUME5 is a steady-state Gaussian plume model applicable to both rural and urban areas in uneven terrain. Pollutant concentrations at 500 receptors from up to 10 sources with up to 15 stacks each can be calculated using up to 5 meteorological inputs. The model in its "basic" mode is similar to CRSTER and MPTER. Several options are available that allow better simulation of atmospheric conditions and improved model outputs. These options allow plume rise into or through a stable layer and crosswind spread of the plume by wind directional shear with height, initial plume expansion, mean (advective) wind speed, terrain considerations, and chemical transformation of pollutants.

Differences that exist between PLUME5 and CRSTER are in the following areas: Stability class determination, hourly mixing height schemes, hourly stable layer data, randomization of wind direction, extent of data set required for preprocessing meteorological data inputs.

a. *Recommendations for Regulatory Use*

PLUME5 can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. PLUME5 must be executed in the equivalent mode.

PLUME5 can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that PLUME5 is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. *Input Requirements*

Source data requirements are: Cartesian or polar coordinates of each source with stack height, diameter, gas temperature, and exit velocity for each stack.

Meteorological data requirements are: Surface data—hourly meteorological data including wind direction, wind speed, temperature, and either ceiling height and total sky cover or sigma A or Delta T depending on how stability is computed; stable layer data—either NCC data or site specific user supplied data.

Receptor data requirements are: cartesian or polar coordinates of each receptor.

c. *Output*

Printed output includes:
Highest and second highest concentrations for the year printed out at each receptor for averaging times of 1, 3, and 24-hours, plus a

user-selected averaging time which may be 2, 4, 6, 8, or 12 hours.

Annual arithmetic average at each receptor.

For each day, the highest 1-hour and 24-hour concentrations over the receptor field is printed.

Hourly effective stack height and effective stack height distributions.

Vertical profiles of maximum pollutant concentrations above a designated height (Z_o) for the data period processed.

Cumulative number of exceedances of 1 hour and 24-hour specified values for all receptors during the entire meteorological data period. These specified values will normally be National and State Ambient Air Quality Standards.

Computer readable output includes:
Hourly concentrations for each receptor on magnetic tape.

Computer file for input to plotting routine. The file stores the highest 1-hour (or other specified time period) concentration at each receptor for the entire meteorological data period for input into a user supplied plotting routine.

d. *Type of Model*

PLUME5 is a Gaussian plume model.

e. *Pollutant Types*

PLUME5 may be used to model primary pollutants. Chemical transformations of pollutants are treated by exponential decay and/or ozone limiting procedures.

f. *Source-Receptor Relationship*

Can input up to 10 separate sources with up to 15 stacks per source.

Unique stack height for each source. Rectangular or circular receptor locations (up to 500) can be either model generated or user input.

Terrain considerations:
When plume rise, H, is above the stable layer top concentration estimates will only be calculated for receptors at or above the stable layer top. If the receptor is below the stable layer top, then the concentration is zero.

When plume rise falls within the stable layer, concentration estimates will be only calculated for receptors located within this region. If the receptor height is above or below the stable top, then the concentration is zero.

When plume rise falls below the stable layer and the receptor height is above the stable layer base, then the concentration is zero. If the receptor is below the stable layer base, the receptor height is redefined.

g. *Plume Behavior*

PLUME5 uses Briggs (1975) final plume rise formulas.

Expansion of plumes within and above a stable layer is treated.

h. *Horizontal Winds*

User-supplied hourly wind directions are read to nearest 1, 5, 10, and 22.5 degrees. (The 5, 10 and 22.5 degree values are randomly modified to nearest whole degree within the intervals).

PLUME5 employs the extrapolated mean wind speed at stack height when the effective stack height is equal to or less than the height

of the inversion base above ground. If the plume rises into a stable layer, a separate algorithm is used.

Constant, uniform (steady state) wind assumed within each hour.

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

j. *Horizontal Dispersion*

Six stability classes are defined by either radiation index and wind speed (STAR), wind direction fluctuation, or temperature lapse rate. Nighttime stability class is based on wind direction fluctuations or temperature lapse rate and may be modified according to the method of Mitchell and Timbre (1979).

Dispersion curves are from Turner (1969).

k. *Vertical Dispersion*

Six stability classes are defined by either radiation index and wind speed (STAR), wind direction fluctuations, or temperature lapse rate.

Nighttime stability class is based on wind direction fluctuations or temperature lapse rate and modified according to the method of Mitchell-Timbre (1979).

Dispersion curves are from Turner (1969).

l. *Chemical Transformation*

Chemical transformations are treated using exponential decay and/or ozone limiting procedures.

m. *Physical Removal*

Physical removal is treated using exponential decay. Half-life is input by user.

n. *Evaluation Studies*

Londergan, R., D. Minott, D. Wackter, T. Kincaid and B. Bonitata, 1983. Evaluation of Rural Air Quality Simulation Models. EPA Publication No. EPA–450/4–83–003, U. S. Environmental Protection Agency, Research Triangle Park, NC.

Wackter, D., and R. Londergan, 1984. Evaluation of Complex Terrain Air Quality Simulation Models. EPA Publication No. EPA 450/4–84–017. U. S. Environmental Protection Agency, Research Triangle Park, NC.

B.18 PLMSTAR Air Quality Simulation Model

Reference

Lurmann, F.W., D.A. Godden, and H. Collins, 1985. User's Guide to the PLMSTAR Air Quality Simulation Model. ERT Document No. M–2206–100, Environmental Research & Technology, Inc., Newbury Park, CA.

Availability

The above report and a computer tape are available from: Computer Products, National Technical Information Service, U.S. Department of Commerce, 5825 Port Royal Road, Springfield, Virginia 22161, phone (703) 487–4650.

Abstract

PLMSTAR is a mesoscale Lagrangian photochemical model designed to predict atmospheric concentrations of O_3, NO_2, HNO_3, PAN, SO_2, and SO^- from reactive

hydrocarbons, NO_x and SO_x emissions. PLMSTAR is intended to simulate the behavior of pollutants in chemically reactive plumes resulting form major point source emissions. The model's Lagrangian air parcel is subdivided into a 5 layer/9 column domain of computational cells. The approach allows for realistic simulation of the combined effects of atmospheric chemical reactions and pollutant dispersion in the horizontal and vertical directions. Other key features of the model include: the capability for generation of trajectories at any level of a three-dimensional, divergence-free wind field; the capability for calculating and utilizing the time and space varying surface deposition of pollutants; an up-to-date $O_3/RHC/NO_x/SO_x$ chemical mechanism that utilizes eight classes of reactive hydrocarbons; the capability for simultaneously handling both point and area source emissions; and the capability to simulate overwater conditions and land/water transitions.

a. *Recommendations for Regulatory Use*

There is no specific recommendation at the present time. The PLMSTAR Model may be used on a case-by-case.

b. *Input Requirements*

Source data requirements are: Emission rates, stack parameters, diurnal emission profiles, and RHC, NO_x, and SO_x partitioning profiles.

Meteorological data requirements are: Station location, grid geometry, surface winds, surface roughness, surface temperature, temperature profiles, mixing heights (optional), cloud cover, solar radiation, and winds aloft.

Receptor data requirements are: Receptor locations and topography.

c. *Output*

Printed output includes:
Computed concentrations at specified times and receptors along the trajectory.

d. *Type of Model*

PLMSTAR is a Lagrangian photochemical model.

e. *Pollutant Types*

The key chemical species included in the model are O_3, NO, NO_2, HNO_3, PAN, SO_2, SO^-_4, CO, and eight classes of reactive hydrocarbons. Twenty additional intermediate species are included in the chemical mechanism.

f. *Source-Receptor Relationships*

Source-receptor relationships for individual sources are calculated using a differencing technique. That is, simulations are made with and without an individual source (or group of collocated sources) in addition to the RHC/NO_x/SO_x emissions from all other sources in the region. The emission processors allow for up to 250 point sources and an unlimited number of area sources (allocated to a grid of 36×36 squares) to be included in the simulation.

g. *Plume Behavior*

Plume rise calculations are based on Briggs (1975).

h. *Horizontal Winds*

Gridded hourly multi-level horizontal wind fields are generated using techniques similar

to those reported by Goodin et al. (1979). These involve wind data interpolation, divergence mimimization, and terrain adjustment. Trajectory path segments are then generated by interpolation from the gridded horizontal wind fields in 15 minute steps at the user selected vertical level. Either source or receptor oriented trajectory may be generated.

j. *Vertical Wind Speed*

Vertical speed is produced by WINDMOD, but is not utilized in the trajectory calculation or the pollutant advection algorithm.

j. *Vertical Dispersion*

Vertical eddy diffusivities (K_z) over land are calculated as a function of wind speed, stability, surface roughness, and boundary layer height. Over water, wind speed, air-to-sea temperature difference, humidity, and boundary layer height are the key parameters.

The effects of vertical dispersion on pollutant concentrations are calculated by numerically integrating finite difference approximations to the diffusion equation.

Mixing heights can be internally calculated or externally specified.

k. *Horizontal Dispersion*

Horizontal eddy diffusivities (K_y) are calculated either as a function of K_z and stability class or as a function of σ_y. The effects of horizontal dispersion on pollutant concentrations are calculated by numerically integrating finite difference approximations to the diffusion equation.

1. *Chemical Transformation*

PLMSTAR incorporates a slightly condensed version of the Atkinson et al. (1982) photochemical mechanism for $O_3/RHC/NO_x/SO_x/$air mixtures. The mechanism contains 62 reactions involving 38 species, including 6 classes of organic precursors. The effects of chemical transormations on pollutant concentrations are computed by numerically integrating the nonlinear kinetic rate equations.

m. *Physical Removal*

Dry deposition of O_3, NO_2, HNO_3, PAN, SO_2, and SO^-_4 is based on the model of Wesely and Hicks (1977).

n. *Evaluation Studies*

Lurmann, F.W.. D.A. Godden and A.C. Lloyd, 1982. The Development and Selected Sensitivity, Tests of the PLMSTAR Reactive Plume Model. Presented at the Third Joint Conference on Applications of Air Pollution Meteorology, San Antonio, TX.

Godden, D. and F. Lurmann, 1983. Development of the PLMSTAR Model and its Application to Ozone Episode Conditions in the South Coast Air Basin, ERT Document No. P–A702–200, Environmental Research & Technology, Inc., Newbury Park, CA.

Blumenthal, D.L., T.B. Smith, D.E. Lehrman, N.L. Alexander, F. Lurman, and D. Godden, 1985. Analysis of Aerometric and Meteorological Data for the Ventura County Region, Ref. #90094–511–FR. Sonoma Technology, Inc., and Environmental Research and Technology, Inc., for the Western Oil and Gas Association, Los Angeles, CA.

B.19   Plume Visibility Model (PLUVUE II)

Reference

Seigneur, C., C. D. Johnson, D. A. Latimer, R. W. Bergstrom and H. Hogo, 1984. User's Manual for the Plume Visibility Model (PLUVUE II). EPA Publication No. EPA 600/8–84–005. U.S. Environmental Protection Agency, Research Triangle Park, NC. (NTIS No. PB 84–158302).

Availability

This model is available as part of UNAMAP (Version 6). The computer code is available on magnetic tape from: Computer Products, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, phone (703) 487–4650.

Abstract

The Plume Visibility Model (PLUVUE II) is a computerized model used for estimating visual range reduction and atmospheric discoloration caused by plumes resulting from the emissions of particles, nitrogen oxides and sulfur oxides from a single emission source. PLUVUE II predicts the transport, dispersion, chemical reactions, optical effects and surface deposition of point or area source emissions. Addenda to the User's Manual were prepared in February 1985 to allow execution of PLUVUE II and the test cases on the UNIVAC computer, the addenda are included in the UNAMAP (Version 6) documentation.

a. *Recommendations for Regulatory Use*

There is no specific recommendation at the present time. The Plume Visibility Model (PLUVUE II) may be used on a case-by case basis.

b. *Input Requirements*

Source data requirements are: Location and elevation; emission rates of SO_2, NO_x, and particulates; flue gas flow rate, exit velocity, and exit temperature; flue gas oxygen content; properties (including density, mass median and standard geometric deviation of radius) of the emitted aerosols in the accumulation (0.1–1.0 μm) and coarse (1.0–10.0 μm) size modes; and deposition velocities for SO_2, NO_x, coarse mode aerosol, and accumulations mode aerosol.

Meterological data requirements are: Stability class, wind direction (for an observer-based run), wind speed, lapse rate, air temperature, relative humidity, and mixing height.

Other data requirements are: Ambient background concentrations of NO_x, O_3, and SO_2, background visual range or sulfate and nitrate concentrations.

Receptor (observer) data requirements are: Location, elevation, terrain which will be observed through the plume (for observer based run with white, gray, and black viewing backgrounds).

c. *Output*

Printed output includes: plume concentrations and visual effects at specified downwind distances for calculated or specified lines of sight.

d. *Type of Model*

PLUVUE is a Gaussian plume model.

e. *Pollutant Types*

PLUVUE II treats NO, NO_2, SO_2, H_2SO_4, HNO_3, O_3, primary and secondary particles to calculate effects on visibility.

f. *Source Receptor Relationship*

PLUVUE treats a single point or area source.

Predicted concentrations and visual effects are obtained at user specified downwind distances.

g. *Plume Behavior*

PLUVUE uses Briggs (1969, 1971, 1972) final plume rise equations.

h. *Horizontal Winds*

User-specified wind speed (and direction for an observer-based run) are assumed constant for the calculation.

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

j. *Horizontal Dispersion*

User specified plume widths, or widths computed from either Pasquill-Gifford-Turner curves (Turner, 1969) or TVA curves (Carpenter, et al., 1971) are used in PLUVUE.

k. *Vertical Dispersion*

User specified plume depths, or computer from Pasquill-Gifford-Turner curves (Turner, 1969) or TVA curves (Carpenter, et al., 1971) are used in PLUVUE.

l. *Chemical Transformation*

PLUVUE II treats the chemistry of NO, NO_2, O_3, OH, $O(^1D)$, SO_2, HNO_3, and H_2SO_4, by means of nine reactions. Steady state approximations are used for radicals and for the $NO/NO_2/O_3$ reactions.

m. *Physical Removal*

Dry deposition of gaseous and particulate pollutants is treated using deposition velocities.

n. *Evaluation Studies*

Bergstrom, R.W., C. Seigneur, B. L. Babson, H. Y. Holman and M. A. Wojcik, 1981. Comparison of the Observed and Predicted Visual Effects Caused by Power Plant Plumes. Atmospheric Environment, 15:2135–2150.

Bergstrom, R.W., C. Seigneur, C. D. Johnson, and L. W. Richards, Measurements and Simulations of the Visual Effects of Particulate Plumes. Systems Applications, Inc., San Rafael, CA.

Seigneur, C., R. W. Bergstrom, and A. B. Hudischewskyj, 1982. Evaluation of the EPA PLUVUE Model and the ERT Visibility Model Based on the 1979 VISTTA Data Base. EPA Publication No. EPA–450/4–82–008, U.S. Environmental Protection Agency, Research Triangle Park, NC.

White, W.H., C. Seigneur, D.W. Heinold, M.W. Eltgroth, L.W. Richards, P.T. Roberts, P. S. Bhardwaja, W. D. Conner and W. E. Wilson, Jr, 1985. Predicting the Visibility of Chimney Plumes: An Intercomparison of Four Models with Observations at a Well-Controlled Power Plant, Atmospheric Environment, 19:515–528.

B.20 Point, Area, Line Source Algorithm (PAL–DS)

Reference

Petersen, W.B., 1978. User's Guide for PAL— A Gaussian-Plume Algorithm for Point, Area, and Line Sources. EPA Publication No. EPA–600/4–78–013. Office of Research and Development, Research Triangle Park, NC. (NTIS PB 281306).

Rao, K.S. and H.F. Snodgrass, 1982. PAL–DS Model: The PAL Model Including Deposition and Sedimentation. EPA Publication No. EPA 600/8–82–023. Office of Research and Development, Research Triangle Park, NC. (NTIS PB 83–117739).

Availability

This model is available as part of UNAMAP (Version 6). The computer code is available on magnetic tape from: Computer Products, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, phone (703) 487–4650.

Abstract

PAL–DS is an acronym for this point, area, and line source algorithm and is a method of estimating short-term dispersion using Gaussian-plume steady-state assumptions. The algorithm can be used for estimating concentrations of non-reactive pollutants at 99 receptors for averaging times of 1 to 24 hours, and for a limited number of point, area, and line sources (99 of each type). This algorithm is not intended for application to entire urban areas but is intended, rather, to assess the impact on air quality, on scales of tens to hundreds of meters, of portions of urban areas such as shopping centers, large parking areas, and airports. Level terrain is assumed. The Gaussian point source equation estimates concentrations from point sources after determining the effective height of emission and the upwind and crosswind distance of the source from the receptor. Numerical integration of the Gaussian point source equation is used to determine concentrations from the four types of line sources. Subroutines are included that estimate concentrations for multiple lane line and curved path sources, special line sources (line sources with endpoints at different heights above ground), and special curved path sources. Integration over the area source, which includes edge effects from the source region, is done by considering finite line sources perpendicular to the wind at intervals upwind from the receptor. The crosswind integration is done analytically; integration upwinds is done numerically by successive approximations.

The PAL–DS model utilizes Gaussian plume-type diffusion-deposition algorithms based on analytical solutions of a gradient-transfer model. The PAL–DS model can treat

deposition of both gaseous and suspended particulate pollutants in the plume since gravitational settling and dry deposition of the particles are explicitly accounted for. The analytical diffusion-reposition expressions listed in this report in the limit when pollutant settling and deposition velocities are zero, they reduce to the usual Gaussian plume diffusion algorithms in the PAL model.

a. *Recommendations for Regulatory Use*

PAL–DS can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. PAL–DS must be executed in the equivalent mode.

PAL–DS can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that PAL–DS is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. *Input Requirements*

Source data: point-sources—emission rate, physical stack height, stack gas temperature, stack gas velocity, stack diameter, stack gas volume flow, coordinates of stack, initial σ_y and σ_z; area sources—source strength, size of area source, coordinates of S.W. corner, and height of area source; and line sources—source strength, number of lanes, height of source, coordinates of end points, initial σ_y and σ_z, width of line source, and width of median. Diurnal variations in emissions are permitted. When applicable, the settling velocity and deposition velocity are also permitted.

Meteorological data: wind profile exponents, anemometer height, wind direction and speed, stability class, mixing height, air temperature, and hourly variations in emission rate.

Receptor data: receptor coordinates.

c. *Output*

Printed output includes:

Hourly concentration and deposition flux for each source type at each receptor; and

Average concentration for up to 24 hrs for each source type at each receptor.

d. *Type of Model*

PAL–DS is a Gaussian plume model.

e. *Pollutant Types*

PAL–DS may be used to model non-reactive pollutants.

f. *Source-Receptor Relationships*

Up to 99 sources of each of 6 source types: point, area, and 4 types of line sources.

Source and receptor coordinates are uniquely defined.

Unique stack height for each source.

Coordinates of receptor locations are user defined.

g. *Plume Behavior*

Briggs final plume rise equations are used. Fumigation and downwash are not treated.

If plume height exceeds mixing height, concentrations are assumed equal to zero.

Surface concentrations are set to zero when the plume centerline exceeds mixing height.

h. *Horizontal Winds*

User-supplied hourly wind data are used. Constant, uniform (steady-state) wind is assumed within each hour.

Wind is assumed to increase with height.

i. *Vertical Wind Speeds*

Assumed equal to zero.

j. *Horizontal Dispersion*

Rural dispersion coefficients from Turner (1969) are used with no adjustments made for surface roughness.

Six stability classes are used.

Dispersion coefficients (Pasquill-Gifford) are assumed based on a 3 cm roughness height.

k. *Vertical Dispersion*

Six stability classes are used.

Rural dispersion coefficients from Turner (1969) are used; no further adjustments are made for variation in surface roughness, transport or averaging time.

Multiple reflection is handled by summation of series until the vertical standard deviation equals 1.6 times mixing height. Uniform vertical mixing is assumed thereafter.

l. *Chemical Transformation*

Not treated.

m. *Physical Removal*

PAL-DS can treat deposition of both gaseous and suspended particulates in the plume since gravitational settling and dry deposition of the particles are explicitly accounted for.

n. *Evaluation Studies*

None.

B.21 Random-Walk Advection and Dispersion Model (RADM)

References

Austin, D.I., A.W. Bealer, and W.R. Goodin, 1981. Random-Walk Advection and Dispersion Model (RADM), User's Manual. Dames & Moore, Los Angeles, CA.

Runchal, A.K., W.R. Goodin, A.W. Bealer, D.I. Austin, 1981. Technical Description of the Random-Walk Advection and Dispersion Model (RADM). Dames & Moore, Los Angeles, CA.

Availability:

A magnetic tape of the compute code and the user's manual are available for a cost of $440.00 from: Mr. C. James Olsten, Dames & Moore, 445 South Figueroa Street, Suite 3500, Los Angeles, California 90071-1665.

Abstract:

RADM is a Lagrangian dispersion model which uses the random-walk method to simulate atmospheric dispersion. The technical procedure involves tracing tracer particles having a given mass through advection by the mean wind and diffusion by the random motions of atmospheric turbulence. Turbulent movement is calculated by determining the probability distribution of particle movement for a user-defined time step. A random number between 0 and 1 is then computed to determine the distance of particle movement according to the

probability distribution. A large number of particles is used to statistically represent the distribution of pollutant mass. Concentrations are calculated by summing the mass in a volume around the receptor of interest and dividing the total mass by the volume. Concentrations can be calculated for any averaging time. RADM is applicable to point and area sources.

a. *Recommendations for Regulatory Use*

There is no specific recommendation at the present time. The RADM model may be used on a case-by-case basis.

b. *Input Requirements*

Source data requirements are: Emission rate, physical stack height, stack gas exit velocity, stack inside diameter, stack gas temperature. Hourly rates may be specified.

Meteorological data requirements are: Gridded wind field including wind speed, wind direction, stability class, temperature and mixing height.

Receptor data requirements are: Coordinates, ground elevation, and receptor cell dimensions.

c. *Output*

Printed output includes:

Average concentration by receptor for user-specified averaging time (concentrations are printed for each block of n hours).

Average concentrations for the entire period of the run.

d. *Type of Model*

RADM is a random-walk Lagrangian dispersion model.

e. *Pollutant Types*

RADM may be used to model inert gases and particles, and pollutants with exponential decay or formation rates.

f. *Source-Receptor Relationship*

Multiple point and area sources may be specified at independent locations.

Unique stack characteristics are used for each source.

No restriction is placed on receptor locations.

Perfect reflection at the surface is assumed for the portion not removed by dry deposition.

Particles leaving the gridded area are removed from simulation.

g. *Plume Behavior*

Briggs (1975) final plume rise equations are used.

Inversion penetration by the plume is allowed.

Fumigation may occur as mixing height rises above a plume which has penetrated an inversion.

h. *Horizontal Winds*

Wind speed, wind direction, stability class, temperature and mixing height are supplied on a gridded array.

Any wind field may be used as long as output is in correct format for RADM input.

Wind field is updated at user-specified intervals, which may be less than one hour if data are available.

Vertical wind speed profile is used based on surface roughness and stability using Monin-Obukhov length.

i. *Vertical Wind Speed*

Assumed equal to zero.

j. *Horizontal Dispersion*

Dispersion is based on diffusivity values calculated from surface roughness, stability class and Monin-Obukhov length.

Diffusivity is a function of height.

k. *Vertical Dispersion*

Dispersion is based on diffusivity values calculated from surface roughness, stability class and Monin-Obukhov length.

Diffusivity is a function of height.

l. *Chemical Transformations*

Simple exponential decay or formation is used.

m. *Physical Removal*

Dry deposition is treated.

n. *Evaluation Studies*

Runchal, A.K., A.W. Bealer, and G.S. Segal, 1978. A Completely Lagrangian Random-Walk Model for Atmospheric Dispersion. Proceedings of the Thirteenth International colloquim on Atmospheric Pollution, National Institute for Applications of Chemical Research, Paris, pp. 137-142.

Goodin, W.R., A.K. Runchal, and G.Y. Lou, 1980. Evaluation and Application of the Random-Walk Advection and Dispersion Model (RADM). Symposium on Intermediate Range Atmospheric Transport Processes and Technology Assessment, DOE/NOAA/ORNL, Gatlinburg, TN.

Goodin, W.R., D.I. Austin and A.K. Runchal, 1980. A Model Verification and Prediction study of SO_2/SO^-_4 Concentrations in the San Francisco Bay Area. Second Joint Conference on Applications of Air Pollution Meteorology, AMS/APCA, New Orleans, LA.

B.22 Reactive Plume Model (RPM-II)

Reference

D. Stewart, M. Yocke, and M-K Liu, 1981. Reactive Plume Model—RPM-II, User's Guide, EPA Publication No. EPA 600/8-81-021 U.S. Environmental Protection Agency, ESRL, Research Triangle Park, NC. (NTIS PB82-230723)

Availability

The above report is available from NTIS ($16.95 for paper copy; $5.95 on microfiche). The accession number for the computer tape for RPM-II is PB83-154898, and the cost is $460.00. Requests should be sent to: Computer Products, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, phone (703) 487-4650.

Abstract

The Reactive Plume Model, RPM-II, is a computerized model used for estimating short-term concentrations of primary and secondary pollutants resulting from point or area source emissions. The model is capable of simulating the complex interaction of plume dispersion and non-linear photochemistry. Two main features of the

model are: (1) The horizontal resolution within the plume, which offers a more realistic treatment of the entrainment process, and (2) its flexibility with regard to choices of chemical kinetic mechanisms.

a. Recommendations for Regulatory Use

There is no specific recommendations at the present time. The RPM–II Model may be used on a case-by-case basis.

b. Input Requirements

Source data requirements are: Emission rates, name, and molecular weight of each species of pollutant emitted; ambient pressure, ambient temperature, stack height, stack diameter, stack exit velocity, stack gas temperature, and location.

Meteorological data requirements are: Wind speeds, plume widths or stability classes, photolytic rate constants, and plume depths or stability classes.

Receptor data requirements are: Downwind distances or travel times at which calculations are to be made.

Initial concentration of all species is required, and the specification of downwind ambient concentrations to be entrained by the plume is optional.

c. Output

Short-term concentrations of primary and secondary pollutants at either user specified time increments, or user specified downwind distances.

d. Type of Model

Reactive plume model.

e. Pollutant Types

Currently, using the Carbon Bond Mechanism (CBM–II), 35 species are simulated (68 reactions), including NO, NO_2, O_3, SO_2, SO_4, five categories of reactive hydrocarbons, secondary nitrogen compounds, organic aerosols, and radical species.

f. Source-Receptor Relationships

Single point source.
Single area or volume source.
Multiple sources can be simulated if they are lined up along the wind trajectory.
Predicted concentrations are obtained at a user specified time increment, or at user specified downwind distances.

g. Plume Behavior

Briggs (1971) plume rise equations are used.

h. Horizontal Winds

User specifies wind speeds as a function of time.

i. Vertical Wind Speed

Not treated.

j. Horizontal Dispersion

User specified plume widths, or user may specify stability and widths will be computed using Turner (1969).

k. Vertical Dispersion

User specified plume depths, or user may specify stability in which case depths will be calculated using Turner (1969). Note that vertical uniformity in plume concentration is assumed.

l. Chemical Transformation

The RPM–II has the flexibility of using any user input chemical kinetic mechanism. Currently it is run using the chemistry of the Carbon Bond Mechanism, CBM–II (Whitten, Killus, and Hogo, 1980). The CBM–II, as incorporated in the RPM–II, contains 35 species and 68 reactions focusing primarily on hydrocarbon-nitrogen oxides-ozone photochemistry.

m. Physical Removal

Not treated.

n. Evaluation Studies

Stewart, D.A. and M–K Liu, 1981. Development and Application of a Reactive Plume Model, Atmospheric Environment, 15:2377–2393.

B.23   Regional Transport Model (RTM–II)

Reference

Morris, R.E., D.A. Stewart, and M–K Liu, 1982. Revised User's Guide to the Regional Transport Model—Version II. Publication No. SYSAPP–83/022, Systems Applications Inc., San Rafael, CA.

Availability

The computer code is available on magnetic tape for a cost of $100 (which includes the User's Manual) from: Systems Applications, Inc., 101 Lucas Valley Road, San Raphael, California 94903.

Abstract

The Regional Transport Model (RTM–II) is a computer based air quality grid model whose primary use is estimating the distribution of air pollution from multiple point sources and area sources at large distances (on the scale of several hundred to a thousand kilometers). RTM–II offers significant advantages over other long-range transport models because it is a quasi-three dimensional hybrid (grid plus Lagrangian puff) approach to the solution of the advection-diffusion equation. Furthermore, its formulation allows the treatment of spatially and temporarily varying wind, mixing depths, diffusivity, and transformation rate fields. It is also capable of treating spatially varying surface depletion processes. While the modeling concept is capable of predicting concentration distributions of many pollutant species (e.g., NO_x, CO, TSP, etc.), the most notable applications of the model to date focus on the long-range transport and transformation of SO_2 and sulfates.

a. Recommendations for Regulatory Use

There is no specific recommendation at the present time. The RTM Model may be used on a case-by-case basis.

b. Input Requirements

Source data requirements are: Major point source SO_2 and primary sulfate emissions, including stack height, diameter, exit velocity, exit temperature, and hourly emission factors; area source SO_2 and primary SO_4 emissions in gridded format.

Meteorological data requirements are: Gridded u, v wind fields at user specified update interval (model configured for separate wind fields in each of two layers), derived from twice daily radiosonde data,

time variation linear between a maximum convectively driven boundary layer and a minimum mechanically driven boundary layer, spatial interpolation by an inverse distance weighted objective scheme; gridded hourly precipitation fields determined either by averaging precipitation rate of all stations in grid (if high density), or by inverse distance weighted interpolation (if low density).

Other data requirements are: Parameter file, containing region definition, starting time, output and averaging time intervals, region top specifications, and various operational flags; horizontal diffusivity fields calculated from wind fields; land use type file; deposition velocities and roughness length determined internally from tabulated values associated with land use types; initial conditions and boundary conditions for both layers (boundary conditions may be time varying).

c. Output

Printed output includes:
Diagnostic information.
Instantaneous SO_2 and sulfate concentration fields for lower and upper layers at pre-specified time intervals.
Average SO_2 and sulfate concentration fields for upper and lower layer, over pre-specified time intervals. Accumulated dry and wet deposition for each species over pre-selected time intervals.

d. Type of Model

RTM–II is a hybrid Eulerian grid and Lagrangian puff model.

e. Pollutant Types

RTM–II is configured for SO_2 and sulfate only. Primary sulfate emissions may be included.

f. Source Receptor Relationships

Area sources and minor point sources are specified at each grid within the modeling domain.

Up to 500 major point sources (modeled with the Gaussian puff submodel) are allowed.

Grid average concentration and deposition totals are provided at each grid within the modeling domain (dry deposition for lower layer grid only). All lower grid average concentration values are assumed to be representative of ground-level receptors.

g. Plume Behavior

Plume rise (Briggs, 1971) is calculated for all major point sources regardless of whether they are treated in the Gaussian puff submodel.

h. Horizontal Winds

Gridded u, v wind fields are used at a user specified update interval for each layer.

Gaussian puff submodel tracks puff centroids horizontally at user specified time intervals.

i. Vertical Wind Speed

Considered implicitly if convergent or divergent winds are provided.

j. Horizontal Dispersion

Plume dispersion is based on σ_y differentials derived from a power law fit to

Turner (1969) dispersion curves. Variable stabilities within adjacent cells are considered.

Horizontal eddy diffusivities are proportional to the wind field deformation and are calculated from the gridded wind fields as ancilliary input. Maximum and minimum constraints are imposed on the magnitude of the diffusivities.

k. Vertical Dispersion

Plume dispersion is based on σ_z differentials derived from a power law fit to Turner (1969) dispersion curves. Variable stabilities within adjacent cells are considered.

Vertical dispersion across the mixed layer-surface layer interface is considered when calculating pollutant deposition.

l. Chemical Transformation

Linear SO_2 oxidation is treated. Rate constant is diurnally and latitudinally variable. A minimum oxidation rate constant is specified to account for heterogeneous oxidation during the nighttime.

m. Physical Removal

Dry deposition of SO_2 and sulfate is treated. Precipitation scavenging of SO_2 (reversible) and sulfate (irreversible) is treated.

n. Evaluation Studies

Stewart, D.A., R.E. Morris, M–K Liu, and D. Henderson, 1983. Evaluation of an Episodic Regional Transport Model for a Multiple Day Episode. Atmospheric Environment, 17:1225–1252.

B.24   SHORTZ

Reference

Bjorklud, J.R., and J.F. Bowers, 1982, User's Instructions for the SHORTZ and LONGZ Computer Programs, Volumes I and II. EPA Publication No. EPA 903/9–82004a and b, U.S. Environmental Protection Agency, Region III, Philadelphia PA.

Availability

This model is available as part of UNAMAP. (Version 6). The computer code is available on magnetic tape from: Computer Products, National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161, phone (703) 487–4650.

Abstract

SHORTZ utilizes the steady state bivariate Gaussian plume formulation for both urban and rural areas in flat or complex terrain to calculate ground-level ambient air concentrations. It can calculate 1-hour, 2-hour, 3-hour etc. average concentrations due to emissions from stacks, buildings and area sources for up to 300 arbitrarily placed sources. The output consists of total concentration at each receptor due to emissions from each user-specified source or group of sources, including all sources. If the option for gravitational settling is invoked, analysis cannot be accomplished in complex terrain without violating mass continuity.

a. Recommendations for Regulatory Use

SHORTZ can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. SHORTZ must be executed in the equivalent mode.

SHORTZ can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that SHORTZ is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. Input Requirements

Source data requirements are: For point, building or area sources, location, elevation, total emission rate (optionally classified by gravitational settling velocity) and decay coefficient; for stack sources, stack height, effluent temperature, effluent exist velocity, stack radius (inner), actual volumetric flow rate, and ground elevation (optional) ; for building sources, height, length and width, and orientation; for area sources, characteristic vertical dimension, and length, width and orientation.

Meteorological data requirements are: Wind speed and measurement height, wind profile exponents, wind direction, standard deviations of vertical and horizontal wind directions, (i.e., vertical and lateral turbulent intensities), mixing height, air temperature, and vertical potential temperature gradient.

Receptor data requirements are: Coordinates, ground elevation.

c. Output

Printed output includes: Total concentration due to emissions from user-specified source groups, including the combined emissions from all sources (with optional allowance for depletion by deposition).

d. Type of Model

SHORTZ is a Gaussian plume model.

e. Pollutant Types

SHORTZ may be used to model primary pollutants. Settling and deposition of particulates are treated.

f. Source-Receptor Relationships

User specified locations for sources and receptors are used.

Receptors are assumed to be at ground level.

g. Plume Behavior

Plume rise equations of Bjorklund and Bowers (1982) are used.

Stack tip downwash (Bjorklund and Bowers, 1982) is included.

All plumes move horizontally and will fully intercept elevated terrain.

Plumes above mixing height are ignored.

Perfect reflection at mixing height is assumed for plumes below the mixing height.

Plume rise is limited when the mean wind at stack height approaches or exceeds stack exit velocity.

Perfect reflection at ground is assumed for pollutants with no settling velocity.

Zero reflection at ground is assumed for pollutants with finite settling velocity.

Tilted plume is used for pollutants with settling velocity specified

Buoyancy-induced dispersion (Briggs, 1972) is included.

h. Horizontal Winds

Winds are assumed homogeneous and steady-state.

Wind speed profile exponents are functions of both stability class and wind speed. Default values are specified in Bjorklund and Bowers (1982).

i. Vertical Wind Speed

Vertical winds are assumed equal to zero.

j. Horizontal Dispersion

Horizontal plume size is derived from input lateral turbulent intensities using adjustments to plume height, and rate plume growth with downwind distance specified in Bjorklund and Bowers (1982).

k. Vertical Dispersion

Vertical plume size is derived from input vertical turbulent intensities using adjustments to plume height and rate of plume growth with downwind distance specified in Bjorklund and Bowers (1982).

l. Chemical Transformation

Chemical transformations are treated using exponential decay. Time constant is input by the user.

m. Physical Removal

Settling and deposition of particulates are treated.

n. Evaluation Studies

Bjorklund, J.R., and J.F. Bowers, 1982. User's instructions for the SHORTZ and LONGZ Computer Programs. EPA Publication No. EPA–903/9–82–004. EPA Environmental Protection Agency, Region III, Philadelphia, PA.

Wackter, D., and R. Londergan, 1984. Evaluation of Complex Terrain Air Quality Simulation Models. EPA Publication No. EPA 450/4–84–017. U.S. Environmental Protection Agency, Research Triangle Park, NC.

B.25   Simple Line-Source Model (GMLINE)

Reference

Chock, D.P., 1980. User's Guide for the Simple Line-Source Model for Vehicle Exhaust Dispersion Near a Road, Environmental Science Department, General Motors Research Laboratories, Warren, MI.

Availability

Copies of the above reference are available without charge from: Dr. D.P. Chock. Environmental Science Department, General Motors Research Laboratories, General Motors Technical Center, Warren, Michigan 48090. The User's Guide contains the short algorithm of the model.

Abstract

GMLINE is a simple steady-state Gaussian plume model which can be used to determine hourly (or half-hourly) averages of exhaust concentrations within 100m from a roadway on a relatively flat terrain. The model allows for plume rise due to the heated exhaust, which can be important when the crossroad wind is very low. It also utilizes a new set of

vertical dispersion parameters which reflects the influence of traffic-induced turbulence.

a. *Recommendations for Regulatory Use*

GMLINE can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. GMLINE must be executed in the equivalent mode.

GMLINE can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that GMLINE is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. *Input Requirements*

Source data requirements are: Emission rate per unit length per lane, the number of lanes on each road, distances from lane centers to the receptor, source and receptor heights.

Meteorological data requirements are: Buoyancy flux, ambient stability condition, ambient wind and its direction relative to the road.

Receptor data requirements are: Distance and height above ground.

c. *Output*

Printed output includes: Hourly or (half-hourly) concentrations at the receptor due to exhaust emission from a road (or a system of roads by summing the results from repeated model applications).

d. *Type of Model*

GMLINE is a Gaussian plume model.

e. *Pollutant Types*

GMLINE can be used to model primary pollutants. Settling and deposition are not treated.

f. *Source-Receptor Relationship*

GMLINE treats arbitrary location of line sources and receptors.

g. *Plume Behavior*

Plume-rise formula adequate for a heated line source is used.

h. *Horizontal Winds*

GMLINE uses user-supplied hourly (or half-hourly) ambient wind speed and direction. The wind measurements are from a height of 5 to 10 m.

i. *Vertical Wind Speed*

Vertical wind speed is assumed equal to zero.

j. *Dispersion Parameters*

Horizontal dispersion parameter is not used.

k. *Vertical Dispersion*

A vertical dispersion parameter is used which is a function of stability and wind-road angle. Three stability classes are used: Unstable, neutral and stable. The parameters take into account the effect of traffic-generated turbulence (Chock, 1980).

l. *Chemical Transformation*

Not treated.

m. *Physical Removal*

Not treated.

n. *Evaluation Studies*

Chock, D.P., 1978. A Simple Line-Source Model for Dispersion Near Roadways, Atmospheric Environment, 12:823–829.

Sistla, G., P. Samson, M. Keenan, and S.T. Rao, 1979. A Study of Pollutant Dispersion Near Highways, Atmospheric Environment 13:669–685.

B.26 TEXAS CLIMATOLOGICAL MODEL (TCM)-2)

Reference

Staff of the Texas Air Control Board, 1980. User's Guide to the TEXAS CLIMATOLOGICAL MODEL (TCM). Texas Air Control Board, Permits Section, 6330 Highway 290 East, Austin, TX.

Availability

The TCM-2 model is available from the Texas Air Control Board at the following cost: User's Manual only—$20.00. User's Manual and Model (Magnetic Tape)—$80.00.

Requests should be directed to: Data Processing Division, Texas Air Control Board, 6330 Highway 290 East, Austin, Texas 78723.

Abstract

TCM is a climatological steady-state Gaussian plume model for determining long-term (seasonal or annual arithmetic) average pollutant concentrations of non-reactive pollutants.

a. *Recommendations for Regulatory Use*

TCM can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. TCM must be executed in the equivalent mode.

TCM can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that TCM is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. *Input Requirements*

Source data requirements are: Point source coordinates emission rates (by pollutant), stack height, stack diameter, stack gas exit velocity, stack gas temperature; area source coordinates (southwest corner), size, emission rate.

Meteorological data requirements are: Stability wind rose and average temperature.

Receptor data requirements are: Size and spacing of the rectangular receptor grid.

c. *Output*

Printed output includes:
Period average concentrations listed, displayed in map format, or punched on cards at the user's options.
Culpability list option provides the contributions of the five highest contributors at each receptor.
Maximum concentration option provides the maximum concentration for each scenario (run).

d. *Type of Model*

TCM is a Gaussian plume model.

e. *Pollutant Types*

TCM may be used to model primary pollutants. Settling and deposition are not treated.

f. *Source-Receptor Relationship*

Arbitrary location of point sources and area sources are treated.

Arbitrary location and spacing of rectangular grid of receptors are used. (Area source grid is best defined in terms of the receptor grid, so that the receptors fall in the center of the area source).

Receptors located in simple terrain may be modeled.

g. *Plume Behavior*

Briggs (1975) plume rise equations, including momentum rise, are used for point sources.

Two-thirds power law is used when transitional rise option is selected.

Flares are treated.

h. *Horizontal Winds*

Characteristic wind speed is calculated for each direction-stability class combination.

This characteristic speed is the inverse of the average inverse speed for the stability-wind direction combination.

Wind speed is adjusted to stack height by a power law using exponents of .10, .15, .20, .25, .30, and .30 for stabilities A through F, respectively.

i. *Vertical Wind Speed*

Vertical wind speed is assumed to be zero.

j. *Horizontal Dispersion*

Uniform distribution within each 22.5 degree sector is assumed

k. *Vertical Dispersion*

Dispersion parameters for point sources are fit to Turner (1969); for area sources in the urban mode the fit is to Gifford and Hanna (1970).

Seven stability classes are used.

Pasquill A through F are treated, with daytime "D" and nighttime "D" given separately.

In the urban mode, E and F stability classes are treated as D-night.

Perfect reflection at the ground is assumed.

l. *Chemical Transformation*

Chemical transformations are treated using exponential decay. Half-life is input by the user.

m. *Physical Removal*

Physical removal is treated using exponential decay. Half-life is input by the user.

n. *Evaluation Studies*

Londergan, R.J., D.H. Minott, D.J. Wachter and R.R. Fizz, 1983. Evaluation of Urban Air Quality Simulation Models. EPA Publication No. EPA-450/4-83-020. U.S. Environmental Protection Agency, Research Triangle Park, NC.

Durrenberger, C.S., B.A. Braberg, and K. Zimmerman, 1983. Development of a Protocol to be Used for Dispersion Model Comparison Studies. Presented at the 76th Annual Meeting of the Air Pollution Control Association, Atlanta, GA.

B.27 TEXAS EPISODIC MODEL (TEM-8)

Reference

Staff of the Texas Air Control Board, 1979. User's Guide to the TEXAS EPISODIC MODEL. Texas Air Control Board, Permits Section, 6330 Highway 290 East, Austin, TX.

Availability

The TEM-8 model is available from the Texas Air Control Board at the following costs: User's Manual only—$20.00. User's Manual and Model (Magnetic Tape)—$80.00.

Requests should be directed to: Data Processing Division, Texas Air Control Board, 6330 Highway 290 East, Austin, Texas 78723.

Abstract:

TEM is a short-term, steady-state Gaussian plume model for determining short-term concentrations of non-reactive pollutants.

a. *Recommendations for Regulatory Use*

TEM can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. TEM must be executed in the equivalent mode.

TEM can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that TEM is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. *Input Requirements*

Source data requirements are: locations, average emission rates and heights of emissions for both point and area sources; stack gas temperature, stack gas exit velocity, and stack inside diameter for point sources for plume rise calculations.

Meteorological data requirements are: hourly surface weather data from the EPA meteorological preprocessor program. Preprocessor output includes hourly stability class, wind direction, wind speed, temperature, and mixing height. Any combination of hourly meteorological data up to 24 hours may be used, (e.g. 1, 3, 5, 8, 24 hours).

Receptor requirements are: size, spacing and location of rectangular grid of receptors.

c. *Output*

Printed output includes: concentration list;

Spatial array (concentrations displayed as on a map);

Punched cards of the concentration list;

Culpability list (percent contributions) of the five highest contributors to each receptor;

Maximum concentration; and

Point source list.

d. *Type of Model*

TEM is a Gaussian plume model.

e. *Pollutant Types*

TEM can be used to model non-reactive pollutants. Settling and deposition are not treated.

f. *Source-Receptor Relationship*

Arbitrary locations of point sources and area sources are treated.

Arbitrary location and spacing of rectangular grid of receptors is treated. Area source grid is best defined in terms of the receptor grid so that the receptors fall in the centers of the area sources.

Receptors located in simple terrain may be modeled.

g. *Plume Behavior*

Briggs (1975) plume rise equations are used, including momentum rise, for point sources.

Transitional rise is calculated.

Stack-tip downwash may be evaluated.

h. *Horizontal Winds*

Wind speeds are adjusted to release height by power law formula, using exponents of .10, .15, .20, .25, .30 and .30 for stabilities A through F respectively.

Steady-state wind is assumed.

i. *Vertical Wind Speed*

Vertical wind is assumed equal to zero.

j. *Horizontal Dispersion*

Gaussian plume coefficients are fitted to Turner (1969). The Turner curves are treated as 10-minute averages and the coefficients are adjusted to represent 30-minute or hourly as appropriate.

In the urban mode, stable cases are shifted to neutral nighttime (D-night) conditions and urban mixing heights are used.

k. *Vertical Dispersion*

Dispersion parameters for point sources are fit to Turner (1969); for area sources, in the urban mode, the fit is to Gifford and Hanna (1970).

Total reflection of the plume at the ground is assumed.

In the urban mode, E and F stability classes are treated as D-nighttime.

l. *Chemical Transformation*

Chemical transformation is treated using exponential decay. Half-life is input by the user.

m. *Physical Removal*

Physical removal is treated using exponential decay. Half-life is input by the user.

n. *Evaluation Studies*

Londergan, R., D. Minott, D. Wachter, T. Kincaid and D. Bonitata, 1983. Evaluation of Rural Air Quality Simulation Models, EPA-450/4-83-003, Environmental Protection Agency, Research Triangle Park, NC.

Durrenberger, C.J., B.A. Broberg, and K. Zimmermann, 1983. Development of a Protocol to be Used for Dispersion Model Comparison Studies. Presented at the 76th Annual Meeting of the Air Pollution Control Association at Atlanta, GA.

B.28 AVACTA II

Reference

Zannetti, P., G. Carboni and R. Lewis, 1985. AVACTA II User's Guide (Release 3). AeroVironment, Inc., Technical Report AV-OM-85/520.

Availability

A magnetic tape copy of the FORTRAN coding and the user's guide are available at a cost of $2,500 (non-profit organization) or

$3,500 (other organizations) from: AeroVironment, Inc., 825 Myrtle Avenue, Monrovia, CA 91016, phone (818) 357-9983.

Abstract

The AVACTA II model is a Gaussian model in which atmospheric dispersion phenomena are described by the evolution of plume elements, either segments or puffs. The model can be applied for short time (e.g., one day) simulations in both transport and calm conditions.

The user is given flexibility in defining the computational domain, the three-dimensional meteorological and emission input, the receptor locations, the plume rise formulas, the sigma formulas, etc. Without explicit user's specifications, standard default values are assumed.

AVACTA II provides both concentration fields on the user specified receptor points, and dry/wet deposition patterns throughout the domain. The model is particularly oriented to the simulation of the dynamics and transformation of sulfur species (SO_2 and SO^-_4), but can handle virtually any pair of primary-secondary pollutants.

a. *Recommendations for Regulatory Use*

AVACTA II can be used if it can be demonstrated to estimate concentrations equivalent to those provided by the preferred model for a given application. AVACTA II must be executed in the equivalent mode.

AVACTA II can be used on a case-by-case basis in lieu of a preferred model if it can be demonstrated, using the criteria in section 3.2, that AVACTA II is more appropriate for the specific application. In this case the model options/modes which are most appropriate for the application should be used.

b. *Input Requirements* (all time-varying)

A time-varying input is required at each computational step. Only those data which have changed need to be input by the user.

Source data requirements are: Coordinates, emission rates of primary and secondary pollutants, initial plume sigmas (for non-point sources), exit temperature, exit velocity, stack inside diameter.

Meteorological data requirements are: surface wind measurements, wind profiles (if available), atmospheric stability profiles, mixing heights.

Receptor data requirements are: receptor coordinates.

Other data requirements: coordinates of the computational domain, grid cell specification, terrain elevations, user's computational and printing options.

c. *Output*

The model's output is provided according to user's printing flags. Hourly, 3-hour and 24-hour concentration averages are computed, together with highest and highest-second-highest concentration values. Both partial and total concentrations are provided.

d. *Type of Model*

AVACTA II is Gaussian plume segment/puff model.

e. *Pollutant Types*

AVACTA II can handle any couple of primary-secondary pollutants (e.g. SO_2 and SO^-_4).

f. Source Receptor Relationship

The AVACTA II approach maintains the basic Gaussian formulation, but allows a numerical simulation of both nonstationary and nonhomogeneous meteorological conditions. The emitted pollutant material is divided into a sequence of "elements," either segments or puffs, which are connected together but whose dynamics are a function of the local meteorological conditions. Since the meteorological parameters vary with time and space, each element evolves according to the different meteorological conditions encountered along its trajectory.

AVACTA II calculates the partial contribution of each source in each receptor during each interval. The partial concentration is the sum of the contribution of all existing puffs, plus that of the closest segment.

g. Plume Behavior

The user can select the following plume rise formulas:

Briggs (1969, 1971, 1972)
CONCAWE (Briggs, 1975)
Lucas-Moore (Briggs, 1975)
User's functions, i.e., a subroutine supplied by the user

With cold plumes, the program uses a special routine for the computation of the jet plume rise. The user can also select several computational options that control plume behavior in complex terrain and its total/partial reflections.

h. Horizontal Winds

A 3D mass-consistent wind field is optionally generated.

i. Vertical Wind Speed

A 3D mass-consistent wind field is optionally generated.

j. Horizontal Dispersion

During each step, the sigmas of each element are increased. The user can select the following sigma functions:

Pasquill-Gifford-Turner (in the functional form specified by Green et al., 1980)
Brookhaven (Gifford, 1975)
Briggs, open country (Gifford, 1975)
Briggs, urban, i.e., McElroy-Pooler (Gifford, 1975)
Irwin (1979)
LO–LOCAT (MacCready et al., 1974)
User-specified function, by points
User-specified function, with a user's subroutine

The virtual distance/age concept is used for incrementing the sigmas at each time step.

k. Vertical Dispersion

During each step, the sigmas of each element are increased. The user can select the following sigma functions:

Pasquill-Gifford-Turner (in the functional form specified by Green et al., 1980)
Brookhaven (Gifford, 1975)
Briggs, open country (Gifford, 1975)
Briggs, urban, i.e., McElroy-Pooler (Gifford, 1975)
LO–LOCAT (MacCready et al., 1974)
User-specified function, with a user's subroutine

The virtual distance/age concept is used for incrementing the sigmas at each time step.

l. Chemical Transformation

First order chemical reactions (primary-to-secondary pollutant)

m. Physical Removal

First order dry and wet deposition schemes.

n. Evaluation Studies

Zannetti, P., G. Carboni and A. Ceriani, 1985. AVACTA II Model Simulations of Worst-Case Air Pollution Scenarios in Northern Italy. 15th International Technical Meeting on Air Pollution Modeling and Its Application, St. Louis, Missouri, April 15–19.

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APPENDIX C TO APPENDIX X TO PART 266—

Example Air Quality Analysis Checklist

C.O INTRODUCTION

This checklist recommends a standardized set of data and a standard basic level of analysis needed for PSD applications and SIP revisions. The checklist implies a level of detail required to assess both PSD increments and the NAAQS. Individual cases may require more or less information and the Regional Meteorologist should be consulted at an early stage in the development of a data base for a modeling analysis.

At pre-application meetings between source owner and reviewing authority, this checklist should prove useful in developing a consensus on the data base, modeling techniques and overall technical approach prior to the actual analyses. Such agreement will help avoid misunderstandings concerning the final results and may reduce the later need for additional analyses.

Example Air Quality Analysis Checklist [1]

1. Source location map(s) showing location with respect to:
   • Urban areas [2]
   • PSD Class I areas
   • Nonattainment areas [2]
   • Topographic features (terrain, lakes, river valleys, etc.) [2]
   • Other major existing sources [2]
   • Other major sources subject to PSD requirements
   • NWS meteorological observations (surface and upper air)
   • On-site/local meteorological observations (surface and upper air)
   • State/local/on-site air quality monitoring location [2]

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[1] The "Guidelines for Air Quality Maintenance Planning and Analysis," Volume 10R, EPA-450/4-77-001, 1977 should be used as a screening tool to determine whether modeling analyses are required. Screening procedures should be refined by the user to be site/problem specific.

[2] Within 50 km or distance to which source has a significant impact, whichever is less.

• Plant layout on a topographic map covering a 1-km radius of the source with information sufficient to determine GEP stack heights

2. Information on urban/rural characteristics:
   • Land use within 3 km of source classified according to Auer, A.H. (1978): Correlation of land use and cover with meteorological anomalies, J. of Applied Meteorology, 17:636-643.
   • Population
   —total
   —density
   • Based on current guidance determination of whether the area should be addressed using urban or rural modeling methodology

3. Emission inventory and operating/design parameters for major sources within region of significant impact of proposed site (same as required for applicant)
   • Actual and allowable annual emission rates (g/s) and operating rates [3]
   • Maximum design load short-term emission rate (g/s) [3]
   • Associated emissions/stack characteristics as a function of load for maximum, average, and nominal operating conditions if stack height is less than GEP or located in complex terrain. Screening analyses as footnoted on page 1 or detailed analyses, if necessary, must be employed to determine the constraining load condition (e.g., 50%, 75%, or 100% load) to be relied upon in the short-term modeling analysis.
   —location (UTM's)
   —height of stack (m) and grade level above MSL
   —stack exit diameter (m)
   —exit velocity (m/s)
   —exit temperature (°K)
   • Area source emissions (rates, size of area, height of area source) [3]
   • Location and dimensions of buildings (plant layout drawing)
   —to determine GEP stack height
   —to determine potential building downwash considerations for stack heights less than GEP
   • Associated parameters
   —boiler size (megawatts, pounds/hr. steam, fuel consumption, etc.)
   —boiler parameters (% excess air, boiler type, type of firing, etc.)
   —operating conditions (pollutant content in fuel, hours of operation, capacity factor, % load for winter, summer, etc.)
   —pollutant control equipment parameters (design efficiency, operation record, e.g., can it be bypassed?, etc.)
   • Anticipated growth changes

4. Air quality monitoring data:
   • Summary of existing observations for latest five years (including any additional quality assured measured data which can be obtained from any state or local agency or company) [4]
   • Comparison with standards
   • Discussion of background due to uninventoried sources and contributions from outside the inventoried area and description

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[3] Particulate emissions should be specified as a function of particulate diameter and density ranges.

[4] See footnote 1.

of the method used for determination of background (should be consistent with the Guideline on Air Quality Models)

5. Meteorological data:
• Five consecutive years of the most recent representative sequential hourly National Weather Service (NWS) data, or one or more years of hourly sequential on-site data
• Discussion of meteorological conditions observed (as applied or modified for the site-specific area, i.e., identify possible variations due to difference between the monitoring site and the specific site of the source)
. • Discussion of topographic/land use influences

6. Air quality modeling analyses:
• Model each individual year for which data are available with a recommended model or model demonstrated to be acceptable on a case-by-case basis
—urban dispersion coefficients for urban areas
—rural dispersion coefficients for rural areas
• Evaluate downwash if stack height is less than GEP

• Define worst case meteorology
• Determine background and document method
—long-term
—short-term
• Provide topographic map(s) of receptor network with respect to location of all sources
• Follow current guidance on selection of receptor sites for refined analyses
• Include receptor terrain heights (if applicable) used in analyses
• Compare model estimates with · measurements considering the upper ends of the frequency distribution
• Determine extent of significant impact—provide maps
• Define areas of maximum and highest, second-highest impacts due to applicant source (refer to format suggested in Air Quality Summary Tables)
—long term
—short term

7. Comparison with acceptable air quality levels:

• NAAQS
• PSD increments
• Emission offset impacts if nonattainment

8. Documentation and guidelines for modeling methodology:
• Follow guidance documents
—Guideline on Air Quality Models, Revised, EPA–450/2–78–027R
—Guidelines for Air Quality Maintenance Planning and Analysis, Volume 10R, EPA–450/4–77–001, 1977
—Guideline for Determination of Good Engineering Practice Stack Height (Technical Support Document for the Stack Height Regulations), EPA–450/4–80–023R, 1985
—Ambient Air Monitoring Guidelines for PSD, EPA–450/4–80–012, 1980
—"Requirements for Preparation, Adoption and Submittal of Implementation Plans; Approval and Promulgation of Implementation Plans," CFR title 40 parts 51, 1982 (Prevention of Significant Deterioration)

AIR QUALITY SUMMARY

For New Source Alone

	Pollutant _____ *				
		**		**	Annual
	Highest	Highest 2nd High	Highest	Highest 2nd High	
Concentration Due to Modeled Source ($\mu g/m^3$)					
Background Concentration ($\mu g/m^3$)					
Total Concentration ($\mu g/m^3$)					
Receptor Distance (Km) (or UTM Easting)					
Receptor Direction (°) (or UTM Northing)					
Receptor Elevation (m)					
Wind Speed (m/s)					
Wind Direction (°)					
Mixing Depth (m)					
Temperature (°K)					
Stability					
Day/Month/Year of Occurrence					
Surface Air Data From_____					
Surface Station Elevation (m)_____					
Anemometer Height Above Local Ground Level (m)_____					
Upper Air Data From_____					
Period of Record Analyzed_____					
Model Used_____					
Recommended Model_____					

*Use separate sheet for each pollutant (SO₂, TSP, CO, NO₂, HC, Pb, Hg, Asbestos, etc.)
**List all appropriate averaging periods (1-hr, 3-hr, 8-hr, 24-hr, 30-day, 90-day, etc.) for which an air quality standard exists.

For All New Sources

	Pollutant _____ *				
		**		**	Annual
	Highest	Highest 2nd High	Highest	Highest 2nd High	
Concentration Due to Modeled Source ($\mu g/m^3$)					
Background Concentration ($\mu g/m^3$)					
Total Concentration ($\mu g/m^3$)					
Receptor Distance (Km) (or UTM Easting)					
Receptor Direction (°) (or UTM Northing)					
Receptor Elevation (m)					
Wind Speed (m/s)					
Wind Direction (°)					
Mixing Depth (m)					
Temperature (°K)					
Stability					

For All New Sources

	Pollutant _____ *				Annual
	**••		**		
	Highest	Highest 2nd High	Highest	Highest 2nd High	

Day/Month/Year of Occurrence...
Surface Air Data From_____
Surface Station Elevation (m)_____
Anemometer Height Above Local Ground Level (m)_____
Upper Air Data From_____
Period of Record Analyzed_____
Model Used_____
Recommended Model_____

*Use separate sheet for each pollutant (SO$_2$, TSP, CO, NO$_x$ HC, Pb, Hg, Asbestos, etc.)
**List all appropriate averaging periods (1-hr, 3-hr, 8-hr, 24-hr, 30-day, 90-day, etc.) for which an air quality standard exists.

For All Sources

•	Pollutant _____ *				Annual
	**••		**		
	Highest	Highest 2nd High	Highest	Highest 2nd High	

Concentration Due to Modeled Source (μg/m^3) ....
Background Concentration (μg/m^3) ....
Total Concentration (μg/m^3) ....
Receptor Distance (Km) (or UTM Easting)..
Receptor Direction (°) (or UTM Northing)..
Receptor Elevation (m) ....
Wind Speed (m/s) ....
Wind Direction (°)..
Mixing Depth (m)..
Temperature (°K) ....
Stability..
Day/Month/Year of Occurrence..
Surface Air Data From_____
Surface Station Elevation (m)_____
Anemometer Height Above Local Ground Level (m)_____
Upper Air Data From_____
Period of Record Analyzed_____
Model Used_____
Recommended Model_____

*Use separate sheet for each pollutant (SO$_2$, TSP, CO, NO$_x$ HC, Pb, Hg, Asbestos, etc.)
**List all appropriate averaging periods (1-hr, 3-hr, 8-hr, 24-hr, 30-day, 90-day, etc.) for which an air quality standard exists.

STACK PARAMETERS FOR ANNUAL MODELING

Stack No.	Serving	Emission Rate for each Pollutant (g/s)	Stack Exit Diameter (m)	Stack Exit Velocity (m/s)	Stack Exit Temperature (°K)	Physical Stack Height (m)	GEP Stack Height (m)	Stack Base Elevation (m)	Building Dimensions (m)		
									Height	Width	Length

STACK PARAMETERS FOR SHORT-TERM MODELING*

Stack No.	Serving	Emission Rate for each Pollutant (g/s)	Stack Exit Diameter (m)	Stack Exit Velocity (m/s)	Stack Exit Temperature (°K)	Physical Stack Height (m)	GEP Stack Height (m)	Stack Base Elevation (m)	Building Dimensions (m)		
									Height	Width	Length

* Separate tables for 50%, 75%, 100% of full load operating condition (and any other operating conditions as determied by screening or detailed modeling analyses to represent constraining operating conditions) should be provided.

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