

US EPA ARCHIVE DOCUMENT

**Part 266 - Standards for the Management of Specific Hazardous Wastes  
and Specific Types of Hazardous Waste Management Facilities**

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**Subparts A, B - [Reserved]**

**Subpart C - Recyclable Materials Used in a Manner Constituting Disposal**

**Section 266.20 Applicability.**

(a) The regulations of this subpart apply to recyclable materials that are applied to or placed on the land:

(1) Without mixing with any other substance(s); or

(2) After mixing or in combination with any other substance(s). These materials will be referred to throughout this subpart as "materials used in a manner that constitutes disposal".

(b) Products produced for the general public's use that are used in a manner that constitutes disposal and that contain recyclable materials are not presently subject to regulation if the recyclable materials have undergone a chemical reaction in the course of producing the products so as to become inseparable by physical means and if such products meet the applicable treatment standards in Subpart D of Part 268 (or applicable prohibition levels in §268.32 or 7 Del. C., Chapter 63, where no treatment standards have been established) for each recyclable material (i.e., hazardous waste) that they contain. Commercial fertilizers that are produced for the general public's use that contain recyclable materials also are not presently subject to regulation provided they meet the same treatment standards or prohibition levels for each recyclable material that they contain. However, zinc-containing fertilizers using hazardous waste KO61 that are produced for the general public's use are not presently subject to regulation.

(c) Anti-skid/deicing uses of slags, which are generated from high temperature metals recovery (HTMR) processing of hazardous waste KO61, KO62, and F006, in a manner constituting disposal are not covered by the exemption in paragraph (b) of this section and remain subject to regulation.

(Amended November 21, 1985; August 29, 1988; June 19, 1992, August 21, 1997)

**Section 266.21 Standards applicable to generators and transporters of materials used in a manner that constitute disposal.**

Generators and transporters of materials that are used in a manner that constitutes disposal are subject to the applicable requirements of Parts 262 and 263 of these regulations, and the notification requirement under 7 Del. C., Chapter 63.

(Amended November 21, 1985)

**Section 266.22 Standards applicable to storers of materials that are to be used in a manner that constitutes disposal who are not the ultimate users.**

Owners or operators of facilities that store recyclable materials that are to be used in a manner that constitutes disposal, but who are not the ultimate users of the materials, are regulated under all applicable provisions of Subparts A through L of Parts 264 and 265 and Parts 122 and 124 of these regulations and the notification requirement under 7 Del. C., Chapter 63.

(Amended November 21, 1985)

**Section 266.23 Standards applicable to users of materials that are used in a manner that constitutes disposal.**

(a) Owners or operators of facilities that use recyclable materials in a manner that constitutes disposal are regulated under all applicable provisions of Subparts A through N of Parts 264 and 265, and Parts 268, 122, and 124 of these regulations and the notification requirement under 7 Del. C., Chapter 63. (These requirements do not apply to products which contain these recyclable materials under the provisions of §266.20(b) of these regulations.)

(b) The use of waste or used oil or other material, which is contaminated with dioxin or any other hazardous waste (other than a waste identified solely on the basis of ignitability), for dust suppression or road treatment is prohibited.

(Amended November 21, 1985; August 29, 1988, July 23, 1996)

**Subpart D - Reserved**

**Subpart E - Reserved**

**Subpart F - Recyclable Materials Utilized for Precious Metal Recovery**

**Section 266.70 Applicability and requirements.**

(a) The regulations of this subpart apply to recyclable materials that are reclaimed to recover economically significant amounts of gold, silver, platinum, palladium, iridium, osmium, rhodium, ruthenium, or any combination of these.

(b) Persons who generate, transport, or store recyclable materials that are regulated under this subpart are subject to the following requirements:

(1) Notification requirements under 7 Del. C., Chapter 63;

(2) Subpart B of Part 262 (for generators), §263.20 and §263.21 (for transporters), and 265.71 and 265.72 (for persons who store) of these regulations;

(c) Persons who store recycled materials that are regulated under this subpart must keep the following records to document that they are not accumulating these materials speculatively (as defined in 261.1(c) of these regulations);

(i) Records showing the volume of these materials stored at the beginning of the calendar year;

(ii) The amount of these materials generated or received during the calendar year; and

(iii) The amount of materials remaining at the end of the calendar year.

(d) Recyclable materials that are regulated under this subpart that are accumulated speculatively (as defined in 261.1(c) of these regulations) are subject to all applicable provisions of Parts 262 through 265, 122 and 124 of these regulations.

(Amended November 21, 1985)

**Subpart G - Spent Lead-Acid Batteries Being Reclaimed**

**Section 266.80 Applicability and requirements.**

(a) The regulations of this subpart apply to persons who reclaim (including regeneration) spent lead-acid batteries that are recyclable materials ("spent batteries"). Persons who generate, transport, or collect spent batteries, who regenerate spent batteries, or who store spent batteries but do not reclaim them (other than spent batteries that are to be regenerated) are not subject to regulation under Parts 262 through 266 or Part 122 or 124 of these regulations, and also are not subject to the requirements of 7 Del. C., Chapter 63.

(b) Owners or operators of facilities that store spent lead acid batteries before reclaiming (other than spent batteries that are to be regenerated) them are subject to the following requirements.

(Amended July 23, 1996)



- (1) Notification requirements under 7 Del. C., Chapter 63;
- (2) All applicable provisions in Subparts A, B (but not §264.13 (waste analysis)), C, D, E (but not §264.71 or §264.72 (dealing with the use of the manifest and manifest discrepancies)), and F through L of Part 264 of these regulations.

(Amended November 21, 1985; August 29, 1988)

### **Subpart H - Hazardous Waste Burned in Boilers and Industrial Furnaces**

#### **Section 266.100 Applicability.**

(a) The regulations of this subpart apply to hazardous waste burned or processed in a boiler or industrial furnace (as defined in §260.10 of these regulations) irrespective of the purpose of burning or processing, except as provided by paragraphs (b), (c), (d), and (f) of this section. In this subpart, the term "burn" means burning for energy recovery or destruction, or processing for materials recovery or as an ingredient. The emissions standards of §§ 266.104, 266.105, 266.106, and 266.107 apply to facilities operating under interim status or under a DNREC operating permit as specified in §§ 266.102 and 266.103.

(b) The following hazardous wastes and facilities are not subject to regulation under this subpart:

(1) Used oil burned for energy recovery that is also a hazardous waste solely because it exhibits a characteristic of hazardous waste identified in Subpart C of Part 261 of these regulations. Such used oil is subject to regulation under Part 279 of these regulations;

(2) Gas recovered from hazardous or solid waste landfills when such gas is burned for energy recovery;

(3) Hazardous wastes that are exempt from regulation under §§ 261.4 and 261.6(a)(3)(iv) through (vi) of these regulations, and hazardous wastes that are subject to the special requirements for conditionally exempt small quantity generators under §261.5 of these regulations; and

(4) Coke ovens, if the only hazardous waste burned is DNREC Hazardous Waste No. K087, decanter tank tar sludge from coking operations.

(c) Owners and operators of smelting, melting, and refining furnaces (including pyrometallurgical devices such as cupolas, sintering machines, roasters, and foundry furnaces, but not including cement kilns, aggregate kilns, or halogen acid furnaces burning hazardous waste) that process hazardous waste solely for metal recovery are conditionally exempt from regulation under this subpart, except for §§ 266.101 and 266.112.

(1) To be exempt from §§ 266.102 through 266.111, an owner or operator of a metal recovery furnace or mercury recovery furnace, must comply with the following requirements, except that an owner or operator of a lead or a nickel-chromium recovery furnace, or a metal recovery furnace that burns baghouse bags used to capture metallic dusts emitted by steel manufacturing, must comply with the requirements of paragraph (c)(3) of this section:

(i) Provide a one-time written notice to the Secretary indicating the following:

(A) The owner or operator claims exemption under this paragraph;

(B) The hazardous waste is burned solely for metal recovery consistent with the provisions of paragraph (c)(2) of this section;

(C) The hazardous waste contains recoverable levels of metals; and

(D) The owner or operator will comply with the sampling and analysis and recordkeeping requirements of this paragraph;

(ii) Sample and analyze the hazardous waste and other feedstocks as necessary to comply with the requirements of this paragraph under procedures specified by Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, incorporated by reference in §260.11 of these regulations or alternative methods that meet or exceed the SW-846 method performance capabilities. If SW-846 does not prescribe a method for a particular determination, the owner or operator shall use the best available method; and

(iii) Maintain at the facility for at least three years records to document compliance with the provisions of this paragraph including limits on levels of toxic organic constituents and Btu value of the

waste, and levels of recoverable metals in the hazardous waste compared to normal nonhazardous waste feedstocks.

(2) A hazardous waste meeting either of the following criteria is not processed solely for metal recovery:

(i) The hazardous waste has a total concentration of organic compounds listed in Part 261, Appendix VIII, of these regulations exceeding 500 ppm by weight, as-fired, and so is considered to be burned for destruction. The concentration of organic compounds in a waste as-generated may be reduced to the 500 ppm limit by bona fide treatment that removes or destroys organic constituents. Blending for dilution to meet the 500 ppm limit is prohibited and documentation that the waste has not been impermissibly diluted must be retained in the records required by paragraph (c)(1)(iii) of this section; or

(ii) The hazardous waste has a heating value of 5,000 Btu/lb or more, as-fired, and so is considered to be burned as fuel. The heating value of a waste as-generated may be reduced to below the 5,000 Btu/lb limit by bona fide treatment that removes or destroys organic constituents. Blending for dilution to meet the 5,000 Btu/lb limit is prohibited and documentation that the waste has not been impermissibly diluted must be retained in the records required by paragraph (c)(1)(iii) of this section.

(3) To be exempt from §§ 266.102 through 266.111, an owner or operator of a lead or nickel-chromium or mercury recovery furnace, or a metal recovery furnace that burns baghouse bags used to capture metallic dusts emitted by steel manufacturing, must provide a one-time written notice to the Secretary identifying each hazardous waste burned and specifying whether the owner or operator claims an exemption for each waste under this paragraph or paragraph (c)(1) of this section. The owner or operator must comply with the requirements of paragraph (c)(1) of this section for those wastes claimed to be exempt under that paragraph and must comply with the requirements below for those wastes claimed to be exempt under this paragraph (c)(3).

(i) The hazardous wastes listed in Appendices XI, XII, and XIII, Part 266, and baghouse bags used to capture metallic dusts emitted by steel manufacturing are exempt from the requirements of paragraph (c)(1) of this section, provided that:

(A) A waste listed in Appendix XI of this part must contain recoverable levels of lead, a waste listed in Appendix XII of this part must contain recoverable levels of nickel or chromium, a waste listed in Appendix XIII of this part must contain recoverable levels of mercury and contain less than 500 ppm of Part 261, Appendix VIII organic constituents, and baghouse bags used to capture metallic dusts emitted by steel manufacturing must contain recoverable levels of metal; and

(B) The waste does not exhibit the Toxicity Characteristic of §261.24 of these regulations for an organic constituent; and

(C) The waste is not a hazardous waste listed in Subpart D of Part 261 of these regulations because it is listed for an organic constituent as identified in Appendix VII of Part 261 of these regulations; and

(D) The owner or operator certifies in the one-time notice that hazardous waste is burned under the provisions of paragraph (c)(3) of this section and that sampling and analysis will be conducted or other information will be obtained as necessary to ensure continued compliance with these requirements. Sampling and analysis shall be conducted according to paragraph (c)(1)(ii) of this section and records to document compliance with paragraph (c)(3) of this section shall be kept for at least three years.

(ii) The Secretary may decide on a case-by-case basis that the toxic organic constituents in a material listed in Appendix XI, XII, or XIII of this part that contains a total concentration of more than 500 ppm toxic organic compounds listed in Appendix VIII, Part 261 of these regulations, may pose a hazard to human health and the environment when burned in a metal recovery furnace exempt from the requirements of this subpart. In that situation, after adequate notice and opportunity for comment, the metal recovery furnace will become subject to the requirements of this subpart when burning that material. In making the hazard determination, the Secretary will consider the following factors:

(A) The concentration and toxicity of organic constituents in the material; and

(B) The level of destruction of toxic organic constituents provided by the furnace; and  
 (C) Whether the acceptable ambient levels established in Appendices IV or V of this part may be exceeded for any toxic organic compound that may be emitted based on dispersion modeling to predict the maximum annual average off-site ground level concentration.

(d) The standards for direct transfer operations under §266.111 apply only to facilities subject to the permit standards of §266.102 or the interim status standards of §266.103.

(e) The management standards for residues under §266.112 apply to any boiler or industrial furnace burning hazardous waste.

(f) Owners and operators of smelting, melting, and refining furnaces (including pyrometallurgical devices such as cupolas, sintering machines, roasters, and foundry furnaces) that process hazardous waste for recovery of economically significant amounts of the precious metals gold, silver, platinum, palladium, iridium, osmium, rhodium, or ruthenium, or any combination of these are conditionally exempt from regulation under this subpart, except for §266.112. To be exempt from §§ 266.101 through 266.111, an owner or operator must:

(1) Provide a one-time written notice to the Secretary indicating the following:

- (i) The owner or operator claims exemption under this paragraph;
- (ii) The hazardous waste is burned for legitimate recovery of precious metal; and
- (iii) The owner or operator will comply with the sampling and analysis and recordkeeping requirements of this paragraph; and

(2) Sample and analyze the hazardous waste as necessary to document that the waste is burned for recovery of economically significant amounts of precious metal using procedures specified by Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, incorporated by reference in §260.11 of these regulations or alternative methods that meet or exceed the SW-846 method performance capabilities. If SW-846 does not prescribe a method for a particular determination, the owner or operator shall use the best available method; and

(3) Maintain at the facility for at least three years records to document that all hazardous wastes burned are burned for recovery of economically significant amounts of precious metal.

(Amended July 26, 1994, August 1, 1995, July 23, 1996, August 21, 1997)

#### **Section 266.101 Management prior to burning.**

(a) Generators. Generators of hazardous waste that is burned in a boiler or industrial furnace are subject to Part 262 of these regulations.

(b) Transporters. Transporters of hazardous waste that is burned in a boiler or industrial furnace are subject to Part 263 of these regulations.

(c) Storage facilities. (1) Owners and operators of facilities that store hazardous waste that is burned in a boiler or industrial furnace are subject to the applicable provisions of Parts 264, 265, and 122 of these regulations, except as provided by paragraph (c)(2) of this section. These standards apply to storage by the burner as well as to storage facilities operated by intermediaries (processors, blenders, distributors, etc.) between the generator and the burner.

(2) Owners and operators of facilities that burn, in an on-site boiler or industrial furnace exempt from regulation under the small quantity burner provisions of §266.108, hazardous waste that they generate are exempt from the regulations of Parts 264, 265, and 122 of these regulations applicable to storage units for those storage units that store mixtures of hazardous waste and the primary fuel to the boiler or industrial furnace in tanks that feed the fuel mixture directly to the burner. Storage of hazardous waste prior to mixing with the primary fuel is subject to regulation as prescribed in paragraph (c)(1) of this section.

(Amended July 26, 1994, August 1, 1995)

## Section 266.102 Permit standards for burners.

(a) Applicability-(1) General. Owners and operators of boilers and industrial furnaces burning hazardous waste and not operating under interim status must comply with the requirements of this section and §§ 122.22 and 122.66 of these regulations, unless exempt under the small quantity burner exemption of §266.108.

(2) Applicability of Part 264 standards. Owners and operators of boilers and industrial furnaces that burn hazardous waste are subject to the following provisions of Part 264 of these regulations, except as provided otherwise by this subpart:

- (i) In Subpart A (General), 264.4;
- (ii) In Subpart B (General facility standards), §§ 264.11-264.18;
- (iii) In Subpart C (Preparedness and prevention), §§ 264.31-264.37;
- (iv) In Subpart D (Contingency plan and emergency procedures), §§ 264.51-264.56;
- (v) In Subpart E (Manifest system, recordkeeping, and reporting), the applicable provisions of §§ 264.71-264.77;
- (vi) In Subpart F (Releases from Solid Waste Management Units), §§ 264.90 and 264.101;
- (vii) In Subpart G (Closure and post-closure), §§ 264.111-264.115;
- (viii) In Subpart H (Financial requirements), §§ 264.141, 264.142, 264.143, and 264.147-264.151, except that States and the Federal government are exempt from the requirements of Subpart H; and
- (ix) Subpart BB (Air emission standards for equipment leaks), except §§ 264.1050(a).

(b) Hazardous waste analysis. (1) The owner or operator must provide an analysis of the hazardous waste that quantifies the concentration of any constituent identified in Appendix VIII of Part 261 of these regulations that may reasonably be expected to be in the waste. Such constituents must be identified and quantified if present, at levels detectable by analytical procedures prescribed by Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (incorporated by reference, see §260.11 of these regulations). Alternative methods that meet or exceed the method performance capabilities of SW-846 methods may be used. If SW-846 does not prescribe a method for a particular determination, the owner or operator shall use the best available method. The Appendix VIII, Part 261 constituents excluded from this analysis must be identified and the basis for their exclusion explained. This analysis will be used to provide all information required by this subpart and §122.22 and §122.66 of these regulations and to enable the permit writer to prescribe such permit conditions as necessary to protect human health and the environment. Such analysis must be included as a portion of the Part B permit application, or, for facilities operating under the interim status standards of this subpart, as a portion of the trial burn plan that may be submitted before the Part B application under provisions of §122.66(g) of these regulations as well as any other analysis required by the permit authority in preparing the permit. Owners and operators of boilers and industrial furnaces not operating under the interim status standards must provide the information required by §§ 122.22 or 122.66(c) of these regulations in the Part B application to the greatest extent possible.

(2) Throughout normal operation, the owner or operator must conduct sampling and analysis as necessary to ensure that the hazardous waste, other fuels, and industrial furnace feedstocks fired into the boiler or industrial furnace are within the physical and chemical composition limits specified in the permit.

(c) Emissions standards. Owners and operators must comply with emissions standards provided by §§ 266.104 through 266.107.

(d) Permits. (1) The owner or operator may burn only hazardous wastes specified in the facility permit and only under the operating conditions specified under paragraph (e) of this section, except in approved trial burns under the conditions specified in §122.66 of these regulations.



(2) Hazardous wastes not specified in the permit may not be burned until operating conditions have been specified under a new permit or permit modification, as applicable. Operating requirements for new wastes may be based on either trial burn results or alternative data included with Part B of a permit application under §122.22 of these regulations.

(3) Boilers and industrial furnaces operating under the interim status standards of §266.103 are permitted under procedures provided by §122.66(g) of these regulations.

(4) A permit for a new boiler or industrial furnace (those boilers and industrial furnaces not operating under the interim status standards) must establish appropriate conditions for each of the applicable requirements of this section, including but not limited to allowable hazardous waste firing rates and operating conditions necessary to meet the requirements of paragraph (e) of this section, in order to comply with the following standards:

(i) For the period beginning with initial introduction of hazardous waste and ending with initiation of the trial burn, and only for the minimum time required to bring the device to a point of operational readiness to conduct a trial burn, not to exceed a duration of 720 hours operating time when burning hazardous waste, the operating requirements must be those most likely to ensure compliance with the emission standards of §§ 266.104 through 266.107, based on the Secretary's engineering judgment. If the applicant is seeking a waiver from a trial burn to demonstrate conformance with a particular emission standard, the operating requirements during this initial period of operation shall include those specified by the applicable provisions of §266.104, §266.105, §266.106, or §266.107. The Secretary may extend the duration of this period for up to 720 additional hours when good cause for the extension is demonstrated by the applicant.

(ii) For the duration of the trial burn, the operating requirements must be sufficient to demonstrate compliance with the emissions standards of §§ 266.104 through 266.107 and must be in accordance with the approved trial burn plan;

(iii) For the period immediately following completion of the trial burn, and only for the minimum period sufficient to allow sample analysis, data computation, submission of the trial burn results by the applicant, review of the trial burn results and modification of the facility permit by the Secretary to reflect the trial burn results, the operating requirements must be those most likely to ensure compliance with the emission standards §§ 266.104 through 266.107 based on the Secretary's engineering judgment.

(iv) For the remaining duration of the permit, the operating requirements must be those demonstrated in a trial burn or by alternative data specified in §122.22 of these regulations, as sufficient to ensure compliance with the emissions standards of §§ 266.104 through 266.107.

(e) Operating requirements-(1) General. A boiler or industrial furnace burning hazardous waste must be operated in accordance with the operating requirements specified in the permit at all times where there is hazardous waste in the unit.

(2) Requirements to ensure compliance with the organic emissions standards- (i) DRE standard. Operating conditions will be specified either on a case-by-case basis for each hazardous waste burned as those demonstrated (in a trial burn or by alternative data as specified in §122.22) to be sufficient to comply with the destruction and removal efficiency (DRE) performance standard of §266.104(a) or as those special operating requirements provided by §266.104(a)(4) for the waiver of the DRE trial burn. When the DRE trial burn is not waived under §266.104(a)(4), each set of operating requirements will specify the composition of the hazardous waste (including acceptable variations in the physical and chemical properties of the hazardous waste which will not affect compliance with the DRE performance standard) to which the operating requirements apply. For each such hazardous waste, the permit will specify acceptable operating limits including, but not limited to, the following conditions as appropriate:

(A) Feed rate of hazardous waste and other fuels measured and specified as prescribed in paragraph (e)(6) of this section;

(B) Minimum and maximum device production rate when producing normal product expressed in appropriate units, measured and specified as prescribed in paragraph (e)(6) of this section;

(C) Appropriate controls of the hazardous waste firing system;

- (D) Allowable variation in boiler and industrial furnace system design or operating procedures;
- (E) Minimum combustion gas temperature measured at a location indicative of combustion chamber temperature, measured and specified as prescribed in paragraph (e)(6) of this section;
- (F) An appropriate indicator of combustion gas velocity, measured and specified as prescribed in paragraph (e)(6) of this section, unless documentation is provided under §122.66 of these regulations demonstrating adequate combustion gas residence time; and
- (G) Such other operating requirements as are necessary to ensure that the DRE performance standard of §266.104(a) is met.

(ii) Carbon monoxide and hydrocarbon standards. The permit must incorporate a carbon monoxide (CO) limit and, as appropriate, a hydrocarbon (HC) limit as provided by paragraphs (b), (c), (d), (e) and (f) of §266.104. The permit limits will be specified as follows:

(A) When complying with the CO standard of §266.104(b)(1), the permit limit is 100 ppmv;

(B) When complying with the alternative CO standard under §266.104(c), the permit limit for CO is based on the trial burn and is established as the average over all valid runs of the highest hourly rolling average CO level of each run, and the permit limit for HC is 20 ppmv (as defined in §266.104(c)(1)), except as provided in §266.104(f).

(C) When complying with the alternative HC limit for industrial furnaces under §266.104(f), the permit limit for HC and CO is the baseline level when hazardous waste is not burned as specified by that paragraph.

(iii) Start-up and shut-down. During start-up and shut-down of the boiler or industrial furnace, hazardous waste (except waste fed solely as an ingredient under the Tier I (or adjusted Tier I) feed rate screening limits for metals and chloride/chlorine, and except low risk waste exempt from the trial burn requirements under §§ 266.104(a)(5), 266.105, 266.106, and 266.107) must not be fed into the device unless the device is operating within the conditions of operation specified in the permit.

(3) Requirements to ensure conformance with the particulate standard. (i) Except as provided in paragraphs (e)(3) (ii) and (iii) of this section, the permit shall specify the following operating requirements to ensure conformance with the particulate standard specified in §266.105:

(A) Total ash feed rate to the device from hazardous waste, other fuels, and industrial furnace feedstocks, measured and specified as prescribed in paragraph (e)(6) of this section;

(B) Maximum device production rate when producing normal product expressed in appropriate units, and measured and specified as prescribed in paragraph (e)(6) of this section;

(C) Appropriate controls on operation and maintenance of the hazardous waste firing system and any air pollution control system;

(D) Allowable variation in boiler and industrial furnace system design including any air pollution control system or operating procedures; and

(E) Such other operating requirements as are necessary to ensure that the particulate standard in §266.111(b) is met.

(ii) Permit conditions to ensure conformance with the particulate matter standard shall not be provided for facilities exempt from the particulate matter standard under §266.105(b);

(iii) For cement kilns and light-weight aggregate kilns, permit conditions to ensure compliance with the particulate standard shall not limit the ash content of hazardous waste or other feed materials.

(4) Requirements to ensure conformance with the metals emissions standard. (i) For conformance with the Tier I (or adjusted Tier I) metals feed rate screening limits of paragraphs (b) or (e) of §266.106, the permit shall specify the following operating requirements:

(A) Total feed rate of each metal in hazardous waste, other fuels, and industrial furnace feedstocks measured and specified under provisions of paragraph (e)(6) of this section;

(B) Total feed rate of hazardous waste measured and specified as prescribed in paragraph (e)(6) of this section;

(C) A sampling and metals analysis program for the hazardous waste, other fuels, and industrial furnace feedstocks;



(ii) For conformance with the Tier II metals emission rate screening limits under §266.106(c) and the Tier III metals controls under §266.106(d), the permit shall specify the following operating requirements:

(A) Maximum emission rate for each metal specified as the average emission rate during the trial burn;

(B) Feed rate of total hazardous waste and pumpable hazardous waste, each measured and specified as prescribed in paragraph (e)(6)(i) of this section;

(C) Feed rate of each metal in the following feedstreams, measured and specified as prescribed in paragraphs (e)(6) of this section:

(1) Total feed streams;

(2) Total hazardous waste feed; and

(3) Total pumpable hazardous waste feed;

(D) Total feed rate of chlorine and chloride in total feed streams measured and specified as prescribed in paragraph (e)(6) of this section;

(E) Maximum combustion gas temperature measured at a location indicative of combustion chamber temperature, and measured and specified as prescribed in paragraph (e)(6) of this section;

(F) Maximum flue gas temperature at the inlet to the particulate matter air pollution control system measured and specified as prescribed in paragraph (e)(6) of this section;

(G) Maximum device production rate when producing normal product expressed in appropriate units and measured and specified as prescribed in paragraph (e)(6) of this section;

(H) Appropriate controls on operation and maintenance of the hazardous waste firing system and any air pollution control system;

(I) Allowable variation in boiler and industrial furnace system design including any air pollution control system or operating procedures; and

(J) Such other operating requirements as are necessary to ensure that the metals standards under §§ 266.106(c) or 266.106(d) are met.

(iii) For conformance with an alternative implementation approach approved by the Secretary under §266.106(f), the permit will specify the following operating requirements:

(A) Maximum emission rate for each metal specified as the average emission rate during the trial burn;

(B) Feed rate of total hazardous waste and pumpable hazardous waste, each measured and specified as prescribed in paragraph (e)(6)(i) of this section;

(C) Feed rate of each metal in the following feedstreams, measured and specified as prescribed in paragraph (e)(6) of this section:

(1) Total hazardous waste feed; and

(2) Total pumpable hazardous waste feed;

(D) Total feed rate of chlorine and chloride in total feed streams measured and specified prescribed in paragraph (e)(6) of this section;

(E) Maximum combustion gas temperature measured at a location indicative of combustion chamber temperature, and measured and specified as prescribed in paragraph (e)(6) of this section;

(F) Maximum flue gas temperature at the inlet to the particulate matter air pollution control system measured and specified as prescribed in paragraph (e)(6) of this section;

(G) Maximum device production rate when producing normal product expressed in appropriate units and measured and specified as prescribed in paragraph (e)(6) of this section;

(H) Appropriate controls on operation and maintenance of the hazardous waste firing system and any air pollution control system;

(I) Allowable variation in boiler and industrial furnace system design including any air pollution control system or operating procedures; and

(J) Such other operating requirements as are necessary to ensure that the metals standards under §§ 266.106(c) or 266.106(d) are met.

(5) Requirements to ensure conformance with the hydrogen chloride and chlorine gas standards. (i) For conformance with the Tier I total chloride and chlorine feed rate screening limits of §266.107(b)(1), the permit will specify the following operating requirements:

(A) Feed rate of total chloride and chlorine in hazardous waste, other fuels, and industrial furnace feedstocks measured and specified as prescribed in paragraph (e)(6) of this section;

(B) Feed rate of total hazardous waste measured and specified as prescribed in paragraph (e)(6) of this section;

(C) A sampling and analysis program for total chloride and chlorine for the hazardous waste, other fuels, and industrial furnace feedstocks;

(ii) For conformance with the Tier II HCl and Cl<sub>2</sub> emission rate screening limits under §266.107(b)(2) and the Tier III HCl and Cl<sub>2</sub> controls under §266.107(c), the permit will specify the following operating requirements:

(A) Maximum emission rate for HCl and for Cl<sub>2</sub> specified as the average emission rate during the trial burn;

(B) Feed rate of total hazardous waste measured and specified as prescribed in paragraph (e)(6) of this section;

(C) Total feed rate of chlorine and chloride in total feed streams, measured and specified as prescribed in paragraph (e)(6) of this section;

(D) Maximum device production rate when producing normal product expressed in appropriate units, measured and specified as prescribed in paragraph (e)(6) of this section;

(E) Appropriate controls on operation and maintenance of the hazardous waste firing system and any air pollution control system;

(F) Allowable variation in boiler and industrial furnace system design including any air pollution control system or operating procedures; and

(G) Such other operating requirements as are necessary to ensure that the HCl and Cl<sub>2</sub> standards under §266.107 (b)(2) or (c) are met.

(6) Measuring parameters and establishing limits based on trial burn data-(i) General requirements. As specified in paragraphs (e)(2) through (e)(5) of this section, each operating parameter shall be measured, and permit limits on the parameter shall be established, according to either of the following procedures:

(A) Instantaneous limits. A parameter may be measured and recorded on an instantaneous basis (i.e., the value that occurs at any time) and the permit limit specified as the time-weighted average during all valid runs of the trial burn; or

(B) Hourly rolling average. (1) The limit for a parameter may be established and continuously monitored on an hourly rolling average basis defined as follows:

(i) A continuous monitor is one which continuously samples the regulated parameter without interruption, and evaluates the detector response at least once each 15 seconds, and computes and records the average value at least every 60 seconds.

(ii) An hourly rolling average is the arithmetic mean of the 60 most recent 1-minute average values recorded by the continuous monitoring system.

(2) The permit limit for the parameter shall be established based on trial burn data as the average over all valid test runs of the highest hourly rolling average value for each run.

(ii) Rolling average limits for carcinogenic metals and lead. Feed rate limits for the carcinogenic metals (i.e., arsenic, beryllium, cadmium and chromium) and lead may be established either on an hourly rolling average basis as prescribed by paragraph (e)(6)(i) of this section or on (up to) a 24 hour rolling average basis. If the owner or operator elects to use an average period from 2 to 24 hours:

(A) The feed rate of each metal shall be limited at any time to ten times the feed rate that would be allowed on an hourly rolling average basis;

(B) The continuous monitor shall meet the following specifications:

(1) A continuous monitor is one which continuously samples the regulated parameter without interruption, and evaluates the detector response at least once each 15 seconds, and computes and records the average value at least every 60 seconds.

(2) The rolling average for the selected averaging period is defined as the arithmetic mean of one hour block averages for the averaging period. A one hour block average is the arithmetic mean of the one minute averages recorded during the 60-minute period beginning at one minute after the beginning of preceding clock hour; and

(C) The permit limit for the feed rate of each metal shall be established based on trial burn data as the average over all valid test runs of the highest hourly rolling average feed rate for each run.

(iii) Feed rate limits for metals, total chloride and chlorine, and ash. Feed rate limits for metals, total chlorine and chloride, and ash are established and monitored by knowing the concentration of the substance (i.e., metals, chloride/chlorine, and ash) in each feedstream and the flow rate of the feedstream. To monitor the feed rate of these substances, the flow rate of each feedstream must be monitored under the continuous monitoring requirements of paragraphs (e)(6) (i) and (ii) of this section.

(iv) Conduct of trial burn testing. (A) If compliance with all applicable emissions standards of §§ 266.104 through 266.107 is not demonstrated simultaneously during a set of test runs, the operating conditions of additional test runs required to demonstrate compliance with remaining emissions standards must be as close as possible to the original operating conditions.

(B) Prior to obtaining test data for purposes of demonstrating compliance with the emissions standards of §§ 266.104 through 266.107 or establishing limits on operating parameters under this section, the facility must operate under trial burn conditions for a sufficient period to reach steady-state operations. The Secretary may determine, however, that industrial furnaces that recycle collected particulate matter back into the furnace and that comply with an alternative implementation approach for metals under §266.106(f) need not reach steady state conditions with respect to the flow of metals in the system prior to beginning compliance testing for metals emissions.

(C) Trial burn data on the level of an operating parameter for which a limit must be established in the permit must be obtained during emissions sampling for the pollutant(s) (i.e., metals, PM, HCl/Cl<sub>2</sub>, organic compounds) for which the parameter must be established as specified by paragraph (e) of this section.

(7) General requirements-(i) Fugitive emissions. Fugitive emissions must be controlled by:

(A) Keeping the combustion zone totally sealed against fugitive emissions; or

(B) Maintaining the combustion zone pressure lower than atmospheric pressure; or

(C) An alternate means of control demonstrated (with Part B of the permit application) to provide fugitive emissions control equivalent to maintenance of combustion zone pressure lower than atmospheric pressure.

(ii) Automatic waste feed cutoff. A boiler or industrial furnace must be operated with a functioning system that automatically cuts off the hazardous waste feed when operating conditions deviate from those established under this section. The Secretary may limit the number of cutoffs per an operating period on a case-by-case basis. In addition:

(A) The permit limit for (the indicator of) minimum combustion chamber temperature must be maintained while hazardous waste or hazardous waste residues remain in the combustion chamber,

(B) Exhaust gases must be ducted to the air pollution control system operated in accordance with the permit requirements while hazardous waste or hazardous waste residues remain in the combustion chamber; and

(C) Operating parameters for which permit limits are established must continue to be monitored during the cutoff, and the hazardous waste feed shall not be restarted until the levels of those parameters comply with the permit limits. For parameters that may be monitored on an instantaneous basis, the Secretary will establish a minimum period of time after a waste feed cutoff during which the parameter must not exceed the permit limit before the hazardous waste feed may be restarted.

(iii) Changes. A boiler or industrial furnace must cease burning hazardous waste when changes in combustion properties, or feed rates of the hazardous waste, other fuels, or industrial furnace feedstocks, or changes in the boiler or industrial furnace design or operating conditions deviate from the limits as specified in the permit.

(8) Monitoring and Inspections. (i) The owner or operator must monitor and record the following, at a minimum, while burning hazardous waste:

(A) If specified by the permit, feed rates and composition of hazardous waste, other fuels, and industrial furnace feedstocks, and feed rates of ash, metals, and total chloride and chlorine;

(B) If specified by the permit, carbon monoxide (CO), hydrocarbons (HC), and oxygen on a continuous basis at a common point in the boiler or industrial furnace downstream of the combustion zone and prior to release of stack gases to the atmosphere in accordance with operating requirements specified in paragraph (e)(2)(ii) of this section. CO, HC, and oxygen monitors must be installed, operated, and maintained in accordance with methods specified in Appendix IX of this part.

(C) Upon the request of the Secretary, sampling and analysis of the hazardous waste (and other fuels and industrial furnace feedstocks as appropriate), residues, and exhaust emissions must be conducted to verify that the operating requirements established in the permit achieve the applicable standards of §§ 266.104, 266.105, 266.106, and 266.107.

(ii) All monitors shall record data in units corresponding to the permit limit unless otherwise specified in the permit.

(iii) The boiler or industrial furnace and associated equipment (pumps, valves, pipes, fuel storage tanks, etc.) must be subjected to thorough visual inspection when it contains hazardous waste, at least daily for leaks, spills, fugitive emissions, and signs of tampering.

(iv) The automatic hazardous waste feed cutoff system and associated alarms must be tested at least once every 7 days when hazardous waste is burned to verify operability, unless the applicant demonstrates to the Secretary that weekly inspections will unduly restrict or upset operations and that less frequent inspections will be adequate. At a minimum, operational testing must be conducted at least once every 30 days.

(v) These monitoring and inspection data must be recorded and the records must be placed in the operating record required by §264.73 of these regulations.

(9) Direct transfer to the burner. If hazardous waste is directly transferred from a transport vehicle to a boiler or industrial furnace without the use of a storage unit, the owner and operator must comply with §266.111.

(10) Recordkeeping. The owner or operator must keep in the operating record of the facility all information and data required by this section until closure of the facility.

(11) Closure. At closure, the owner or operator must remove all hazardous waste and hazardous waste residues (including, but not limited to, ash, scrubber waters, and scrubber sludges) from the boiler or industrial furnace.

(Amended July 26, 1994, August 21, 1997)

#### Section 266.103 Interim status standards for burners.

(a) Purpose, scope, applicability.-(1) General. (i) The purpose of this section is to establish minimum national standards for owners and operators of "existing" boilers and industrial furnaces that burn hazardous waste where such standards define the acceptable management of hazardous waste during the period of interim status. The standards of this section apply to owners and operators of existing facilities until either a permit is issued under §266.102(d) or until closure responsibilities identified in this section are fulfilled.

(ii) "Existing or in existence" means a boiler or industrial furnace that on or before August 21, 1991 is either in operation burning or processing hazardous waste or for which construction (including the ancillary facilities to burn or to process the hazardous waste) has commenced. A facility has



commenced construction if the owner or operator has obtained the Federal, State, and local approvals or permits necessary to begin physical construction; and either:

(A) A continuous on-site, physical construction program has begun; or

(B) The owner or operator has entered into contractual obligations-which cannot be canceled or modified without substantial loss-for physical construction of the facility to be completed within a reasonable time.

(iii) If a boiler or industrial furnace is located at a facility that already has a permit or interim status, then the facility must comply with the applicable regulations dealing with permit modifications in §122.42 or changes in interim status in §122.72 of these regulations.

(2) Exemptions. The requirements of this section do not apply to hazardous waste and facilities exempt under §§ 266.100(b), or 266.108.

(3) Prohibition on burning dioxin-listed wastes. The following hazardous waste listed for dioxin and hazardous waste derived from any of these wastes may not be burned in a boiler or industrial furnace operating under interim status: F020, F021, F022, F023, F026, and F027.

(4) Applicability of Part 265 standards. Owners and operators of boilers and industrial furnaces that burn hazardous waste and are operating under interim status are subject to the following provisions of Part 265 of these regulations, except as provided otherwise by this section:

(i) In Subpart A (General), §265.4;

(ii) In Subpart B (General facility standards), §§ 265.11-265.17;

(iii) In Subpart C (Preparedness and prevention), §§ 265.31-265.37;

(iv) In Subpart D (Contingency plan and emergency procedures), §§ 265.51-265.56;

(v) In Subpart E (Manifest system, recordkeeping, and reporting), §§ 265.71-265.77, except that §§ 265.71, 265.72, and 265.76 do not apply to owners and operators of on-site facilities that do not receive any hazardous waste from off-site sources;

(vi) In Subpart G (Closure and post-closure), §§ 265.111-265.115;

(vii) In Subpart H (Financial requirements), §§ 265.141, 265.142, 265.143, and 265.147-265.148 and 265.151, except that States and the Federal government are exempt from the requirements of Subpart H; and

(viii) Subpart BB (Air emission standards for equipment leaks), except §265.1050(a).

(5) Special requirements for furnaces. The following controls apply during interim status to industrial furnaces (e.g., kilns, cupolas) that feed hazardous waste for a purpose other than solely as an ingredient (see paragraph (a)(5)(ii) of this section) at any location other than the hot end where products are normally discharged or where fuels are normally fired:

(i) Controls. (A) The hazardous waste shall be fed at a location where combustion gas temperatures are at least 1800 °F;

(B) The owner or operator must determine that adequate oxygen is present in combustion gases to combust organic constituents in the waste and retain documentation of such determination in the facility record;

(C) For cement kiln systems, the hazardous waste shall be fed into the kiln; and

(D) The hydrocarbon controls of §266.104(c) or paragraph (c)(5) of this section apply upon certification of compliance under paragraph (c) of this section irrespective of the CO level achieved during the compliance test.

(ii) Burning hazardous waste solely as an ingredient. A hazardous waste is burned for a purpose other than solely as an ingredient if it meets either of these criteria:

(A) The hazardous waste has a total concentration of nonmetal compounds listed in Part 261, Appendix VIII, of these regulations exceeding 500 ppm by weight, as-fired, and so is considered to be burned for destruction. The concentration of nonmetal compounds in a waste as-generated may be reduced to the 500 ppm limit by bona fide treatment that removes or destroys nonmetal constituents. Blending for dilution to meet the 500 ppm limit is prohibited and documentation that the waste has not been impermissibly diluted must be retained in the facility record; or

(B) The hazardous waste has a heating value of 5,000 Btu/lb or more, as-fired, and so is considered to be burned as fuel. The heating value of a waste as-generated may be reduced to below the 5,000 Btu/lb limit by bona fide treatment that removes or destroys organic constituents. Blending to augment the heating value to meet the 5,000 Btu/lb limit is prohibited and documentation that the waste has not been impermissibly blended must be retained in the facility record.

(6) Restrictions on burning hazardous waste that is not a fuel. Prior to certification of compliance under paragraph (c) of this section, owners and operators shall not feed hazardous waste that has a heating value less than 5,000 Btu/lb, as-generated, (except that the heating value of a waste as-generated may be increased to above the 5,000 Btu/lb limit by bona fide treatment; however, blending to augment the heating value to meet the 5,000 Btu/lb limit is prohibited and records must be kept to document that impermissible blending has not occurred) in a boiler or industrial furnace, except that:

- (i) Hazardous waste may be burned solely as an ingredient; or
- (ii) Hazardous waste may be burned for purposes of compliance testing (or testing prior to compliance testing) for a total period of time not to exceed 720 hours; or
- (iii) Such waste may be burned if the Secretary has documentation to show that, prior to August 21, 1991:

(A) The boiler or industrial furnace is operating under the interim status standards for incinerators provided by Subpart O of Part 265 of these regulations, or the interim status standards for thermal treatment units provided by Subpart P of Part 265 of these regulations; and

(B) The boiler or industrial furnace met the interim status eligibility requirements under §122.70 of these regulations for Subpart O or Subpart P of Part 265 of these regulations; and

(C) Hazardous waste with a heating value less than 5,000 Btu/lb was burned prior to that date; or

(iv) Such waste may be burned in a halogen acid furnace if the waste was burned as an excluded ingredient under §261.2(e) of these regulations prior to February 21, 1991 and documentation is kept on file supporting this claim.

(7) Direct transfer to the burner. If hazardous waste is directly transferred from a transport vehicle to a boiler or industrial furnace without the use of a storage unit, the owner and operator must comply with §266.111.

(b) Certification of precompliance-(1) General. The owner or operator must provide complete and accurate information specified in paragraph (b)(2) of this section to the Secretary on or before August 21, 1991, and must establish limits for the operating parameters specified in paragraph (b)(3) of this section. Such information is termed a "certification of precompliance" and constitutes a certification that the owner or operator has determined that, when the facility is operated within the limits specified in paragraph (b)(3) of this section, the owner or operator believes that, using best engineering judgment, emissions of particulate matter, metals, and HCl and Cl<sub>2</sub> are not likely to exceed the limits provided by §§ 266.105, 266.106, and 266.107. The facility may burn hazardous waste only under the operating conditions that the owner or operator establishes under paragraph (b)(3) of this section until the owner or operator submits a revised certification of precompliance under paragraph (b)(8) of this section or a certification of compliance under paragraph (c) of this section, or until a permit is issued.

(2) Information required. The following information must be submitted with the certification of precompliance to support the determination that the limits established for the operating parameters identified in paragraph (b)(3) of this section are not likely to result in an exceedance of the allowable emission rates for particulate matter, metals, and HCl and Cl<sub>2</sub>:

(i) General facility information:

(A) EPA facility ID number;

(B) Facility name, contact person, telephone number, and address;

(C) Description of boilers and industrial furnaces burning hazardous waste, including type and capacity of device;



(D) A scaled plot plan showing the entire facility and location of the boilers and industrial furnaces burning hazardous waste; and

(E) A description of the air pollution control system on each device burning hazardous waste, including the temperature of the flue gas at the inlet to the particulate matter control system.

(ii) Except for facilities complying with the Tier I or Adjusted Tier I feed rate screening limits for metals or total chlorine and chloride provided by §§ 266.106 (b) or (e) and 266.107 (b)(1) or (e) respectively, the estimated uncontrolled (at the inlet to the air pollution control system) emissions of particulate matter, each metal controlled by §266.106, and hydrogen chloride and chlorine, and the following information to support such determinations:

(A) The feed rate (lb/hr) of ash, chlorine, antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium in each feedstream (hazardous waste, other fuels, and industrial furnace feedstocks);

(B) The estimated partitioning factor to the combustion gas for the materials identified in paragraph (b)(2)(ii)(A) of this section and the basis for the estimate and an estimate of the partitioning to HCl and Cl<sub>2</sub> of total chloride and chlorine in feed materials. To estimate the partitioning factor, the owner or operator must use either best engineering judgment or the procedures specified in Appendix IX of this part.

(C) For industrial furnaces that recycle collected particulate matter (PM) back into the furnace and that will certify compliance with the metals emissions standards under paragraph (c)(3)(ii)(A), the estimated enrichment factor for each metal. To estimate the enrichment factor, the owner or operator must use either best engineering judgment or the procedures specified in "Alternative Methodology for Implementing Metals Controls" in Appendix IX of this part.

(D) If best engineering judgment is used to estimate partitioning factors or enrichment factors under paragraphs (b)(2)(ii)(B) or (b)(2)(ii)(C) respectively, the basis for the judgment. When best engineering judgment is used to develop or evaluate data or information and make determinations under this section, the determinations must be made by a qualified, registered professional engineer and a certification of his/her determinations in accordance with §122.11(d) of these regulations must be provided in the certification of precompliance.

(iii) For facilities complying with the Tier I or Adjusted Tier I feed rate screening limits for metals or total chlorine and chloride provided by §§ 266.106 (b) or (e) and 266.107 (b)(1) or (e), the feed rate (lb/hr) of total chloride and chlorine, antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium in each feedstream (hazardous waste, other fuels, industrial furnace feedstocks).

(iv) For facilities complying with the Tier II or Tier III emission limits for metals or HCl and Cl<sub>2</sub> (under §§ 266.106 (c) or (d) or 266.107(b)(2) or (c)), the estimated controlled (outlet of the air pollution control system) emissions rates of particulate matter, each metal controlled by §266.106, and HCl and Cl<sub>2</sub>, and the following information to support such determinations:

(A) The estimated air pollution control system (APCS) removal efficiency for particulate matter, HCl, Cl<sub>2</sub>, antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium.

(B) To estimate APCS removal efficiency, the owner or operator must use either best engineering judgment or the procedures prescribed in Appendix IX of this part.

(C) If best engineering judgment is used to estimate APCS removal efficiency, the basis for the judgment. Use of best engineering judgment must be in conformance with provisions of paragraph (b)(2)(ii)(D) of this section.

(v) Determination of allowable emissions rates for HCl, Cl<sub>2</sub>, antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium, and the following information to support such determinations:

(A) For all facilities:

(1) Physical stack height;

(2) Good engineering practice stack height as defined by 40 CFR 51.100(ii);

(3) Maximum flue gas flow rate;

- (4) Maximum flue gas temperature;
- (5) Attach a US Geological Service topographic map (or equivalent) showing the facility location and surrounding land within 5 km of the facility;
- (6) Identify terrain type: complex or noncomplex; and
- (7) Identify land use: urban or rural.

(B) For owners and operators using Tier III site specific dispersion modeling to determine allowable levels under §266.106(d) or §266.107(c), or adjusted Tier I feed rate screening limits under §§ 266.106(e) or 266.107(e):

- (1) Dispersion model and version used;
- (2) Source of meteorological data;
- (3) The dilution factor in micrograms per cubic meter per gram per second of emissions for the maximum annual average off-site (unless on-site is required) ground level concentration (MEI location); and

(4) Indicate the MEI location on the map required under paragraph (b)(2)(v)(A)(5);

(vi) For facilities complying with the Tier II or III emissions rate controls for metals or HCl and Cl<sub>2</sub>, a comparison of the estimated controlled emissions rates determined under paragraph (b)(2)(iv) with the allowable emission rates determined under paragraph (b)(2)(v);

(vii) For facilities complying with the Tier I (or adjusted Tier I) feed rate screening limits for metals or total chloride and chlorine, a comparison of actual feed rates of each metal and total chlorine and chloride determined under paragraph (b)(2)(iii) of this section to the Tier I allowable feed rates; and

(viii) For industrial furnaces that feed hazardous waste for any purpose other than solely as an ingredient (as defined by paragraph (a)(5)(ii) of this section) at any location other than the product discharge end of the device, documentation of compliance with the requirements of paragraphs (a)(5)(i) (A), (B), and (C) of this section.

(ix) For industrial furnaces that recycle collected particulate matter (PM) back into the furnace and that will certify compliance with the metals emissions standards under paragraph (c)(3)(ii) (A) of this section:

(A) The applicable particulate matter standard in lb/hr; and

(B) The precompliance limit on the concentration of each metal in collected PM.

(3) Limits on operating conditions. The owner and operator shall establish limits on the following parameters consistent with the determinations made under paragraph (b)(2) of this section and certify (under provisions of paragraph (b)(9) of this section) to the Secretary that the facility will operate within the limits during interim status when there is hazardous waste in the unit until revised certification of precompliance under paragraph (b)(8) of this section or certification of compliance under paragraph (c) of this section:

(i) Feed rate of total hazardous waste and (unless complying with the Tier I or adjusted Tier I metals feed rate screening limits under §266.106(b) or (e)) pumpable hazardous waste;

(ii) Feed rate of each metal in the following feed streams:

(A) Total feed streams, except that industrial furnaces that comply with the alternative metals implementation approach under paragraph (b)(4) of this section must specify limits on the concentration of each metal in collected particulate matter in lieu of feed rate limits for total feedstreams;

(B) Total hazardous waste feed, unless complying with the Tier I or Adjusted Tier I metals feed rate screening limits under §266.106(b) or (e); and

(C) Total pumpable hazardous waste feed, unless complying with the Tier I or adjusted Tier I metals feed rate screening limits under §266.106 (b) or (e);

(iii) Total feed rate of chlorine and chloride in total feed streams;

(iv) Total feed rate of ash in total feed streams, except that the ash feed rate for cement kilns and light-weight aggregate kilns is not limited; and

(v) Maximum production rate of the device in appropriate units when producing normal product, unless complying with the Tier I or Adjusted Tier I feed rate screening limits for chlorine under

§266.107(b)(1) or (e) and for all metals under §266.106(b) or (e), and the uncontrolled particulate emissions do not exceed the standard under §266.105.

(4) Operating requirements for furnaces that recycle PM. Owners and operators of furnaces that recycle collected particulate matter (PM) back into the furnace and that will certify compliance with the metals emissions controls under paragraph (c)(3)(ii)(A) of this section must comply with the special operating requirements provided in "Alternative Methodology for Implementing Metals Controls" in Appendix IX of this part.

(5) Measurement of feed rates and production rate-(i) General requirements. Limits on each of the parameters specified in paragraph (b)(3) of this section (except for limits on metals concentrations in collected particulate matter (PM) for industrial furnaces that recycle collected PM) shall be established and continuously monitored under either of the following methods:

(A) Instantaneous limits. A limit for a parameter may be established and continuously monitored and recorded on an instantaneous basis (i.e., the value that occurs at any time) not to be exceeded at any time; or

(B) Hourly rolling average limits. A limit for a parameter may be established and continuously monitored on an hourly rolling average basis defined as follows:

(1) A continuous monitor is one which continuously samples the regulated parameter without interruption, and evaluates the detector response at least once each 15 seconds, and computes and records the average value at least every 60 seconds.

(2) An hourly rolling average is the arithmetic mean of the 60 most recent 1-minute average values recorded by the continuous monitoring system.

(ii) Rolling average limits for carcinogenic metals and lead. Feed rate limits for the carcinogenic metals (arsenic, beryllium, cadmium, and chromium) and lead may be established either on an hourly rolling average basis as prescribed by paragraph (b)(5)(i)(B) or on (up to) a 24 hour rolling average basis. If the owner or operator elects to use an averaging period from 2 to 24 hours:

(A) The feed rate of each metal shall be limited at any time to ten times the feed rate that would be allowed on an hourly rolling average basis;

(B) The continuous monitor shall meet the following specifications:

(1) A continuous monitor is one which continuously samples the regulated parameter without interruption, and evaluates the detector response at least once each 15 seconds, and computes and records the average value at least every 60 seconds.

(2) The rolling average for the selected averaging period is defined as the arithmetic mean of one hour block averages for the averaging period. A one hour block average is the arithmetic mean of the one minute averages recorded during the 60-minute period beginning at one minute after the beginning of preceding clock hour.

(iii) Feed rate limits for metals, total chloride and chlorine, and ash. Feed rate limits for metals, total chlorine and chloride, and ash are established and monitored by knowing the concentration of the substance (i.e., metals, chloride/chlorine, and ash) in each feedstream and the flow rate of the feedstream. To monitor the feed rate of these substances, the flow rate of each feedstream must be monitored under the continuous monitoring requirements of paragraphs (b)(5) (i) and (ii) of this section.

(6) Public notice requirements at precompliance. On or before August 21, 1991, the owner or operator must submit a notice with the following information for publication in a major local newspaper of general circulation and send a copy of the notice to the appropriate units of State and local government. The owner and operator must provide to the Secretary with the certification of precompliance evidence of submitting the notice for publication. The notice, which shall be entitled "Notice of Certification of Precompliance with Hazardous Waste Burning Requirements of 40 CFR 266.103(b)", must include:

(i) Name and address of the owner and operator of the facility as well as the location of the device burning hazardous waste;

(ii) Date that the certification of precompliance is submitted to the Secretary;

(iii) Brief description of the regulatory process required to comply with the interim status requirements of this section including required emissions testing to demonstrate conformance with emissions standards for organic compounds, particulate matter, metals, and HCl and Cl<sub>2</sub>;

(iv) Types and quantities of hazardous waste burned including, but not limited to, source, whether solids or liquids, as well as an appropriate description of the waste;

(v) Type of device(s) in which the hazardous waste is burned including a physical description and maximum production rate of each device;

(vi) Types and quantities of other fuels and industrial furnace feedstocks fed to each unit;

(vii) Brief description of the basis for this certification of precompliance as specified in paragraph (b)(2) of this section;

(viii) Locations where the record for the facility can be viewed and copied by interested parties. These records and locations shall at a minimum include:

(A) The administrative record kept by DNREC where the supporting documentation was submitted or another location designated by the Secretary; and

(B) The BIF correspondence file kept at the facility site where the device is located. The correspondence file must include all correspondence between the facility and the Secretary, State and local regulatory officials, including copies of all certifications and notifications, such as the precompliance certification, precompliance public notice, notice of compliance testing, compliance test report, compliance certification, time extension requests and approvals or denials, enforcement notifications of violations, and copies of EPA and State site visit reports submitted to the owner or operator.

(ix) Notification of the establishment of a facility mailing list whereby interested parties shall notify the DNREC that they wish to be placed on the mailing list to receive future information and notices about this facility; and

(x) Location (mailing address) of the DNREC Office, Hazardous Waste Branch, where further information can be obtained on regulation of hazardous waste burning.

(7) Monitoring other operating parameters. When the monitoring systems for the operating parameters listed in paragraphs (c)(1)(v through xiii) of this section are installed and operating in conformance with vendor specifications or (for CO, HC, and oxygen) specifications provided by Appendix IX of this part, as appropriate, the parameters shall be continuously monitored and records shall be maintained in the operating record.

(8) Revised certification of precompliance. The owner or operator may revise at any time the information and operating conditions documented under paragraphs (b)(2) and (b)(3) of this section in the certification of precompliance by submitting a revised certification of precompliance under procedures provided by those paragraphs.

(i) The public notice requirements of paragraph (b)(6) of this section do not apply to recertifications.

(ii) The owner and operator must operate the facility within the limits established for the operating parameters under paragraph (b)(3) of this section until a revised certification is submitted under this paragraph or a certification of compliance is submitted under paragraph (c) of this section.

(9) Certification of precompliance statement. The owner or operator must include the following signed statement with the certification of precompliance submitted to the Secretary:

"I certify under penalty of law that this information was prepared under my direction or supervision in accordance with a system designed to ensure that qualified personnel properly gathered and evaluated the information and supporting documentation. Copies of all emissions tests, dispersion modeling results and other information used to determine conformance with the requirements of §266.103(b) are available at the facility and can be obtained from the facility contact person listed above. Based on my inquiry of the person or persons who manages the facility, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

I also acknowledge that the operating limits established in this certification pursuant to §266.103(b) (3) and (4) are enforceable limits at which the facility can legally operate during interim status until: (1) A revised certification of precompliance is submitted, (2) a certification of compliance is submitted, or (3) an operating permit is issued."



(c) Certification of compliance. The owner or operator shall conduct emissions testing to document compliance with the emissions standards of §§ 266.104 (b) through (e), 266.105, 266.106, 266.107, and paragraph (a)(5)(i)(D) of this section, under the procedures prescribed by this paragraph, except under extensions of time provided by paragraph (c)(7). Based on the compliance test, the owner or operator shall submit to the Secretary on or before August 21, 1992 a complete and accurate "certification of compliance" (under paragraph (c)(4) of this section) with those emission standards establishing limits on the operating parameters specified in paragraph (c)(1).

(1) Limits on operating conditions. The owner or operator shall establish limits on the following parameters based on operations during the compliance test (under procedures prescribed in paragraph (c)(4)(iv) of this section) or as otherwise specified and include these limits with the certification of compliance. The boiler or industrial furnace must be operated in accordance with these operating limits and the applicable emissions standards of §§ 266.104(b) through (e), 266.105, 266.106, 266.107, and 266.103(a)(5)(i)(D) at all times when there is hazardous waste in the unit.

(i) Feed rate of total hazardous waste and (unless complying with the Tier I or Adjusted Tier I metals feed rate screening limits under §266.106 (b) or (e)), pumpable hazardous waste;

(ii) Feed rate of each metal in the following feedstreams:

(A) Total feedstreams, except that:

(1) Facilities that comply with Tier I or Adjusted Tier I metals feed rate screening limits may set their operating limits at the metals feed rate screening limits determined under §266.106(b) or (e); and

(2) Industrial furnaces that must comply with the alternative metals implementation approach under paragraph (c)(3)(ii) of this section must specify limits on the concentration of each metal in the collected particulate matter in lieu of feed rate limits for total feedstreams;

(B) Total hazardous waste feed (unless complying with the Tier I or Adjusted Tier I metals feed rate screening limits under §266.106(b) or (e)); and

(C) Total pumpable hazardous waste feed (unless complying with the Tier I or Adjusted Tier I metals feed rate screening limits under §266.106(b) or (e));

(iii) Total feed rate of chlorine and chloride in total feed streams, except that facilities that comply with Tier I or Adjusted Tier I feed rate screening limits may set their operating limits at the total chlorine and chloride feed rate screening limits determined under §266.107(b)(1) or (e);

(iv) Total feed rate of ash in total feed streams, except that the ash feed rate for cement kilns and light-weight aggregate kilns is not limited;

(v) Carbon monoxide concentration, and where required, hydrocarbon concentration in stack gas. When complying with the CO controls of §266.104(b), the CO limit is 100 ppmv, and when complying with the HC controls of §266.104(c), the HC limit is 20 ppmv. When complying with the CO controls of §266.104(c), the CO limit is established based on the compliance test;

(vi) Maximum production rate of the device in appropriate units when producing normal product, unless complying with the Tier I or Adjusted Tier I feed rate screening limits for chlorine under §266.107(b)(1) or (e) and for all metals under §266.106(b) or (e), and the uncontrolled particulate emissions do not exceed the standard under §266.105;

(vii) Maximum combustion chamber temperature where the temperature measurement is as close to the combustion zone as possible and is upstream of any quench water injection (unless complying with the Tier I or Adjusted Tier I metals feed rate screening limits under §266.106(b) or (e));

(viii) Maximum flue gas temperature entering a particulate matter control device (unless complying with Tier I or Adjusted Tier I metals feed rate screening limits under §266.106(b) or (e) and the total chlorine and chloride feed rate screening limits under §266.107(b) or (e));

(ix) For systems using wet scrubbers, including wet ionizing scrubbers (unless complying with the Tier I or Adjusted Tier I metals feed rate screening limits under §266.106(b) or (e) and the total chlorine and chloride feed rate screening limits under §266.107(b)(1) or (e));

(A) Minimum liquid to flue gas ratio;

(B) Minimum scrubber blowdown from the system or maximum suspended solids content of scrubber water; and

(C) Minimum pH level of the scrubber water;

(x) For systems using venturi scrubbers, the minimum differential gas pressure across the venturi (unless complying with the Tier I or Adjusted Tier I metals feed rate screening limits under §266.106(b) or (e) and the total chlorine and chloride feed rate screening limits under §266.107(b)(1) or (e));

(xi) For systems using dry scrubbers (unless complying with the Tier I or Adjusted Tier I metals feed rate screening limits under §266.106(b) or (e) and the total chlorine and chloride feed rate screening limits under §266.107(b)(1) or (e)):

(A) Minimum caustic feed rate; and

(B) Maximum flue gas flow rate;

(xii) For systems using wet ionizing scrubbers or electrostatic precipitators (unless complying with the Tier I or Adjusted Tier I metals feed rate screening limits under §266.106(b) or (e) and the total chlorine and chloride feed rate screening limits under §266.107(b)(1) or (e)):

(A) Minimum electrical power in kilovolt amperes (kVA) to the precipitator plates; and

(B) Maximum flue gas flow rate;

(xiii) For systems using fabric filters (baghouses), the minimum pressure drop (unless complying with the Tier I or Adjusted Tier I metals feed rate screening limits under §266.106(b) or (e) and the total chlorine and chloride feed rate screening limits under §266.107(b)(1) or (e)).

(2) Prior notice of compliance testing. At least 30 days prior to the compliance testing required by paragraph (c)(3) of this section, the owner or operator shall notify the Secretary and submit the following information:

(i) General facility information including:

(A) EPA facility ID number;

(B) Facility name, contact person, telephone number, and address;

(C) Person responsible for conducting compliance test, including company name, address, and telephone number, and a statement of qualifications;

(D) Planned date of the compliance test;

(ii) Specific information on each device to be tested including:

(A) Description of boiler or industrial furnace;

(B) A scaled plot plan showing the entire facility and location of the boiler or industrial furnace;

(C) A description of the air pollution control system;

(D) Identification of the continuous emission monitors that are installed, including:

(1) Carbon monoxide monitor;

(2) Oxygen monitor;

(3) Hydrocarbon monitor, specifying the minimum temperature of the system and, if the temperature is less than 150°C, an explanation of why a heated system is not used (see paragraph (c)(5) of this section) and a brief description of the sample gas conditioning system.

(E) Indication of whether the stack is shared with another device that will be in operation during the compliance test;

(F) Other information useful to an understanding of the system design or operation.

(iii) Information on the testing planned, including a complete copy of the test protocol and Quality Assurance/Quality Control (QA/QC) plan, and a summary description for each test providing the following information at a minimum:

(A) Purpose of the test (e.g., demonstrate compliance with emissions of particulate matter); and

(B) Planned operating conditions, including levels for each pertinent parameter specified in paragraph (c)(1) of this section.

(3) Compliance testing-(i) General. Compliance testing must be conducted under conditions for which the owner or operator has submitted a certification of precompliance under paragraph (b) of this section and under conditions established in the notification of compliance testing required by paragraph (c)(2) of this section. The owner or operator may seek approval on a case-by-case basis to use compliance data from one unit in lieu of testing a similar onsite unit. To support the request, the owner or operator must provide a comparison of the hazardous waste burned and other feedstreams, and the



design, operation, and maintenance of both the tested unit and similar unit. The Secretary shall provide written approval to use compliance test data in lieu of testing a similar unit if he finds that the hazardous wastes, the devices, and the operating conditions are sufficiently similar, and the data from the other compliance test is adequate to meet the requirements of §266.103(c).

(ii) Special requirements for industrial furnaces that recycle collected PM. Owners and operators of industrial furnaces that recycle back into the furnace particulate matter (PM) from the air pollution control system must comply with one of the following procedures for testing to determine compliance with the metals standards of §266.106(c) or (d):

(A) The special testing requirements prescribed in "Alternative Method for Implementing Metals Controls" in Appendix IX of this part; or

(B) Stack emissions testing for a minimum of 6 hours each day while hazardous waste is burned during interim status. The testing must be conducted when burning normal hazardous waste for that day at normal feed rates for that day and when the air pollution control system is operated under normal conditions. During interim status, hazardous waste analysis for metals content must be sufficient for the owner or operator to determine if changes in metals content may affect the ability of the facility to meet the metals emissions standards established under §266.106(c) or (d). Under this option, operating limits (under paragraph (c)(1) of this section) must be established during compliance testing under paragraph (c)(3) of this section only on the following parameters:

(1) Feed rate of total hazardous waste;

(2) Total feed rate of chlorine and chloride in total feed streams;

(3) Total feed rate of ash in total feed streams, except that the ash feed rate for cement kilns and light-weight aggregate kilns is not limited;

(4) Carbon monoxide concentration, and where required, hydrocarbon concentration in stack gas;

(5) Maximum production rate of the device in appropriate units when producing normal product;

or

(C) Conduct compliance testing to determine compliance with the metals standards to establish limits on the operating parameters of paragraph (c)(1) of this section only after the kiln system has been conditioned to enable it to reach equilibrium with respect to metals fed into the system and metals emissions. During conditioning, hazardous waste and raw materials having the same metals content as will be fed during the compliance test must be fed at the feed rates that will be fed during the compliance test.

(iii) Conduct of compliance testing. (A) If compliance with all applicable emissions standards of §§ 266.104 through 266.107 is not demonstrated simultaneously during a set of test runs, the operating conditions of additional test runs required to demonstrate compliance with remaining emissions standards must be as close as possible to the original operating conditions.

(B) Prior to obtaining test data for purposes of demonstrating compliance with the applicable emissions standards of §§ 266.104 through 266.107 or establishing limits on operating parameters under this section, the facility must operate under compliance test conditions for a sufficient period to reach steady-state operations. Industrial furnaces that recycle collected particulate matter back into the furnace and that comply with paragraphs (c)(3)(ii)(A) or (B) of this section, however, need not reach steady state conditions with respect to the flow of metals in the system prior to beginning compliance testing for metals.

(C) Compliance test data on the level of an operating parameter for which a limit must be established in the certification of compliance must be obtained during emissions sampling for the pollutant(s) (i.e., metals, PM, HCl/Cl<sub>2</sub>, organic compounds) for which the parameter must be established as specified by paragraph (c)(1) of this section.

(4) Certification of compliance. Within 90 days of completing compliance testing, the owner or operator must certify to the Secretary compliance with the emissions standards of §§ 266.104(b), (c), and (e), 266.105, 266.106, 266.107, and paragraph (a)(5)(i)(D) of this section. The certification of compliance must include the following information:

(i) General facility and testing information including:

- (A) EPA facility ID number;
- (B) Facility name, contact person, telephone number, and address;
- (C) Person responsible for conducting compliance testing, including company name, address, and telephone number, and a statement of qualifications;
- (D) Date(s) of each compliance test;
- (E) Description of boiler or industrial furnace tested;
- (F) Person responsible for quality assurance/quality control (QA/QC), title, and telephone number, and statement that procedures prescribed in the QA/QC plan submitted under §266.103(c)(2)(iii) have been followed, or a description of any changes and an explanation of why changes were necessary.
- (G) Description of any changes in the unit configuration prior to or during testing that would alter any of the information submitted in the prior notice of compliance testing under paragraph (c)(2) of this section, and an explanation of why the changes were necessary;
- (H) Description of any changes in the planned test conditions prior to or during the testing that alter any of the information submitted in the prior notice of compliance testing under paragraph (c)(2) of this section, and an explanation of why the changes were necessary; and
- (I) The complete report on results of emissions testing.
- (ii) Specific information on each test including:
  - (A) Purpose(s) of test (e.g., demonstrate conformance with the emissions limits for particulate matter, metals, HCl, Cl<sub>2</sub>, and CO)
  - (B) Summary of test results for each run and for each test including the following information:
    - (1) Date of run;
    - (2) Duration of run;
    - (3) Time-weighted average and highest hourly rolling average CO level for each run and for the test;
    - (4) Highest hourly rolling average HC level, if HC monitoring is required for each run and for the test;
    - (5) If dioxin and furan testing is required under §266.104(e), time-weighted average emissions for each run and for the test of chlorinated dioxin and furan emissions, and the predicted maximum annual average ground level concentration of the toxicity equivalency factor;
    - (6) Time-weighted average particulate matter emissions for each run and for the test;
    - (7) Time-weighted average HCl and Cl<sub>2</sub> emissions for each run and for the test;
    - (8) Time-weighted average emissions for the metals subject to regulation under §266.106 for each run and for the test; and
    - (9) QA/QC results.
  - (iii) Comparison of the actual emissions during each test with the emissions limits prescribed by §§ 266.104 (b), (c), and (e), 266.105, 266.106, and 266.107 and established for the facility in the certification of precompliance under paragraph (b) of this section.
  - (iv) Determination of operating limits based on all valid runs of the compliance test for each applicable parameter listed in paragraph (c)(1) of this section using either of the following procedures:
    - (A) Instantaneous limits. A parameter may be measured and recorded on an instantaneous basis (i.e., the value that occurs at any time) and the operating limit specified as the time-weighted average during all runs of the compliance test; or
    - (B) Hourly rolling average basis. (1) The limit for a parameter may be established and continuously monitored on an hourly rolling average basis defined as follows:
      - (i) A continuous monitor is one which continuously samples the regulated parameter without interruption, and evaluates the detector response at least once each 15 seconds, and computes and records the average value at least every 60 seconds.
      - (ii) An hourly rolling average is the arithmetic mean of the 60 most recent 1-minute average values recorded by the continuous monitoring system.
    - (2) The operating limit for the parameter shall be established based on compliance test data as the average over all test runs of the highest hourly rolling average value for each run.

(C) Rolling average limits for carcinogenic metals and lead. Feed rate limits for the carcinogenic metals (i.e., arsenic, beryllium, cadmium and chromium) and lead may be established either on an hourly rolling average basis as prescribed by paragraph (c)(4)(iv)(B) of this section or on (up to) a 24 hour rolling average basis. If the owner or operator elects to use an averaging period from 2 to 24 hours:

(1) The feed rate of each metal shall be limited at any time to ten times the feed rate that would be allowed on a hourly rolling average basis;

(2) The continuous monitor shall meet the following specifications:

(i) A continuous monitor is one which continuously samples the regulated parameter without interruption, and evaluates the detector response at least once each 15 seconds, and computes and records the average value at least every 60 seconds.

(ii) The rolling average for the selected averaging period is defined as the arithmetic mean of one hour block averages for the averaging period. A one hour block average is the arithmetic mean of the one minute averages recorded during the 60-minute period beginning at one minute after the beginning of preceding clock hour; and

(3) The operating limit for the feed rate of each metal shall be established based on compliance test data as the average over all test runs of the highest hourly rolling average feed rate for each run.

(D) Feed rate limits for metals, total chloride and chlorine, and ash. Feed rate limits for metals, total chlorine and chloride, and ash are established and monitored by knowing the concentration of the substance (i.e., metals, chloride/chlorine, and ash) in each feedstream and the flow rate of the feedstream. To monitor the feed rate of these substances, the flow rate of each feedstream must be monitored under the continuous monitoring requirements of paragraphs (c)(4)(iv) (A) through (C) of this section.

(v) Certification of compliance statement. The following statement shall accompany the certification of compliance:

"I certify under penalty of law that this information was prepared under my direction or supervision in accordance with a system designed to ensure that qualified personnel properly gathered and evaluated the information and supporting documentation. Copies of all emissions tests, dispersion modeling results and other information used to determine conformance with the requirements of §266.103(c) are available at the facility and can be obtained from the facility contact person listed above. Based on my inquiry of the person or persons who manages the facility, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

I also acknowledge that the operating conditions established in this certification pursuant to §266.103(c)(4)(iv) are enforceable limits at which the facility can legally operate during interim status until a revised certification of compliance is submitted."

(5) Special requirements for HC monitoring systems. When an owner or operator is required to comply with the hydrocarbon (HC) controls provided by §266.104(c) or paragraph (a)(5)(i)(D) of this section, a conditioned gas monitoring system may be used in conformance with specifications provided in Appendix IX of this part provided that the owner or operator submits a certification of compliance without using extensions of time provided by paragraph (c)(7) of this section. However, owners and operators of facilities electing to comply with the alternative hydrocarbon revision of §266.104(f) and requesting a time extension under §266.103(c)(7)(ii)(B) may establish the baseline HC level and comply with the interim HC limit established by the time extension using a conditioned gas monitoring system if the Director determines that the owner or operator has demonstrated that they have made a good faith effort to operate a heated monitoring system but found it to be impracticable.

(6) Special operating requirements for industrial furnaces that recycle collected PM. Owners and operators of industrial furnaces that recycle back into the furnace particulate matter (PM) from the air pollution control system must:

(i) When complying with the requirements of paragraph (c)(3)(ii)(A) of this section, comply with the operating requirements prescribed in "Alternative Method to Implement the Metals Controls" in Appendix IX of this part; and

(ii) When complying with the requirements of paragraph (c)(3)(ii)(B) of this section, comply with the operating requirements prescribed by that paragraph.

(7) Extensions of time. (i) If the owner or operator does not submit a complete certification of compliance for all of the applicable emissions standards of §§ 266.104, 266.105, 266.106, and 266.107 by August 21, 1992, he/she must either:

(A) Stop burning hazardous waste and begin closure activities under paragraph (I) of this section for the hazardous waste portion of the facility; or

(B) Limit hazardous waste burning only for purposes of compliance testing (and pretesting to prepare for compliance testing) a total period of 720 hours for the period of time beginning August 21, 1992, submit a notification to the Secretary by August 21, 1992 stating that the facility is operating under restricted interim status and intends to resume burning hazardous waste, and submit a complete certification of compliance by August 23, 1993; or

(C) Obtain a case-by-case extension of time under paragraph (c)(7)(ii) of this section.

(ii) The owner or operator may request a case-by-case extension of time to extend any time limit provided by paragraph (c) of this section if compliance with the time limit is not practicable for reasons beyond the control of the owner or operator.

(A) In granting an extension, the Secretary may apply conditions as the facts warrant to ensure timely compliance with the requirements of this section and that the facility operates in a manner that does not pose a hazard to human health and the environment;

(B) When an owner or operator requests an extension of time to enable the facility to comply with the alternative hydrocarbon provisions of §266.104(f) and obtain a DNREC operating permit because the facility cannot meet the HC limit of §266.104(c) of these regulations:

(1) The Secretary shall, in considering whether to grant the extension:

(i) Determine whether the owner and operator have submitted in a timely manner a complete Part B permit application that includes information required under §122.22(b) of these regulations; and

(iii) Consider whether the owner and operator have made a good faith effort to certify compliance with all other emission controls, including the controls on dioxins and furans of §266.104(e) and the controls on PM, metals, and HCl/Cl<sub>2</sub>.

(2) If an extension is granted, the Secretary shall, as a condition of the extension, require the facility to operate under flue gas concentration limits on CO and HC that, based on available information, including information in the Part B permit application, are baseline CO and HC levels as defined by §266.104(f)(1).

(8) Revised certification of compliance. The owner or operator may submit at any time a revised certification of compliance (recertification of compliance) under the following procedures:

(i) Prior to submittal of a revised certification of compliance, hazardous waste may not be burned for more than a total of 720 hours under operating conditions that exceed those established under a current certification of compliance, and such burning may be conducted only for purposes of determining whether the facility can operate under revised conditions and continue to meet the applicable emissions standards of §§ 266.104, 266.105, 266.106, and 266.107;

(ii) At least 30 days prior to first burning hazardous waste under operating conditions that exceed those established under a current certification of compliance, the owner or operator shall notify the Secretary and submit the following information:

(A) EPA facility ID number, and facility name, contact person, telephone number, and address;

(B) Operating conditions that the owner or operator is seeking to revise and description of the changes in facility design or operation that prompted the need to seek to revise the operating conditions;



(C) A determination that when operating under the revised operating conditions, the applicable emissions standards of §§ 266.104, 266.105, 266.106, and 266.107 are not likely to be exceeded. To document this determination, the owner or operator shall submit the applicable information required under paragraph (b)(2) of this section; and

(D) Complete emissions testing protocol for any pretesting and for a new compliance test to determine compliance with the applicable emissions standards of §§ 266.104, 266.105, 266.106, and 266.107 when operating under revised operating conditions. The protocol shall include a schedule of pre-testing and compliance testing. If the owner and operator revises the scheduled date for the compliance test, he/she shall notify the Secretary in writing at least 30 days prior to the revised date of the compliance test;

(iii) Conduct a compliance test under the revised operating conditions and the protocol submitted to the Secretary to determine compliance with the applicable emissions standards of §§ 266.104, 266.105, 266.106, and 266.107; and

(iv) Submit a revised certification of compliance under paragraph (c)(4) of this section.

(d) Periodic Recertifications. The owner or operator must conduct compliance testing and submit to the Secretary a recertification of compliance under provisions of paragraph (c) of this section within three years from submitting the previous certification or recertification. If the owner or operator seeks to recertify compliance under new operating conditions, he/she must comply with the requirements of paragraph (c)(8) of this section.

(e) Noncompliance with certification schedule. If the owner or operator does not comply with the interim status compliance schedule provided by paragraphs (b), (c), and (d) of this section, hazardous waste burning must terminate on the date that the deadline is missed, closure activities must begin under paragraph (l) of this section, and hazardous waste burning may not resume except under an operating permit issued under §122.66 of these regulations. For purposes of compliance with the closure provisions of paragraph (l) of this section and §§ 265.112(d)(2) and 265.113 of these regulations the boiler or industrial furnace has received "the known final volume of hazardous waste" on the date that the deadline is missed.

(f) Start-up and shut-down. Hazardous waste (except waste fed solely as an ingredient under the Tier I (or adjusted Tier I) feed rate screening limits for metals and chloride/chlorine) must not be fed into the device during start-up and shut-down of the boiler or industrial furnace, unless the device is operating within the conditions of operation specified in the certification of compliance.

(g) Automatic waste feed cutoff. During the compliance test required by paragraph (c)(3) of this section, and upon certification of compliance under paragraph (c) of this section, a boiler or industrial furnace must be operated with a functioning system that automatically cuts off the hazardous waste feed when the applicable operating conditions specified in paragraphs (c)(1) (i) and (v through xiii) of this section deviate from those established in the certification of compliance. In addition:

(1) To minimize emissions of organic compounds, the minimum combustion chamber temperature (or the indicator of combustion chamber temperature) that occurred during the compliance test must be maintained while hazardous waste or hazardous waste residues remain in the combustion chamber, with the minimum temperature during the compliance test defined as either:

(i) If compliance with the combustion chamber temperature limit is based on a hourly rolling average, the minimum temperature during the compliance test is considered to be the average over all runs of the lowest hourly rolling average for each run; or

(ii) If compliance with the combustion chamber temperature limit is based on an instantaneous temperature measurement, the minimum temperature during the compliance test is considered to be the time-weighted average temperature during all runs of the test; and

(2) Operating parameters limited by the certification of compliance must continue to be monitored during the cutoff, and the hazardous waste feed shall not be restarted until the levels of those parameters comply with the limits established in the certification of compliance.

(h) Fugitive emissions. Fugitive emissions must be controlled by:

(1) Keeping the combustion zone totally sealed against fugitive emissions; or

(2) Maintaining the combustion zone pressure lower than atmospheric pressure; or

(3) An alternate means of control that the owner or operator can demonstrate provide fugitive emissions control equivalent to maintenance of combustion zone pressure lower than atmospheric pressure. Support for such demonstration shall be included in the operating record.

(i) Changes. A boiler or industrial furnace must cease burning hazardous waste when changes in combustion properties, or feed rates of the hazardous waste, other fuels, or industrial furnace feedstocks, or changes in the boiler or industrial furnace design or operating conditions deviate from the limits specified in the certification of compliance.

(j) Monitoring and Inspections. (1) The owner or operator must monitor and record the following, at a minimum, while burning hazardous waste:

(i) Feed rates and composition of hazardous waste, other fuels, and industrial furnace feed stocks, and feed rates of ash, metals, and total chloride and chlorine as necessary to ensure conformance with the certification of precompliance or certification of compliance;

(ii) Carbon monoxide (CO), oxygen, and if applicable, hydrocarbons (HC), on a continuous basis at a common point in the boiler or industrial furnace downstream of the combustion zone and prior to release of stack gases to the atmosphere in accordance with the operating limits specified in the certification of compliance. CO, HC, and oxygen monitors must be installed, operated, and maintained in accordance with methods specified in Appendix IX of this part.

(iii) Upon the request of the Secretary, sampling and analysis of the hazardous waste (and other fuels and industrial furnace feed stocks as appropriate) and the stack gas emissions must be conducted to verify that the operating conditions established in the certification of precompliance or certification of compliance achieve the applicable standards of §§ 266.104, 266.105, 266.106, and 266.107.

(2) The boiler or industrial furnace and associated equipment (pumps, valves, pipes, fuel storage tanks, etc.) must be subjected to thorough visual inspection when they contain hazardous waste, at least daily for leaks, spills, fugitive emissions, and signs of tampering.

(3) The automatic hazardous waste feed cutoff system and associated alarms must be tested at least once every 7 days when hazardous waste is burned to verify operability, unless the owner or operator can demonstrate that weekly inspections will unduly restrict or upset operations and that less frequent inspections will be adequate. Support for such demonstration shall be included in the operating record. At a minimum, operational testing must be conducted at least once every 30 days.

(4) These monitoring and inspection data must be recorded and the records must be placed in the operating log.

(k) Recordkeeping. The owner or operator must keep in the operating record of the facility all information and data required by this section until closure of the boiler or industrial furnace unit.

(l) Closure. At closure, the owner or operator must remove all hazardous waste and hazardous waste residues (including, but not limited to, ash, scrubber waters, and scrubber sludges) from the boiler or industrial furnace and must comply with §§ 265.111-265.115 of these regulations.

(Amended July 26, 1994, August 1, 1995, August 21, 1997)

#### Section 266.104 Standards to control organic emissions.

(a) DRE standard-(1) General. Except as provided in paragraph (a)(3) of this section, a boiler or industrial furnace burning hazardous waste must achieve a destruction and removal efficiency (DRE) of 99.99% for all organic hazardous constituents in the waste feed. To demonstrate conformance with this requirement, 99.99% DRE must be demonstrated during a trial burn for each principal organic hazardous constituent (POHC) designated (under paragraph (a)(2) of this section) in its permit for each waste feed. DRE is determined for each POHC from the following equation:

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



where:

$W_{in}$  = Mass feed rate of one principal organic hazardous constituent (POHC) in the hazardous waste fired to the boiler or industrial furnace; and

$W_{out}$  = Mass emission rate of the same POHC present in stack gas prior to release to the atmosphere.

(2) Designation of POHCs. Principal organic hazardous constituents (POHCs) are those compounds for which compliance with the DRE requirements of this section shall be demonstrated in a trial burn in conformance with procedures prescribed in §122.66 of these regulations. One or more POHCs shall be designated by the Secretary for each waste feed to be burned. POHCs shall be designated based on the degree of difficulty of destruction of the organic constituents in the waste and on their concentrations or mass in the waste feed considering the results of waste analyses submitted with Part B of the permit application. POHCs are most likely to be selected from among those compounds listed in Part 261, Appendix VIII of these regulations that are also present in the normal waste feed. However, if the applicant demonstrates to the Secretary's satisfaction that a compound not listed in Appendix VIII or not present in the normal waste feed is a suitable indicator of compliance with the DRE requirements of this section, that compound may be designated as a POHC. Such POHCs need not be toxic or organic compounds.

(3) Dioxin-listed waste. A boiler or industrial furnace burning hazardous waste containing (or derived from) DNREC Hazardous Wastes Nos. F020, F021, F022, F023, F026, or F027 must achieve a destruction and removal efficiency (DRE) of 99.9999% for each POHC designated (under paragraph (a)(2) of this section) in its permit. This performance must be demonstrated on POHCs that are more difficult to burn than tetra-, penta-, and hexachlorodibenzo-p-dioxins and dibenzofurans. DRE is determined for each POHC from the equation in paragraph (a)(1) of this section. In addition, the owner or operator of the boiler or industrial furnace must notify the Secretary of intent to burn DNREC Hazardous Waste Nos. F020, F021, F022, F023, F026, or F027.

(4) Automatic waiver of DRE trial burn. Owners and operators of boilers operated under the special operating requirements provided by §266.110 are considered to be in compliance with the DRE standard of paragraph (a)(1) of this section and are exempt from the DRE trial burn.

(5) Low risk waste. Owners and operators of boilers or industrial furnaces that burn hazardous waste in compliance with the requirements of §266.109(a) are considered to be in compliance with the DRE standard of paragraph (a)(1) of this section and are exempt from the DRE trial burn.

(b) Carbon monoxide standard. (1) Except as provided in paragraph (c) of this section, the stack gas concentration of carbon monoxide (CO) from a boiler or industrial furnace burning hazardous waste cannot exceed 100 ppmv on an hourly rolling average basis (i.e., over any 60 minute period), continuously corrected to 7 percent oxygen, dry gas basis.

(2) CO and oxygen shall be continuously monitored in conformance with "Performance Specifications for Continuous Emission Monitoring of Carbon Monoxide and Oxygen for Incinerators, Boilers, and Industrial Furnaces Burning Hazardous Waste" in Appendix IX of this part.

(3) Compliance with the 100 ppmv CO limit must be demonstrated during the trial burn (for new facilities or an interim status facility applying for a permit) or the compliance test (for interim status facilities). To demonstrate compliance, the highest hourly rolling average CO level during any valid run of the trial burn or compliance test must not exceed 100 ppmv.

(c) Alternative carbon monoxide standard. (1) The stack gas concentration of carbon monoxide (CO) from a boiler or industrial furnace burning hazardous waste may exceed the 100 ppmv limit provided that stack gas concentrations of hydrocarbons (HC) do not exceed 20 ppmv, except as provided by paragraph (f) of this section for certain industrial furnaces.

(2) HC limits must be established under this section on an hourly rolling average basis (i.e., over any 60 minute period), reported as propane, and continuously corrected to 7 percent oxygen, dry gas basis.

(3) HC shall be continuously monitored in conformance with "Performance Specifications for Continuous Emission Monitoring of Hydrocarbons for Incinerators, Boilers, and Industrial Furnaces Burning Hazardous Waste" in Appendix IX of this part. CO and oxygen shall be continuously monitored in conformance with paragraph (b)(2) of this section.

(4) The alternative CO standard is established based on CO data during the trial burn (for a new facility) and the compliance test (for an interim status facility). The alternative CO standard is the average over all valid runs of the highest hourly average CO level for each run. The CO limit is implemented on an hourly rolling average basis, and continuously corrected to 7 percent oxygen, dry gas basis.

(d) Special requirements for furnaces. Owners and operators of industrial furnaces (e.g., kilns, cupolas) that feed hazardous waste for a purpose other than solely as an ingredient (see §266.103(a)(5)(ii)) at any location other than the end where products are normally discharged and where fuels are normally fired must comply with the hydrocarbon limits provided by paragraphs (c) or (f) of this section irrespective of whether stack gas CO concentrations meet the 100 ppmv limit of paragraph (b) of this section.

(e) Controls for dioxins and furans. Owners and operators of boilers and industrial furnaces that are equipped with a dry particulate matter control device that operates within the temperature range of 450-750 °F, and industrial furnaces operating under an alternative hydrocarbon limit established under paragraph (f) of this section must conduct a site-specific risk assessment as follows to demonstrate that emissions of chlorinated dibenzo-p-dioxins and dibenzofurans do not result in an increased lifetime cancer risk to the hypothetical maximum exposed individual (MEI) exceeding 1 in 100,000:

(1) During the trial burn (for new facilities or an interim status facility applying for a permit) or compliance test (for interim status facilities), determine emission rates of the tetra-octa congeners of chlorinated dibenzo-p-dioxins and dibenzofurans (CDDs/CDFs) using Method 23, "Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) from Stationary Sources", in Appendix IX of this part;

(2) Estimate the 2,3,7,8-TCDD toxicity equivalence of the tetra-octa CDDs/CDFs congeners using "Procedures for Estimating the Toxicity Equivalence of Chlorinated Dibenzo-p-Dioxin and Dibenzofuran Congeners" in Appendix IX of this part. Multiply the emission rates of CDD/CDF congeners with a toxicity equivalence greater than zero (see the procedure) by the calculated toxicity equivalence factor to estimate the equivalent emission rate of 2,3,7,8-TCDD;

(3) Conduct dispersion modeling using methods recommended in Appendix W of Part 51 of 40 CFR ("Guideline on Air Quality Models (Revised)" (1986) and its supplements), the "Hazardous Waste Combustion Air Quality Screening Procedure", provided in Appendix IX of this part, or in Screening Procedures for Estimating the Air Quality Impact of Stationary Sources, Revised (incorporated by reference in §260.11) to predict the maximum annual average off-site ground level concentration of 2,3,7,8-TCDD equivalents determined under paragraph (e)(2) of this section. The maximum annual average concentration must be used when a person resides on-site; and

(4) The ratio of the predicted maximum annual average ground level concentration of 2,3,7,8-TCDD equivalents to the risk-specific dose for 2,3,7,8-TCDD provided in Appendix V of this part ( $2.2 \times 10^{-7}$ ) shall not exceed 1.0.

(f) Alternative HC limit for furnaces with organic matter in raw material. For industrial furnaces that cannot meet the 20 ppmv HC limit because of organic matter in normal raw material, the Secretary may establish an alternative HC limit on a case-by-case basis (under a Part B permit proceeding) at a level that ensures that flue gas HC (and CO) concentrations when burning hazardous waste are not greater than when not burning hazardous waste (the baseline HC level) provided that the owner or operator complies with the following requirements. However, cement kilns equipped with a by-pass duct meeting the requirements of paragraph (g) of this section, are not eligible for an alternative HC limit.

(1) When the baseline HC (and CO) level is determined, the owner or operator must demonstrate that the facility is designed and operated to minimize hydrocarbon emissions from fuels and raw materials and that the facility is producing normal products under normal operating conditions feeding normal feedstocks and fuels. The baseline HC level is defined as the average over all valid test runs of the highest hourly rolling average HC value for each run when the facility does not burn hazardous waste, adjusted as appropriate to consider the variability of hydrocarbon levels under good combustion operating conditions. The baseline CO level is determined based on the test runs used to establish the baseline HC level and is defined as the average over all test runs of the highest hourly rolling average CO value for each run. More than one baseline level must be determined if the facility operates under different modes that may generate significantly lower HC (and CO) levels;

(2) The owner or operator must develop an approach to monitor over time changes in the operation of the facility that could reduce the baseline HC level;

(3) The owner or operator must conduct emissions testing during the trial burn to:

(i) Determine the baseline HC (and CO) level;

(ii) Demonstrate that, when hazardous waste is burned, HC (and CO) levels do not exceed the baseline level; and

(iii) Identify the types and concentrations of organic compounds listed in Appendix VIII, Part 261 of these regulations, that are emitted and conduct dispersion modeling to predict the maximum annual average ground level concentration of each organic compound. On-site ground level concentrations must be considered for this evaluation if a person resides on site.

(A) Sampling and analysis of organic emissions shall be conducted using procedures prescribed by the Secretary.

(B) Dispersion modeling shall be conducted according to procedures provided by paragraph (e)(3) of this section; and

(iv) Demonstrate that maximum annual average ground level concentrations of the organic compounds identified in paragraph (f)(3)(iii) of this section do not exceed the following levels:

(A) For the noncarcinogenic compounds listed in Appendix IV of this part, the levels established in Appendix IV;

(B) For the carcinogenic compounds listed in Appendix V of this part, the sum for all compounds of the ratios of the actual ground level concentration to the level established in Appendix V cannot exceed 1.0. To estimate the health risk from chlorinated dibenzo-p-dioxins and dibenzofuran congeners, use the procedures prescribed by paragraph (e)(2) of this section to estimate the 2,3,7,8-TCDD toxicity equivalence of the congeners.

(C) For compounds not listed in Appendix IV or V, 0.1 micrograms per cubic meter.

(4) All hydrocarbon levels specified under this paragraph are to be monitored and reported as specified in paragraphs (c)(1) and (c)(2) of this section.

(g) Monitoring CO and HC in the by-pass duct of a cement kiln. Cement kilns may comply with the carbon monoxide and hydrocarbon limits provided by paragraphs (b), (c), and (d) of this section by monitoring in the by-pass duct provided that:

(1) Hazardous waste is fired only into the kiln and not at any location downstream from the kiln exit relative to the direction of gas flow; and

(2) The by-pass duct diverts a minimum of 10% of kiln off-gas into the duct.

(h) Use of emissions test data to demonstrate compliance and establish operating limits. Compliance with the requirements of this section must be demonstrated simultaneously by emissions testing or during separate runs under identical operating conditions. Further, data to demonstrate compliance with the CO and HC limits of this section or to establish alternative CO or HC limits under this section must be obtained during the time that DRE testing, and where applicable, CDD/CDF testing under paragraph (e) of this section and comprehensive organic emissions testing under paragraph (f) is conducted.

(i) Enforcement. For the purposes of permit enforcement, compliance with the operating requirements specified in the permit (under §266.102) will be regarded as compliance with this section. However, evidence that compliance with those permit conditions is insufficient to ensure compliance with the requirements of this section may be "information" justifying modification or revocation and re-issuance of a permit under §122.41 of these regulations.

(Amended July 26, 1994, August 1, 1995, July 23, 1996)

#### Section 266.105 Standards to control particulate matter:

(a) A boiler or industrial furnace burning hazardous waste may not emit particulate matter in excess of 180 milligrams per dry standard cubic meter (0.08 grains per dry standard cubic foot) after correction to a stack gas concentration of 7% oxygen, using procedures prescribed in 40 CFR Part 60, Appendix A, methods 1 through 5, and Appendix IX of this part.

(b) An owner or operator meeting the requirements of §266.109(b) for the low risk waste exemption is exempt from the particulate matter standard.

(c) For the purposes of permit enforcement, compliance with the operating requirements specified in the permit (under §266.102) will be regarded as compliance with this section. However, evidence that compliance with those permit conditions is insufficient to ensure compliance with the requirements of this section may be "information" justifying modification or revocation and re-issuance of a permit under §122.41 of these regulations.

(Amended July 26, 1994)

#### Section 266.106 Standards to control metals emissions.

(a) General. The owner or operator must comply with the metals standards provided by paragraphs (b), (c), (d), (e), or (f) of this section for each metal listed in paragraph (b) of this section that is present in the hazardous waste at detectable levels using analytical procedures specified in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), incorporated by reference in §260.11 of these regulations.

(b) Tier I feed rate screening limits. Feed rate screening limits for metals are specified in Appendix I of this part as a function of terrain-adjusted effective stack height and terrain and land use in the vicinity of the facility. Criteria for facilities that are not eligible to comply with the screening limits are provided in paragraph (b)(7) of this section.

(1) Noncarcinogenic metals. The feed rates of antimony, barium, lead, mercury, thallium, and silver in all feed streams, including hazardous waste, fuels, and industrial furnace feed stocks shall not exceed the screening limits specified in Appendix I of this part.

(i) The feed rate screening limits for antimony, barium, mercury, thallium, and silver are based on either:

(A) An hourly rolling average as defined in §266.102(e)(6)(i)(B); or

(B) An instantaneous limit not to be exceeded at any time.

(ii) The feed rate screening limit for lead is based on one of the following:

(A) An hourly rolling average as defined in §266.102(e)(6)(i)(B);

(B) An averaging period of 2 to 24 hours as defined in §266.102(e)(6)(ii) with an instantaneous feed rate limit not to exceed 10 times the feed rate that would be allowed on an hourly rolling average basis; or

(C) An instantaneous limit not to be exceeded at any time.

(2) Carcinogenic metals. (i) The feed rates of arsenic, cadmium, beryllium, and chromium in all feed streams, including hazardous waste, fuels, and industrial furnace feed stocks shall not exceed values derived from the screening limits specified in Appendix I of this part. The feed rate of each of these metals is limited to a level such that the sum of the ratios of the actual feed rate to the feed rate screening limit specified in Appendix I shall not exceed 1.0, as provided by the following equation:



$$\sum_{i=1}^n \frac{AFR_{(i)}}{FRSL_{(i)}} \leq 1.0$$

where:

n = number of carcinogenic metals

AFR = actual feed rate to the device for metal "i"

FRSL = feed rate screening limit provided by Appendix I of this part for metal "i".

(ii) The feed rate screening limits for the carcinogenic metals are based on either:

(A) An hourly rolling average; or

(B) An averaging period of 2 to 24 hours as defined in §266.102(e)(6)(ii) with an instantaneous feed rate limit not to exceed 10 times the feed rate that would be allowed on an hourly rolling average basis.

(3) TESH. (i) The terrain-adjusted effective stack height is determined according to the following equation:

$$TESH = H_a + H_1 - Tr$$

where:

H<sub>a</sub> = Actual physical stack height

H<sub>1</sub> = Plume rise as determined from Appendix VI of this part as a function of stack flow rate and stack gas exhaust temperature.

Tr = Terrain rise within five kilometers of the stack.

(ii) The stack height (H<sub>a</sub>) may not exceed good engineering practice as specified in 40 CFR 51.100(ii).

(iii) If the TESH for a particular facility is not listed in the table in the appendices, the nearest lower TESH listed in the table shall be used. If the TESH is four meters or less, a value of four meters shall be used.

(4) Terrain type. The screening limits are a function of whether the facility is located in noncomplex or complex terrain. A device located where any part of the surrounding terrain within 5 kilometers of the stack equals or exceeds the elevation of the physical stack height (H<sub>a</sub>) is considered to be in complex terrain and the screening limits for complex terrain apply. Terrain measurements are to be made from U.S. Geological Survey 7.5-minute topographic maps of the area surrounding the facility.

(5) Land use. The screening limits are a function of whether the facility is located in an area where the land use is urban or rural. To determine whether land use in the vicinity of the facility is urban or rural, procedures provided in Appendices IX or X of this part shall be used.

(6) Multiple stacks. Owners and operators of facilities with more than one on-site stack from a boiler, industrial furnace, incinerator, or other thermal treatment unit subject to controls of metals emissions under a DNREC operating permit or interim status controls must comply with the screening limits for all such units assuming all hazardous waste is fed into the device with the worst-case stack based on dispersion characteristics. The worst-case stack is determined from the following equation as applied to each stack:

$$K = HVT$$

Where:

K = a parameter accounting for relative influence of stack height and plume rise;

H = physical stack height (meters);

V = stack gas flow rate (m<sup>3</sup>/second); and

T = exhaust temperature (°K).

The stack with the lowest value of K is the worst-case stack.

(7) Criteria for facilities not eligible for screening limits. If any criteria below are met, the Tier I and Tier II screening limits do not apply. Owners and operators of such facilities must comply with either the Tier III standards provided by paragraph (d) of this section or with the adjusted Tier I feed rate screening limits provided by paragraph (e) of this section.

- (i) The device is located in a narrow valley less than one kilometer wide;
- (ii) The device has a stack taller than 20 meters and is located such that the terrain rises to the physical height within one kilometer of the facility;
- (iii) The device has a stack taller than 20 meters and is located within five kilometers of a shoreline of a large body of water such as an ocean or large lake;
- (iv) The physical stack height of any stack is less than 2.5 times the height of any building within five building heights or five projected building widths of the stack and the distance from the stack to the closest boundary is within five building heights or five projected building widths of the associated building; or

(v) The Secretary determines that standards based on site-specific dispersion modeling are required.

(8) Implementation. The feed rate of metals in each feedstream must be monitored to ensure that the feed rate screening limits are not exceeded.

(c) Tier II emission rate screening limits. Emission rate screening limits are specified in Appendix I as a function of terrain-adjusted effective stack height and terrain and land use in the vicinity of the facility. Criteria for facilities that are not eligible to comply with the screening limits are provided in paragraph (b)(7) of this section.

(1) Noncarcinogenic metals. The emission rates of antimony, barium, lead, mercury, thallium, and silver shall not exceed the screening limits specified in Appendix I of this part.

(2) Carcinogenic metals. The emission rates of arsenic, cadmium, beryllium, and chromium shall not exceed values derived from the screening limits specified in Appendix I of this part. The emission rate of each of these metals is limited to a level such that the sum of the ratios of the actual emission rate to the emission rate screening limit specified in Appendix I shall not exceed 1.0, as provided by the following equation:

$$\sum_{i=1}^n \frac{AER_{(i)}}{ERSL_{(i)}} \leq 1.0$$

where: n = number of carcinogenic metals

AER = actual emission rate for metal "i"

ERSL = emission rate screening limit provided by Appendix I of this part for metal "i".

(3) Implementation. The emission rate limits must be implemented by limiting feed rates of the individual metals to levels during the trial burn (for new facilities or an interim status facility applying for a permit) or the compliance test (for interim status facilities). The feed rate averaging periods are the same as provided by paragraphs (b)(1)(i) and (ii) and (b)(2)(ii) of this section. The feed rate of metals in each feedstream must be monitored to ensure that the feed rate limits for the feedstreams specified under §§ 266.102 or 266.103 are not exceeded.

(4) Definitions and limitations. The definitions and limitations provided by paragraph (b) of this section for the following terms also apply to the Tier II emission rate screening limits provided by paragraph (c) of this section: terrain-adjusted effective stack height, good engineering practice stack height, terrain type, land use, and criteria for facilities not eligible to use the screening limits.

(5) Multiple stacks. (i) Owners and operators of facilities with more than one onsite stack from a boiler, industrial furnace, incinerator, or other thermal treatment unit subject to controls on metals emissions under a DNREC operating permit or interim status controls must comply with the emissions screening limits for any such stacks assuming all hazardous waste is fed into the device with the worst-case stack based on dispersion characteristics.

(ii) The worst-case stack is determined by procedures provided in paragraph (b)(6) of this section.  
 (iii) For each metal, the total emissions of the metal from those stacks shall not exceed the screening limit for the worst-case stack.

(d) Tier III and Adjusted Tier I site-specific risk assessment. The requirements of this paragraph apply to facilities complying with either the Tier III or Adjusted Tier I controls, except where specified otherwise.

(1) General. Conformance with the Tier III metals controls must be demonstrated by emissions testing to determine the emission rate for each metal. In addition, conformance with either the Tier III or Adjusted Tier I metals controls must be demonstrated by air dispersion modeling to predict the maximum annual average off-site ground level concentration for each dispersion modeling to predict the maximum annual average off-site ground level concentration for each metal, and a demonstration that acceptable ambient levels are not exceeded.

(2) Acceptable ambient levels. Appendices IV and V of this part list the acceptable ambient levels for purposes of this rule. Reference air concentrations (RACs) are listed for the noncarcinogenic metals and  $10^{-5}$  risk-specific doses (RSDs) are listed for the carcinogenic metals. The RSD for a metal is the acceptable ambient level for that metal provided that only one of the four carcinogenic metals is emitted. If more than one carcinogenic metal is emitted, the acceptable ambient level for the carcinogenic metals is a fraction of the RSD as described in paragraph (d)(3) of this section.

(3) Carcinogenic metals. For the carcinogenic metals, arsenic, cadmium, beryllium, and chromium, the sum of the ratios of the predicted maximum annual average off-site ground level concentrations (except that on-site concentrations must be considered if a person resides on site) to the risk-specific dose (RSD) for all carcinogenic metals emitted shall not exceed 1.0 as determined by the following equation:

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

where: n = number of carcinogenic metals

(4) Noncarcinogenic metals. For the noncarcinogenic metals, the predicted maximum annual average off-site ground level concentration for each metal shall not exceed the reference air concentration (RAC).

(5) Multiple stacks. Owners and operators of facilities with more than one on-site stack from a boiler, industrial furnace, incinerator, or other thermal treatment unit subject to controls on metals emissions under a DNREC operating permit or interim status controls must conduct emissions testing (except that facilities complying with Adjusted Tier I controls need not conduct emissions testing) and dispersion modeling to demonstrate that the aggregate emissions from all such on-site stacks do not result in an exceedance of the acceptable ambient levels.

(6) Implementation. Under Tier III, the metals controls must be implemented by limiting feed rates of the individual metals to levels during the trial burn (for new facilities or an interim status facility applying for a permit) or the compliance test (for interim status facilities). The feed rate averaging periods are the same as provided by paragraphs (b)(1) (i) and (ii) and (b)(2)(ii) of this section. The feed rate of metals in each feedstream must be monitored to ensure that the feed rate limits for the feedstreams specified under §§ 266.102 or 266.103 are not exceeded.

(e) Adjusted Tier I feed rate screening limits. The owner or operator may adjust the feed rate screening limits provided by Appendix I of this part to account for site-specific dispersion modeling. Under this approach, the adjusted feed rate screening limit for a metal is determined by back-calculating from the acceptable ambient level provided by Appendices IV and V of this part using dispersion modeling to determine the maximum allowable emission rate. This emission rate becomes the adjusted Tier I feed rate screening limit. The feed rate screening limits for carcinogenic metals are implemented as prescribed in paragraph (b)(2) of this section.

(f) Alternative implementation approaches. (1) The Secretary may approve on a case-by-case basis approaches to implement the Tier II or Tier III metals emission limits provided by paragraphs (c) or (d) of this section alternative to monitoring the feed rate of metals in each feedstream.

(2) The emission limits provided by paragraph (d) of this section must be determined as follows:

(i) For each noncarcinogenic metal, by back-calculating from the RAC provided in Appendix IV of this part to determine the allowable emission rate for each metal using the dilution factor for the maximum annual average ground level concentration predicted by dispersion modeling in conformance with paragraph (h) of this section; and

(ii) For each carcinogenic metal by:

(A) Back-calculating from the RSD provided in Appendix V of this part to determine the allowable emission rate for each metal if that metal were the only carcinogenic metal emitted using the dilution factor for the maximum annual average ground level concentration predicted by dispersion modeling in conformance with paragraph (h) of this section; and

(B) If more than one carcinogenic metal is emitted, selecting an emission limit for each carcinogenic metal not to exceed the emission rate determined by paragraph (f)(2)(ii)(A) of this section such that the sum for all carcinogenic metals of the ratios of the selected emission limit to the emission rate determined by that paragraph does not exceed 1.0.

(g) Emission testing-(1) General. Emission testing for metals shall be conducted using the Multiple Metals Train as described in Appendix IX of this part.

(2) Hexavalent chromium. Emissions of chromium are assumed to be hexavalent chromium unless the owner or operator conducts emissions testing to determine hexavalent chromium emissions using procedures prescribed in Appendix IX of this part.

(h) Dispersion Modeling. Dispersion modeling required under this section shall be conducted according to methods recommended in Appendix W of Part 51 of 40 CFR ("Guideline on Air Quality Models (Revised)" (1986) and its supplements), the "Hazardous Waste Combustion Air Quality Screening Procedure", provided in Appendix IX of this part, or in Screening Procedures for Estimating the Air Quality Impact of Stationary Sources, Revised (incorporated by reference in §260.11) to predict the maximum annual average off-site ground level concentration. However, on-site concentrations must be considered when a person resides on-site.

(i) Enforcement. For the purposes of permit enforcement, compliance with the operating requirements specified in the permit (under §266.102) will be regarded as compliance with this section. However, evidence that compliance with those permit conditions is insufficient to ensure compliance with the requirements of this section may be "information" justifying modification or revocation and re-issuance of a permit under §122.41 of these regulations.

(Amended July 26, 1994, August 1, 1995, July 23, 1996)

#### **Section 266.107 Standards to control hydrogen chloride (HCl) and chlorine gas (Cl<sub>2</sub>) emissions.**

(a) General. The owner or operator must comply with the hydrogen chloride (HCl) and chlorine (Cl<sub>2</sub>) controls provided by paragraph (b), (c), or (e) of this section.

(b) Screening limits-(1) Tier I feed rate screening limits. Feed rate screening limits are specified for total chlorine in Appendix II of this part as a function of terrain-adjusted effective stack height and terrain and land use in the vicinity of the facility. The feed rate of total chlorine and chloride, both organic and inorganic, in all feed streams, including hazardous waste, fuels, and industrial furnace feed stocks shall not exceed the levels specified.

(2) Tier II emission rate screening limits. Emission rate screening limits for HCl and Cl<sub>2</sub> are specified in Appendix III of this part as a function of terrain-adjusted effective stack height and terrain and land use in the vicinity of the facility. The stack emission rates of HCl and Cl<sub>2</sub> shall not exceed the levels specified.

(3) Definitions and limitations. The definitions and limitations provided by §266.106(b) for the following terms also apply to the screening limits provided by this paragraph: terrain-adjusted effective



stack height, good engineering practice stack height, terrain type, land use, and criteria for facilities not eligible to use the screening limits.

(4) Multiple stacks. Owners and operators of facilities with more than one on-site stack from a boiler, industrial furnace, incinerator, or other thermal treatment unit subject to controls on HCl or Cl<sub>2</sub> emissions under a DNREC operating permit or interim status controls must comply with the Tier I and Tier II screening limits for those stacks assuming all hazardous waste is fed into the device with the worst-case stack based on dispersion characteristics.

(i) The worst-case stack is determined by procedures provided in §266.106(b)(6).

(ii) Under Tier I, the total feed rate of chlorine and chloride to all subject devices shall not exceed the screening limit for the worst-case stack.

(iii) Under Tier II, the total emissions of HCl and Cl<sub>2</sub> from all subject stacks shall not exceed the screening limit for the worst-case stack.

(c) Tier III site-specific risk assessments-(1) General. Conformance with the Tier III controls must be demonstrated by emissions testing to determine the emission rate for HCl and Cl<sub>2</sub>, air dispersion modeling to predict the maximum annual average off-site ground level concentration for each compound, and a demonstration that acceptable ambient levels are not exceeded.

(2) Acceptable ambient levels. Appendix IV of this part lists the reference air concentrations (RACs) for HCl (7 micrograms per cubic meter) and Cl<sub>2</sub> (0.4 micrograms per cubic meter).

(3) Multiple stacks. Owners and operators of facilities with more than one on-site stack from a boiler, industrial furnace, incinerator, or other thermal treatment unit subject to controls on HCl or Cl<sub>2</sub> emissions under a DNREC operating permit or interim status controls must conduct emissions testing and dispersion modeling to demonstrate that the aggregate emissions from all such on-site stacks do not result in an exceedance of the acceptable ambient levels for HCl and Cl<sub>2</sub>.

(d) Averaging periods. The HCl and Cl<sub>2</sub> controls are implemented by limiting the feed rate of total chlorine and chloride in all feedstreams, including hazardous waste, fuels, and industrial furnace feed stocks. Under Tier I, the feed rate of total chloride and chlorine is limited to the Tier I Screening Limits. Under Tier II and Tier III, the feed rate of total chloride and chlorine is limited to the feed rates during the trial burn (for new facilities or an interim status facility applying for a permit) or the compliance test (for interim status facilities). The feed rate limits are based on either:

(1) An hourly rolling average as defined in §266.102(e)(6); or

(2) An instantaneous basis not to be exceeded at any time.

(e) Adjusted Tier I feed rate screening limits. The owner or operator may adjust the feed rate screening limit provided by Appendix II of this part to account for site-specific dispersion modeling. Under this approach, the adjusted feed rate screening limit is determined by back-calculating from the acceptable ambient level for Cl<sub>2</sub> provided by Appendix IV of this part using dispersion modeling to determine the maximum allowable emission rate. This emission rate becomes the adjusted Tier I feed rate screening limit.

(f) Emissions testing. Emissions testing for HCl and Cl<sub>2</sub> shall be conducted using the procedures described in Appendix IX of this part.

(g) Dispersion modeling. Dispersion modeling shall be conducted according to the provisions of §266.106(h).

(h) Enforcement. For the purposes of permit enforcement, compliance with the operating requirements specified in the permit (under §266.102) will be regarded as compliance with this section. However, evidence that compliance with those permit conditions is insufficient to ensure compliance with the requirements of this section may be "information" justifying modification or revocation and re-issuance of a permit under §122.41 of these regulations.

(Amended July 26, 1994, August 1, 1995)

## Section 266.108 Small quantity on-site burner exemption.

(a) Exempt quantities. Owners and operators of facilities that burn hazardous waste in an on-site boiler or industrial furnace are exempt from the requirements of this subpart provided that:

(1) The quantity of hazardous waste burned in a device for a calendar month does not exceed the limits provided in the following table based on the terrain-adjusted effective stack height as defined in §266.106(b)(3):

**Exempt Quantities for Small Quantity Burner Exemption**

Terrain-adjusted effective stack height of device (meters)	Allowable hazardous waste burning rate (gallons/month)	Terrain-adjusted effective stack height of device (meters)	Allowable hazardous waste burning rate (Gallons/month)
0 to 3.9	0	40.0 to 44.9	210
4.0 to 5.9	13	45.0 to 49.9	260
6.0 to 7.9	18	50.0 to 54.9	330
8.0 to 9.9	27	55.0 to 59.9	400
10.0 to 11.9	40	60.0 to 64.9	490
12.0 to 13.9	48	65.0 to 69.9	610
14.0 to 15.9	59	70.0 to 74.9	680
16.0 to 17.9	69	75.0 to 79.9	760
18.0 to 19.9	76	80.0 to 84.9	850
20.0 to 21.9	84	85.0 to 89.9	960
22.0 to 23.9	93	90.0 to 94.9	1,100
24.0 to 25.9	100	95.0 to 99.9	1,200
26.0 to 27.9	110	100.0 to 104.9	1,300
28.0 to 29.9	130	105.0 to 109.9	1,500
30.0 to 34.9	140	110.0 to 114.9	1,700
35.0 to 39.9	170	115.0 or greater	1,900

(2) The maximum hazardous waste firing rate does not exceed at any time 1 percent of the total fuel requirements for the device (hazardous waste plus other fuel) on a total heat input or mass input basis, whichever results in the lower mass feed rate of hazardous waste.

(3) The hazardous waste has a minimum heating value of 5,000 Btu/lb, as generated; and

(4) The hazardous waste fuel does not contain (and is not derived from) DNREC Hazardous Waste Nos. F020, F021, F022, F023, F026, or F027.

(b) Mixing with nonhazardous fuels. If hazardous waste fuel is mixed with a nonhazardous fuel, the quantity of hazardous waste before such mixing is used to comply with paragraph (a).

(c) Multiple stacks. If an owner or operator burns hazardous waste in more than one on-site boiler or industrial furnace exempt under this section, the quantity limits provided by paragraph (a)(1) of this section are implemented according to the following equation:

$$\sum_{i=1}^n \frac{\text{Actual Quantity Burned}_{(i)}}{\text{Allowable Quantity Burned}_{(i)}} \leq 1.0$$

where:

n means the number of stacks;

Actual Quantity Burned means the waste quantity burned per month in device "i";

Allowable Quantity Burned means the maximum allowable exempt quantity for stack "i" from the table in (a)(1) above.

Note: Hazardous wastes that are subject to the special requirements for small quantity generators under §261.5 of these regulations may be burned in an off-site device under the exemption provided by §266.108, but must be included in the quantity determination for the exemption.

(d) Notification requirements. The owner or operator of facilities qualifying for the small quantity burner exemption under this section must provide a one-time signed, written notice to DNREC indicating the following:

- (1) The combustion unit is operating as a small quantity burner of hazardous waste;
- (2) The owner and operator are in compliance with the requirements of this section; and
- (3) The maximum quantity of hazardous waste that the facility may burn per month as provided by §266.108(a)(1).

(e) Recordkeeping requirements. The owner or operator must maintain at the facility for at least three years sufficient records documenting compliance with the hazardous waste quantity, firing rate, and heating value limits of this section. At a minimum, these records must indicate the quantity of hazardous waste and other fuel burned in each unit per calendar month, and the heating value of the hazardous waste.

(Amended July 26, 1994, August 1, 1995)

#### Section 266.109 Low risk waste exemption.

(a) Waiver of DRE standard. The DRE standard of §266.104(a) does not apply if the boiler or industrial furnace is operated in conformance with (a)(1) of this section and the owner or operator demonstrates by procedures prescribed in (a)(2) of this section that the burning will not result in unacceptable adverse health effects.

(1) The device shall be operated as follows:

(i) A minimum of 50 percent of fuel fired to the device shall be fossil fuel, fuels derived from fossil fuel, tall oil, or, if approved by the Secretary on a case-by-case basis, other nonhazardous fuel with combustion characteristics comparable to fossil fuel. Such fuels are termed "primary fuel" for purposes of this section. (Tall oil is a fuel derived from vegetable and rosin fatty acids.) The 50 percent primary fuel firing rate shall be determined on a total heat or mass input basis, whichever results in the greater mass feed rate of primary fuel fired;

(ii) Primary fuels and hazardous waste fuels shall have a minimum as-fired heating value of 8,000 Btu/lb;

(iii) The hazardous waste is fired directly into the primary fuel flame zone of the combustion chamber; and

(iv) The device operates in conformance with the carbon monoxide controls provided by §266.104(b)(1). Devices subject to the exemption provided by this section are not eligible for the alternative carbon monoxide controls provided by §266.104(c).

(2) Procedures to demonstrate that the hazardous waste burning will not pose unacceptable adverse public health effects are as follows:

(i) Identify and quantify those nonmetal compounds listed in Appendix VIII, Part 261 of these regulations that could reasonably be expected to be present in the hazardous waste. The constituents excluded from analysis must be identified and the basis for their exclusion explained;

(ii) Calculate reasonable, worst case emission rates for each constituent identified in paragraph (a)(2)(i) of this section by assuming the device achieves 99.9 percent destruction and removal efficiency. That is, assume that 0.1 percent of the mass weight of each constituent fed to the device is emitted.

(iii) For each constituent identified in paragraph (a)(2)(i) of this section, use emissions dispersion modeling to predict the maximum annual average ground level concentration of the constituent.

(A) Dispersion modeling shall be conducted using methods specified in §266.106(h).

(B) Owners and operators of facilities with more than one on-site stack from a boiler or industrial furnace that is exempt under this section must conduct dispersion modeling of emissions from all stacks exempt under this section to predict ambient levels prescribed by this paragraph.

(iv) Ground level concentrations of constituents predicted under paragraph (a)(2)(iii) of this section must not exceed the following levels:

(A) For the noncarcinogenic compounds listed in Appendix IV of this part, the levels established in Appendix IV;

(B) For the carcinogenic compounds listed in Appendix V of this part, the sum for all constituents of the ratios of the actual ground level concentration to the level established in Appendix V cannot exceed 1.0; and

(C) For constituents not listed in Appendix IV or V, 0.1 micrograms per cubic meter.

(b) Waiver of particular matter standard. The particulate matter standard of §266.105 does not apply if:

(1) The DRE standard is waived under paragraph (a) of this section; and

(2) The owner or operator complies with the Tier I or adjusted Tier I metals feed rate screening limits provided by §266.106(b) or (e).

(Amended July 26, 1994)

#### **Section 266.110 Waiver of DRE trial burn for boilers.**

Boilers that operate under the special requirements of this section, and that do not burn hazardous waste containing (or derived from) DNREC Hazardous Waste Nos. F020, F021, F022, F023, F026, or F027, are considered to be in conformance with the DRE standard of §266.104(a), and a trial burn to demonstrate DRE is waived. When burning hazardous waste:

(a) A minimum of 50 percent of fuel fired to the device shall be fossil fuel, fuels derived from fossil fuel, tall oil, or, if approved by the Secretary on a case-by-case basis, other nonhazardous fuel with combustion characteristics comparable to fossil fuel. Such fuels are termed "primary fuel" for purposes of this section. (Tall oil is a fuel derived from vegetable and rosin fatty acids.) The 50 percent primary fuel firing rate shall be determined on a total heat or mass input basis, whichever results in the greater mass feed rate of primary fuel fired;

(b) Boiler load shall not be less than 40 percent. Boiler load is the ratio at any time of the total heat input to the maximum design heat input;

(c) Primary fuels and hazardous waste fuels shall have a minimum as-fired heating value of 8,000 Btu/lb, and each material fired in a burner where hazardous waste is fired must have a heating value of at least 8,000 Btu/lb, as-fired;

(d) The device shall operate in conformance with the carbon monoxide standard provided by §266.104(b)(1). Boilers subject to the waiver of the DRE trial burn provided by this section are not eligible for the alternative carbon monoxide standard provided by §266.104(c);

(e) The boiler must be a watertube type boiler that does not feed fuel using a stoker or stoker type mechanism; and

(f) The hazardous waste shall be fired directly into the primary fuel flame zone of the combustion chamber with an air or steam atomization firing system, mechanical atomization system, or a rotary cup atomization system under the following conditions:

(1) Viscosity. The viscosity of the hazardous waste fuel as-fired shall not exceed 300 SSU;

(2) Particle size. When a high pressure air or steam atomizer, low pressure atomizer, or mechanical atomizer is used, 70% of the hazardous waste fuel must pass through a 200 mesh (74 micron) screen, and when a rotary cup atomizer is used, 70% of the hazardous waste must pass through a 100 mesh (150 micron) screen;

(3) Mechanical atomization systems. Fuel pressure within a mechanical atomization system and fuel flow rate shall be maintained within the design range taking into account the viscosity and volatility of the fuel;

(4) Rotary cup atomization systems. Fuel flow rate through a rotary cup atomization system must be maintained within the design range taking into account the viscosity and volatility of the fuel.

(Amended July 26, 1994)



## Section 266.111 Standards for direct transfer.

(a) Applicability. The regulations in this section apply to owners and operators of boilers and industrial furnaces subject to §§ 266.102 or 266.103 if hazardous waste is directly transferred from a transport vehicle to a boiler or industrial furnace without the use of a storage unit.

(b) Definitions. (1) When used in this section, the following terms have the meanings given below:

"Direct transfer equipment" means any device (including but not limited to, such devices as piping, fittings, flanges, valves, and pumps) that is used to distribute, meter, or control the flow of hazardous waste between a container (i.e., transport vehicle) and a boiler or industrial furnace.

"Container" means any portable device in which hazardous waste is transported, stored, treated, or otherwise handled, and includes transport vehicles that are containers themselves (e.g., tank trucks, tanker-trailers, and rail tank cars), and containers placed on or in a transport vehicle.

(2) This section references several requirements provided in Subparts I and J of Parts 264 and 265. For purposes of this section, the term "tank systems" in those referenced requirements means direct transfer equipment as defined in paragraph (b)(1) of this section.

(c) General operating requirements. (1) No direct transfer of a pumpable hazardous waste shall be conducted from an open-top container to a boiler or industrial furnace.

(2) Direct transfer equipment used for pumpable hazardous waste shall always be closed, except when necessary to add or remove the waste, and shall not be opened, handled, or stored in a manner that may cause any rupture or leak.

(3) The direct transfer of hazardous waste to a boiler or industrial furnace shall be conducted so that it does not:

- (i) Generate extreme heat or pressure, fire, explosion, or violent reaction;
- (ii) Produce uncontrolled toxic mists, fumes, dusts, or gases in sufficient quantities to threaten human health;
- (iii) Produce uncontrolled flammable fumes or gases in sufficient quantities to pose a risk of fire or explosions;
- (iv) Damage the structural integrity of the container or direct transfer equipment containing the waste;
- (v) Adversely affect the capability of the boiler or industrial furnace to meet the standards provided by §§ 266.104 through 266.107; or
- (vi) Threaten human health or the environment.

(4) Hazardous waste shall not be placed in direct transfer equipment, if it could cause the equipment or its secondary containment system to rupture, leak, corrode, or otherwise fail.

(5) The owner or operator of the facility shall use appropriate controls and practices to prevent spills and overflows from the direct transfer equipment or its secondary containment systems. These include at a minimum:

- (i) Spill prevention controls (e.g., check valves, dry discount couplings); and
  - (ii) Automatic waste feed cutoff to use if a leak or spill occurs from the direct transfer equipment.
- (d) Areas where direct transfer vehicles (containers) are located. Applying the definition of container under this section, owners and operators must comply with the following requirements:

- (1) The containment requirements of §264.175 of these regulations;
- (2) The use and management requirements of Subpart I, Part 265 of these regulations, except for §§ 265.170 and 265.174, and except that in lieu of the special requirements of §265.176 for ignitable or reactive waste, the owner or operator may comply with the requirements for the maintenance of protective distances between the waste management area and any public ways, streets, alleys, or an adjacent property line that can be built upon as required in Tables 2-1 through 2-6 of the National Fire Protection Association's (NFPA) "Flammable and Combustible Liquids Code," (1977 or 1981), (incorporated by reference, see §260.11). The owner or operator must obtain and keep on file at the facility a written certification by the local Fire Marshall that the installation meets the subject NFPA codes; and

(3) The closure requirements of §264.178 of these regulations.

(e) Direct transfer equipment. Direct transfer equipment must meet the following requirements:

(1) Secondary containment. Owners and operators shall comply with the secondary containment requirements of §265.193 of these regulations, except for paragraphs 265.193 (a), (d), (e), and (i) as follows:

(i) For all new direct transfer equipment, prior to their being put into service; and

(ii) For existing direct transfer equipment within 2 years after August 21, 1991.

(2) Requirements prior to meeting secondary containment requirements. (i) For existing direct transfer equipment that does not have secondary containment, the owner or operator shall determine whether the equipment is leaking or is unfit for use. The owner or operator shall obtain and keep on file at the facility a written assessment reviewed and certified by a qualified, registered professional engineer in accordance with §122.11(d) of these regulations that attests to the equipment's integrity by August 21, 1992.

(ii) This assessment shall determine whether the direct transfer equipment is adequately designed and has sufficient structural strength and compatibility with the waste(s) to be transferred to ensure that it will not collapse, rupture, or fail. At a minimum, this assessment shall consider the following:

(A) Design standard(s), if available, according to which the direct transfer equipment was constructed;

(B) Hazardous characteristics of the waste(s) that have been or will be handled;

(C) Existing corrosion protection measures;

(D) Documented age of the equipment, if available, (otherwise, an estimate of the age); and

(E) Results of a leak test or other integrity examination such that the effects of temperature variations, vapor pockets, cracks, leaks, corrosion, and erosion are accounted for.

(iii) If, as a result of the assessment specified above, the direct transfer equipment is found to be leaking or unfit for use, the owner or operator shall comply with the requirements of §§ 265.196 (a) and (b) of these regulations.

(3) Inspections and recordkeeping. (i) The owner or operator must inspect at least once each operating hour when hazardous waste is being transferred from the transport vehicle (container) to the boiler or industrial furnace:

(A) Overfill/spill control equipment (e.g., waste-feed cutoff systems, bypass systems, and drainage systems) to ensure that it is in good working order;

(B) The above ground portions of the direct transfer equipment to detect corrosion, erosion, or releases of waste (e.g., wet spots, dead vegetation); and

(C) Data gathered from monitoring equipment and leak-detection equipment, (e.g., pressure and temperature gauges) to ensure that the direct transfer equipment is being operated according to its design.

(ii) The owner or operator must inspect cathodic protection systems, if used, to ensure that they are functioning properly according to the schedule provided by §265.195(b) of these regulations.

(iii) Records of inspections made under this paragraph shall be maintained in the operating record at the facility, and available for inspection for at least 3 years from the date of the inspection.

(4) Design and installation of new ancillary equipment. Owners and operators must comply with the requirements of §265.192 of these regulations.

(5) Response to leaks or spills. Owners and operators must comply with the requirements of §265.196 of these regulations.

(6) Closure. Owners and operators must comply with the requirements of §265.197 of these regulations, except for §265.197 (c)(2) through (c)(4).

(Amended July 26, 1994)

**Section 266.112 Regulation of residues.**

A residue derived from the burning or processing of hazardous waste in a boiler or industrial furnace is not excluded from the definition of a hazardous waste under §261.4(b) (4), (7), or (8) unless the device and the owner or operator meet the following requirements:

(a) The device meets the following criteria:

(1) Boilers. Boilers must burn at least 50% coal on a total heat input or mass input basis, whichever results in the greater mass feed rate of coal;

(2) Ore or mineral furnaces. Industrial furnaces subject to §261.4(b)(7) must process at least 50% by weight normal, nonhazardous raw materials;

(3) Cement kilns. Cement kilns must process at least 50% by weight normal cement-production raw materials;

(b) The owner or operator demonstrates that the hazardous waste does not significantly affect the residue by demonstrating conformance with either of the following criteria:

(1) Comparison of waste-derived residue with normal residue. The waste-derived residue must not contain Appendix VIII, Part 261 constituents (toxic constituents) that could reasonably be attributable to the hazardous waste at concentrations significantly higher than in residue generated without burning or processing of hazardous waste, using the following procedure. Toxic compounds that could reasonably be attributable to burning or processing the hazardous waste (constituents of concern) include toxic constituents in the hazardous waste, and the organic compounds listed in Appendix VIII of this part that may be generated as products of incomplete combustion. Sampling and analyses shall be in conformance with procedures prescribed in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, incorporated by reference in §260.11(a) of these regulations.

(i) Normal residue. Concentrations of toxic constituents of concern in normal residue shall be determined based on analyses of a minimum of 10 samples representing a minimum of 10 days of operation. Composite samples may be used to develop a sample for analysis provided that the compositing period does not exceed 24 hours. The upper tolerance limit (at 95% confidence with a 95% proportion of the sample distribution) of the concentration in the normal residue shall be considered the statistically-derived concentration in the normal residue. If changes in raw materials or fuels reduce the statistically-derived concentrations of the toxic constituents of concern in the normal residue, the statistically-derived concentrations must be revised or statistically-derived concentrations of toxic constituents in normal residue must be established for a new mode of operation with the new raw material or fuel. To determine the upper tolerance limit in the normal residue, the owner or operator shall use statistical procedures prescribed in "Statistical Methodology for Bevill Residue Determinations" in Appendix IX of this part.

(ii) Waste-derived residue. Waste-derived residue shall be sampled and analyzed as often as necessary to determine whether the residue generated during each 24-hour period has concentrations of toxic constituents that are higher than the concentrations established for the normal residue under paragraph (b)(1)(i) of this section. If so, hazardous waste burning has significantly affected the residue and the residue shall not be excluded from the definition of a hazardous waste. Concentrations of toxic constituents of concern in the waste-derived residue shall be determined based on analysis of one or more samples obtained over a 24-hour period. Multiple samples may be analyzed, and multiple samples may be taken to form a composite sample for analysis provided that the sampling period does not exceed 24 hours. If more than one sample is analyzed to characterize waste-derived residues generated over a 24-hour period, the concentration of each toxic constituent shall be the arithmetic mean of the concentrations in the samples. No results may be disregarded; or

(2) Comparison of waste-derived residue concentrations with health-based limits.

(i) Nonmetal constituents. The concentration of each nonmetal toxic constituent of concern (specified in paragraph (b)(1) of this section) in the waste-derived residue must not exceed the health-based level specified in Appendix VII of this part, or the level of detection (using analytical procedures prescribed in SW-846), whichever is higher. If a health-based limit for a constituent of concern is not

listed in Appendix VII of this part, then a limit of 0.002 micrograms per kilogram or the level of detection (using analytical procedures prescribed in SW-846), whichever is higher, shall be used. The levels specified in Appendix VII of this part (and the default level of 0.002 micrograms per kilogram or the level of detection for constituents as identified in Note 1 of Appendix VII of this part) are administratively stayed under the condition, for those constituents specified in paragraph (b)(1) of this section, that the owner or operator complies with alternative levels defined as the land disposal restriction limits specified in §268.43 of these regulations for F039 nonwastewaters. In complying with those alternative levels, if an owner or operator is unable to detect a constituent despite documenting use of best good-faith efforts as defined by applicable DNREC guidance or standards, the owner or operator is deemed to be in compliance for that constituent. Until new guidance or standards are developed, the owner or operator may demonstrate such good-faith efforts by achieving a detection limit for the constituent that does not exceed an order of magnitude above the level provided by §268.43 for F039 nonwastewaters.

(ii) Metal constituents. The concentration of metals in an extract obtained using the Toxicity Characteristic Leaching Procedure of §261.24 of these regulations must not exceed the levels specified in Appendix VII of this part; and

(iii) Sampling and analysis. Waste-derived residue shall be sampled and analyzed as often as necessary to determine whether the residue generated during each 24-hour period has concentrations of toxic constituents that are higher than the health-based levels. Concentrations of toxic constituents of concern in the waste-derived residue shall be determined based on analysis of one or more samples obtained over a 24-hour period. Multiple samples may be analyzed, and multiple samples may be taken to form a composite sample for analysis provided that the sampling period does not exceed 24 hours. If more than one sample is analyzed to characterize waste-derived residues generated over a 24-hour period, the concentration of each toxic constituent shall be the arithmetic mean of the concentrations in the samples. No results may be disregarded; and

(c) Records sufficient to document compliance with the provisions of this section shall be retained until closure of the boiler or industrial furnace unit. At a minimum, the following shall be recorded.

(1) Levels of constituents in Appendix VIII, Part 261, that are present in waste-derived residues;

(2) If the waste-derived residue is compared with normal residue under paragraph (b)(1) of this section:

(i) The levels of constituents in Appendix VIII, Part 261, that are present in normal residues; and

(ii) Data and information, including analyses of samples as necessary, obtained to determine if changes in raw materials or fuels would reduce the concentration of toxic constituents of concern in the normal residue.

(Amended July 26, 1994, August 1, 1995, July 23, 1996, August 21, 1997)

#### Appendix I. - Tier I and Tier II Feed Rate and Emissions Screening Limits for Metals

Table I-A. - Tier I and Tier II Feed Rate and Emissions Screening Limits for Noncarcinogenic Metals for Facilities in Noncomplex Terrain

[Values for urban areas]

Terrain adjusted eff. stack ht. (m)	Antimony (g/hr)	Barium (g/hr)	Lead (g/hr)	Mercury (g/hr)	Silver (g/hr)	Thallium (g/hr)
4	6.0E+01	1.0E+04	1.8E+01	6.0E+01	6.0E+02	6.0E+01
6	6.8E+01	1.1E+04	2.0E+01	6.8E+01	6.8E+02	6.8E+01
8	7.6E+01	1.3E+04	2.3E+01	7.6E+01	7.6E+02	7.6E+01
10	8.6E+01	1.4E+04	2.6E+01	8.6E+01	8.6E+02	8.6E+01
12	9.6E+01	1.7E+04	3.0E+01	9.6E+01	9.6E+02	9.6E+01
14	1.1E+02	1.8E+04	3.4E+01	1.1E+02	1.1E+03	1.1E+02



16	1.3E+02	2.1E+04	3.6E+01	1.3E+02	1.3E+03	1.3E+02
18	1.4E+02	2.4E+04	4.3E+01	1.4E+02	1.4E+03	1.4E+02
20	1.6E+02	2.7E+04	4.6E+01	1.6E+02	1.6E+03	1.6E+02
22	1.8E+02	3.0E+04	5.4E+01	1.8E+02	1.8E+03	1.8E+02
24	2.0E+02	3.4E+04	6.0E+01	2.0E+02	2.0E+03	2.0E+02
26	2.3E+02	3.9E+04	6.8E+01	2.3E+02	2.3E+03	2.3E+02
28	2.6E+02	4.3E+04	7.8E+01	2.6E+02	2.6E+03	2.6E+02
30	3.0E+02	5.0E+04	9.0E+01	3.0E+02	3.0E+03	3.0E+02
35	4.0E+02	6.6E+04	1.1E+02	4.0E+02	4.0E+03	4.0E+02
40	4.6E+02	7.8E+04	1.4E+02	4.6E+02	4.6E+03	4.6E+02
45	6.0E+02	1.0E+05	1.8E+02	6.0E+02	6.0E+03	6.0E+02
50	7.8E+02	1.3E+05	2.3E+02	7.8E+02	7.8E+03	7.8E+02
55	9.6E+02	1.7E+05	3.0E+02	9.6E+02	9.6E+03	9.6E+02
60	1.2E+03	2.0E+05	3.6E+02	1.2E+03	1.2E+04	1.2E+03
65	1.5E+03	2.5E+05	4.3E+02	1.5E+03	1.5E+04	1.5E+03
70	1.7E+03	2.8E+05	5.0E+02	1.7E+03	1.7E+04	1.7E+03
75	1.9E+03	3.2E+05	5.8E+02	1.9E+03	1.9E+04	1.9E+03
80	2.2E+03	3.6E+05	6.4E+02	2.2E+03	2.2E+04	2.2E+03
85	2.5E+03	4.0E+05	7.6E+02	2.5E+03	2.5E+04	2.5E+03
90	2.8E+03	4.6E+05	8.2E+02	2.8E+03	2.8E+04	2.8E+03
95	3.2E+03	5.4E+05	9.6E+02	3.2E+03	3.2E+04	3.2E+03
100	3.6E+03	6.0E+05	1.1E+03	3.6E+03	3.6E+04	3.6E+03
105	4.0E+03	6.8E+05	1.2E+03	4.0E+03	4.0E+04	4.0E+03
110	4.6E+03	7.8E+05	1.4E+03	4.6E+03	4.6E+04	4.6E+03
115	5.4E+03	8.6E+05	1.6E+03	5.4E+03	5.4E+04	5.4E+03
120	6.0E+03	1.0E+06	1.8E+03	6.0E+03	6.0E+04	6.0E+03

(Amended July 26, 1994)

Table I-B. - Tier I and Tier II Feed Rate and Emissions Screening Limits for Noncarcinogenic Metals for Facilities in Noncomplex Terrain

[Values for rural areas]

Terrain adjusted eff. stack ht. (m)	Antimony (g/hr)	Barium (g/hr)	Lead (g/hr)	Mercury (g/hr)	Silver (g/hr)	Thallium (g/hr)
4	3.1E+01	5.2E+03	9.4E+00	3.1E+01	3.1E+02	3.1E+01
6	3.6E+01	6.0E+03	1.1E+01	3.6E+01	3.6E+02	3.6E+01
8	4.0E+01	6.8E+03	1.2E+01	4.0E+01	4.0E+02	4.0E+01
10	4.6E+01	7.8E+03	1.4E+01	4.6E+01	4.6E+02	4.6E+01
12	5.8E+01	9.6E+03	1.7E+01	5.8E+01	5.8E+02	5.8E+01
14	6.8E+01	1.1E+04	2.1E+01	6.8E+01	6.8E+02	6.8E+01
16	8.6E+01	1.4E+04	2.6E+01	8.6E+01	8.6E+02	8.6E+01
18	1.1E+02	1.8E+04	3.2E+01	1.1E+02	1.1E+03	1.1E+02
20	1.3E+02	2.2E+04	4.0E+01	1.3E+02	1.3E+03	1.3E+02
22	1.7E+02	2.8E+04	5.0E+01	1.7E+02	1.7E+03	1.7E+02
24	2.2E+02	3.6E+04	6.4E+01	2.2E+02	2.2E+03	2.2E+02
26	2.8E+02	4.6E+04	8.2E+01	2.8E+02	2.8E+03	2.8E+02
28	3.5E+02	5.8E+04	1.0E+02	3.5E+02	3.5E+03	3.5E+02
30	4.3E+02	7.6E+04	1.3E+02	4.3E+02	4.3E+03	4.3E+02
35	7.2E+02	1.2E+05	2.1E+02	7.2E+02	7.2E+03	7.2E+02
40	1.1E+03	1.8E+05	3.2E+02	1.1E+03	1.1E+04	1.1E+03
45	1.5E+03	2.5E+05	4.6E+02	1.5E+03	1.5E+04	1.5E+03
50	2.0E+03	3.3E+05	6.0E+02	2.0E+03	2.0E+04	2.0E+03
55	2.6E+03	4.4E+05	7.8E+02	2.6E+03	2.6E+04	2.6E+03
60	3.4E+03	5.8E+05	1.0E+03	3.4E+03	3.4E+04	3.4E+03
65	4.6E+03	7.6E+05	1.4E+03	4.6E+03	4.6E+04	4.6E+03
70	5.4E+03	9.0E+05	1.6E+03	5.4E+03	5.4E+04	5.4E+03
75	6.4E+03	1.1E+06	1.9E+03	6.4E+03	6.4E+04	6.4E+03
80	7.6E+03	1.3E+06	2.3E+03	7.6E+03	7.6E+04	7.6E+03
85	9.4E+03	1.5E+06	2.8E+03	9.4E+03	9.4E+04	9.4E+03
90	1.1E+04	1.8E+06	3.8E+03	1.1E+04	1.1E+05	1.1E+04
95	1.3E+04	2.2E+06	3.9E+03	1.3E+04	1.3E+05	1.3E+04

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100	1.5E+04	2.6E+06	4.6E+03	1.5E+04	1.5E+05	1.5E+04
105	1.8E+04	3.0E+06	5.4E+03	1.8E+04	1.8E+05	1.8E+04
110	2.2E+04	3.6E+06	6.6E+03	2.2E+04	2.2E+05	2.2E+04
115	2.6E+04	4.4E+06	7.8E+03	2.6E+04	2.6E+05	2.6E+04
120	3.1E+04	5.0E+06	9.2E+03	3.1E+04	3.1E+05	3.1E+04

(Amended July 26, 1994)

**Table I-C. - Tier I and Tier II Feed Rate and Emissions Screening Limits for Noncarcinogenic Metals for Facilities in Complex Terrain**

Values for urban and rural areas

Terrain adjusted eff. stack ht. (m)	Antimony (g/hr)	Barium (g/hr)	Lead (g/hr)	Mercury (g/hr)	Silver (g/hr)	Thallium (g/hr)
4	1.4E+01	2.4E+03	4.3E+00	1.4E+01	1.4E+02	1.4E+01
6	2.1E+01	3.5E+03	6.2E+00	2.1E+01	2.1E+02	2.1E+01
8	3.0E+01	5.0E+03	9.2E+00	3.0E+01	3.0E+02	3.0E+01
10	4.3E+01	7.6E+03	1.3E+01	4.3E+01	4.3E+02	4.3E+01
12	5.4E+01	9.0E+03	1.7E+01	5.4E+01	5.4E+02	5.4E+01
14	6.8E+01	1.1E+04	2.0E+01	6.8E+01	6.8E+02	6.8E+01
16	7.8E+01	1.3E+04	2.4E+01	7.8E+01	7.8E+02	7.8E+01
18	8.6E+01	1.4E+04	2.6E+01	8.6E+01	8.6E+02	8.6E+01
20	9.6E+01	1.6E+04	2.9E+01	9.6E+01	9.6E+02	9.6E+01
22	1.0E+02	1.8E+04	3.2E+01	1.0E+02	1.0E+03	1.0E+02
24	1.2E+02	1.9E+04	3.5E+01	1.2E+02	1.2E+03	1.2E+02
26	1.3E+02	2.2E+04	3.6E+01	1.3E+02	1.3E+03	1.3E+02
28	1.4E+02	2.4E+04	4.3E+01	1.4E+02	1.4E+03	1.4E+02
30	1.6E+02	2.7E+04	4.6E+01	1.6E+02	1.6E+03	1.6E+02
35	2.0E+02	3.3E+04	5.8E+01	2.0E+02	2.0E+03	2.0E+02
40	2.4E+02	4.0E+04	7.2E+01	2.4E+02	2.4E+03	2.4E+02
45	3.0E+02	5.0E+04	9.0E+01	3.0E+02	3.0E+03	3.0E+02
50	3.6E+02	6.0E+04	1.1E+02	3.6E+02	3.6E+03	3.6E+02
55	4.6E+02	7.6E+04	1.4E+02	4.6E+02	4.6E+03	4.6E+02
60	5.8E+02	9.4E+04	1.7E+02	5.8E+02	5.8E+03	5.8E+02
65	6.8E+02	1.1E+05	2.1E+02	6.8E+02	6.8E+03	6.8E+02
70	7.8E+02	1.3E+05	2.4E+02	7.8E+02	7.8E+03	7.8E+02
75	8.6E+02	1.4E+05	2.6E+02	8.6E+02	8.6E+03	8.6E+02
80	9.6E+02	1.6E+05	2.9E+02	9.6E+02	9.6E+03	9.6E+02
85	1.1E+03	1.8E+05	3.3E+02	1.1E+03	1.1E+04	1.1E+03
90	1.2E+03	2.0E+05	3.6E+02	1.2E+03	1.2E+04	1.2E+03
95	1.4E+03	2.3E+05	4.0E+02	1.4E+03	1.4E+04	1.4E+03
100	1.5E+03	2.6E+05	4.6E+02	1.5E+03	1.5E+04	1.5E+03
105	1.7E+03	2.8E+05	5.0E+02	1.7E+03	1.7E+04	1.7E+03
110	1.9E+03	3.2E+05	5.8E+02	1.9E+03	1.9E+04	1.9E+03
115	2.1E+03	3.6E+05	6.4E+02	2.1E+03	2.1E+04	2.1E+03
120	2.4E+03	4.0E+05	7.2E+02	2.4E+03	2.4E+04	2.4E+03

(Amended July 26, 1994)

**Table I-D. - Tier I and Tier II Feed Rate and Emissions Screening Limits for Carcinogenic Metals for Facilities in Noncomplex Terrain**

Values for use in urban areas

Values for use in rural areas

Terrain adjusted eff. stack ht. (m)	Arsenic (g/hr)	Cadmium (g/hr)	Chromium (g/hr)	Beryllium (g/hr)	Arsenic (g/hr)	Cadmium (g/hr)	Chromium (g/hr)	Beryllium (g/hr)
4	4.6E-01	1.1E+00	1.7E-01	8.2E-01	2.4E-01	5.8E-01	8.6E-02	4.3E-01
6	5.4E-01	1.3E+00	1.9E-01	9.4E-01	2.8E-01	6.6E-01	1.0E-01	5.0E-01
8	6.0E-01	1.4E+00	2.2E-01	1.1E+00	3.2E-01	7.6E-01	1.1E-01	5.6E-01
10	6.8E-01	1.6E+00	2.4E-01	1.2E+00	3.6E-01	8.6E-01	1.3E-01	6.4E-01
12	7.6E-01	1.8E+00	2.7E-01	1.4E+00	4.3E-01	1.1E+00	1.6E-01	7.8E-01
14	8.6E-01	2.1E+00	3.1E-01	1.5E+00	5.4E-01	1.3E+00	2.0E-01	9.6E-01

16	9.6E-01	2.3E+00	3.5E-01	1.7E+00	6.8E-01	1.6E+00	2.4E-01	1.2E+00
18	1.1E+00	2.6E+00	4.0E-01	2.0E+00	8.2E-01	2.0E+00	3.0E-01	1.5E+00
20	1.2E+00	3.0E+00	4.4E-01	2.2E+00	1.0E+00	2.5E+00	3.7E-01	1.9E+00
22	1.4E+00	3.4E+00	5.0E-01	2.5E+00	1.3E+00	3.2E+00	4.8E-01	2.4E+00
24	1.6E+00	3.9E+00	5.8E-01	2.8E+00	1.7E+00	4.0E+00	6.0E-01	3.0E+00
26	1.8E+00	4.3E+00	6.4E-01	3.2E+00	2.1E+00	5.0E+00	7.6E-01	3.9E+00
28	2.0E+00	4.8E+00	7.2E-01	3.6E+00	2.7E+00	6.4E+00	9.8E-01	5.0E+00
30	2.3E+00	5.4E+00	8.2E-01	4.0E+00	3.5E+00	8.2E+00	1.2E+00	6.2E+00
35	3.0E+00	6.8E+00	1.0E+00	5.4E+00	5.4E+00	1.3E+01	1.9E+00	9.6E+00
40	3.6E+00	9.0E+00	1.3E+00	6.8E+00	8.2E+00	2.0E+01	3.0E+00	1.5E+01
45	4.6E+00	1.1E+01	1.7E+00	8.6E+00	1.1E+01	2.8E+01	4.2E+00	2.1E+01
50	6.0E+00	1.4E+01	2.2E+00	1.1E+01	1.5E+01	3.7E+01	5.4E+00	2.8E+01
55	7.6E+00	1.8E+01	2.7E+00	1.4E+01	2.0E+01	5.0E+01	7.2E+00	3.6E+01
60	9.4E+00	2.2E+01	3.4E+00	1.7E+01	2.7E+01	6.4E+01	9.6E+00	4.8E+01
65	1.1E+01	2.8E+01	4.2E+00	2.1E+01	3.6E+01	8.6E+01	1.3E+01	6.4E+01
70	1.3E+01	3.1E+01	4.6E+00	2.4E+01	4.3E+01	1.0E+02	1.5E+01	7.6E+01
75	1.5E+01	3.6E+01	5.4E+00	2.7E+01	5.0E+01	1.2E+02	1.8E+01	9.0E+01
80	1.7E+01	4.0E+01	6.0E+00	3.0E+01	6.0E+01	1.4E+02	2.2E+01	1.1E+02
85	1.9E+01	4.6E+01	6.8E+00	3.4E+01	7.2E+01	1.7E+02	2.6E+01	1.3E+02
90	2.2E+01	5.0E+01	7.8E+00	3.9E+01	8.6E+01	2.0E+02	3.0E+01	1.5E+02
95	2.5E+01	5.8E+01	9.0E+00	4.4E+01	1.0E+02	2.4E+02	3.6E+01	1.8E+02
100	2.8E+01	6.8E+01	1.0E+01	5.0E+01	1.2E+02	2.9E+02	4.3E+01	2.2E+02
105	3.2E+01	7.6E+01	1.1E+01	5.6E+01	1.4E+02	3.4E+02	5.0E+01	2.6E+02
110	3.6E+01	8.6E+01	1.3E+01	6.4E+01	1.7E+02	4.0E+02	6.0E+01	3.0E+02
115	4.0E+01	9.6E+01	1.5E+01	7.2E+01	2.0E+02	4.8E+02	7.2E+01	3.6E+02
120	4.6E+01	1.1E+02	1.7E+01	8.2E+01	2.4E+02	5.8E+02	8.6E+01	4.3E+02

(Amended July 26, 1994)

Table I-E. - Tier I and Tier II Feed Rate and Emissions Screening Limits for Carcinogenic Metals for Facilities in Complex Terrain

Values for use in urban and rural areas

Terrain adjusted eff. stack ht. (m)	Arsenic (g/hr)	Cadmium (g/hr)	Chromium (g/hr)	Beryllium (g/hr)
4	1.1E-01	2.6E-01	4.0E-02	2.0E-01
6	1.6E-01	3.9E-01	5.8E-02	2.9E-01
8	2.4E-01	5.8E-01	8.6E-02	4.3E-01
10	3.5E-01	8.2E-01	1.3E-01	6.2E-01
12	4.3E-01	1.0E+00	1.5E-01	7.6E-01
14	5.0E-01	1.3E+00	1.9E-01	9.4E-01
16	6.0E-01	1.4E+00	2.2E-01	1.1E+00
18	6.8E-01	1.6E+00	2.4E-01	1.2E+00
20	7.6E-01	1.8E+00	2.7E-01	1.3E+00
22	8.2E-01	1.9E+00	3.0E-01	1.5E+00
24	9.0E-01	2.1E+00	3.3E-01	1.6E+00
26	1.0E+00	2.4E+00	3.6E-01	1.8E+00
28	1.1E+00	2.7E+00	4.0E-01	2.0E+00
30	1.2E+00	3.0E+00	4.4E-01	2.2E+00
35	1.5E+00	3.7E+00	5.4E-01	2.7E+00
40	1.9E+00	4.6E+00	6.8E-01	3.4E+00
45	2.4E+00	5.4E+00	8.4E-01	4.2E+00
50	2.9E+00	6.8E+00	1.0E+00	5.0E+00
55	3.5E+00	8.4E+00	1.3E+00	6.4E+00
60	4.3E+00	1.0E+01	1.5E+00	7.8E+00
65	5.4E+00	1.3E+01	1.9E+00	9.6E+00
70	6.0E+00	1.4E+01	2.2E+00	1.1E+01
75	6.8E+00	1.6E+01	2.4E+00	1.2E+01
80	7.6E+00	1.8E+01	2.7E+00	1.3E+01
85	8.2E+00	2.0E+01	3.0E+00	1.5E+01
90	9.4E+00	2.3E+01	3.4E+00	1.7E+01
95	1.0E+01	2.5E+01	4.0E+00	1.9E+01
100	1.2E+01	2.8E+01	4.3E+00	2.1E+01
105	1.3E+01	3.2E+01	4.8E+00	2.4E+01



110	1.5E+01	3.5E+01	5.4E+00	2.7E+01
115	1.7E+01	4.0E+01	6.0E+00	3.0E+01
120	1.9E+01	4.4E+01	6.4E+00	3.3E+01

(Amended July 26, 1994)

**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	4.8E + 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
115	7.2E + 03	3.5E + 04	2.8E + 03
120	8.2E + 03	4.1E + 04	3.2E + 03

(Amended July 26, 1994)

**Appendix III. - Tier II Emission Rate Screening Limits for Free Chlorine and Hydrogen Chloride**

Terrain-adjusted effective stack height (m)	Noncomplex terrain Values for urban areas		Values for rural areas		Complex terrain Values for use in urban and rural areas	
	Cl <sub>2</sub> (g/hr)	HC1 (g/hr)	Cl <sub>2</sub> (g/hr)	HC1 (g/hr)	Cl <sub>2</sub> (g/hr)	HC1 (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

(Amended July 26, 1994)

#### Appendix IV. - Reference Air Concentrations\*

Constituent	CAS No.	RAC (ug/m <sup>3</sup> )
Acetaldehyde	75-07-0	10
Acetonitrile	75-05-8	10
Acetophenone	98-86-2	100
Acrolein	107-02-8	20
Aldicarb	116-06-3	1
Aluminum Phosphide	20859-73-8	0.3
Allyl Alcohol	107-18-6	5
Antimony	7440-36-0	0.3
Barium	7440-39-3	50
Barium Cyanide	542-62-1	50
Bromomethane	74-83-9	0.8
Calcium Cyanide	592-01-8	30
Carbon Disulfide	75-15-0	200
Chloral	75-87-6	2
Chlorine (free)		0.4
2-Chloro-1,3-butadiene	126-99-8	3
Chromium III	16065-83-1	1000
Copper Cyanide	544-92-3	5
Cresols	1319-77-3	50
Cumene	98-82-8	1
Cyanide (free)	57-12-15	20
Cyanogen	460-19-5	30
Cyanogen Bromide	506-68-3	80
Di-n-butyl Phthalate	84-74-2	100
o-Dichlorobenzene	95-50-1	10
p-Dichlorobenzene	106-46-7	10
Dichlorodifluoromethane	75-71-8	200
2,4-Dichlorophenol	120-83-2	3
Diethyl Phthalate	84-66-2	800
Dimethoate	60-51-5	0.8
2,4-Dinitrophenol	51-28-5	2
Dinoseb	88-85-7	0.9
Diphenylamine	122-39-4	20
Endosulfan	115-29-1	0.05
Endrin	72-20-8	0.3
Fluorine	7782-41-4	50
Formic Acid	64-18-6	2000
Glycidyaldehyde	765-34-4	0.3
Hexachlorocyclopentadiene	77-47-4	5
Hexachlorophene	70-30-4	0.3

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Hydrocyanic Acid	74-90-8	20
Hydrogen Chloride	7647-01-1	7
Hydrogen Sulfide	7783-06-4	3
Isobutyl Alcohol	78-83-1	300
Lead	7439-92-1	0.09
Maleic Anhydride	108-31-6	100
Mercury	7439-97-6	0.3
Methacrylonitrile	126-98-7	0.1
Methomyl	16752-77-5	20
Methoxychlor	72-43-5	50
Methyl Chlorocarbonate	79-22-1	1000
Methyl Ethyl Ketone	78-93-3	80
Methyl Parathion	298-00-0	0.3
Nickel Cyanide	557-19-7	20
Nitric Oxide	10102-43-9	100
Nitrobenzene	98-95-3	0.8
Pentachlorobenzene	608-93-5	0.8
Pentachlorophenol	87-86-5	30
Phenol	108-95-2	30
M-Phenylenediamine	108-45-2	5
Phenylmercuric Acetate	62-38-4	0.075
Phosphine	7803-51-2	0.3
Phthalic Anhydride	85-44-9	2000
Potassium Cyanide	151-50-8	50
Potassium Silver Cyanide	506-61-6	200
Pyridine	110-86-1	1
Selenious Acid	7783-60-8	3
Selenourea	630-10-4	5
Silver	7440-22-4	3
Silver Cyanide	506-64-9	100
Sodium Cyanide	143-33-9	30
Strychnine	57-24-9	0.3
1,2,4,5-Tetrachlorobenzene	95-94-3	0.3
2,3,4,6-Tetrachlorophenol	58-90-2	30
Tetraethyl Lead	78-00-2	0.0001
Tetrahydrofuran	109-99-9	10
Thallic Oxide	1314-32-5	0.3
Thallium	7440-28-0	0.5
Thallium (I) Acetate	563-68-8	0.5
Thallium (I) Carbonate	6533-73-9	0.3
Thallium (I) Chloride	7791-12-0	0.3
Thallium (I) Nitrate	10102-45-1	0.5
Thallium Selenite	12039-52-0	0.5
Thallium (I) Sulfate	7446-18-6	0.075
Thiram	137-26-8	5
Toluene	108-88-3	300
1,2,4-Trichlorobenzene	120-82-1	20
Trichloromonofluoromethane	75-69-4	300
2,4,5-Trichlorophenol	95-95-4	100
Vanadium Pentoxide	1314-62-1	20
Warfarin	81-81-2	0.3
Xylenes	1330-20-7	80
Zinc Cyanide	557-21-1	50
Zinc Phosphide	1314-84-7	0.3

\*The RAC for other Appendix VIII Part 261 constituents not listed herein or in Appendix V of this part is 0.1 ug/m<sup>3</sup>.  
(Amended July 26, 1994)

Appendix V.-Risk Specific Doses ( $10^{-5}$ )

Constituent	CAS No.	Unit risk ( $m^3/ug$ )	RsD ( $ug/m^3$ )
Acrylamide	79-06-1	1.3E-03	7.7E-03
Acrylonitrile	107-13-1	6.8E-05	1.5E-01
Aldrin	309-00-2	4.9E-03	2.0E-03
Aniline	62-53-3	7.4E-06	1.4E+00
Arsenic	7440-38-2	4.3E-03	2.3E-03
Benz(a)anthracene	56-55-3	8.9E-04	1.1E-02
Benzene	71-43-2	8.3E-06	1.2E+00
Benzidine	92-87-5	6.7E-02	1.5E-04
Benzo(a)pyrene	50-32-8	3.3E-03	3.0E-03
Beryllium	7440-41-7	2.4E-03	4.2E-03
Bis(2-chloroethyl)ether	111-44-4	3.3E-04	3.0E-02
Bis(chloromethyl)ether	542-88-1	6.2E-02	1.6E-04
Bis(2-ethylhexyl)- phthalate	117-81-7	2.4E-07	4.2E+01
1,3-Butadiene	106-99-0	2.8E-04	3.6E-02
Cadmium	7440-43-9	1.8E-03	5.6E-03
Carbon Tetrachloride	56-23-5	1.5E-05	6.7E-01
Chlordane	57-74-9	3.7E-04	2.7E-02
Chloroform	67-66-3	2.3E-05	4.3E-01
Chloromethane	74-87-3	3.6E-06	2.8E+00
Chromium VI	7440-47-3	1.2E-02	8.3E-04
DDT	50-29-3	9.7E-05	1.0E-01
Dibenz(a,h)anthracene	53-70-3	1.4E-02	7.1E-04
1,2-Dibromo-3-chloro- propane	96-12-8	6.3E-03	1.6E-03
1,2-Dibromoethane	106-93-4	2.2E-04	4.5E-02
1,1-Dichloroethane	75-34-3	2.6E-05	3.8E-01
1,2-Dichloroethane	107-06-2	2.6E-05	3.8E-01
1,1-Dichloroethylene	75-35-4	5.0E-05	2.0E-01
1,3-Dichloropropene	542-75-6	3.5E-01	2.9E-05
Dieldrin	60-57-1	4.6E-03	2.2E-03
Diethylstilbestrol	56-53-1	1.4E-01	7.1E-05
Dimethylnitrosamine	62-75-9	1.4E-02	7.1E-04
2,4-Dinitrotoluene	121-14-2	8.8E-05	1.1E-01
1,2-Diphenylhydrazine	122-66-7	2.2E-04	4.5E-02
1,4-Dioxane	123-91-1	1.4E-06	7.1E+00
Epichlorohydrin	106-89-8	1.2E-06	8.3E+00
Ethylene Oxide	75-21-8	1.0E-04	1.0E-01
Ethylene Dibromide	106-93-4	2.2E-04	4.5E-02
Formaldehyde	50-00-0	1.3E-05	7.7E-01
Heptachlor	76-44-8	1.3E-03	7.7E-03
Heptachlor Epoxide	1024-57-3	2.6E-03	3.8E-03
Hexachlorobenzene	118-74-1	4.9E-04	2.0E-02
Hexachlorobutadiene	87-68-3	2.0E-05	5.0E-01
Alpha-hexachloro-cyclo- hexane	319-84-6	1.8E-03	5.6E-03
Beta-hexachloro-cyclo- hexane	319-85-7	5.3E-04	1.9E-02
Gamma-hexachloro-cyclo- hexane	58-89-9	3.8E-04	2.6E-02
Hexachlorocyclohexane, Technical		5.1E-04	2.0E-02
Hexachlorodibenzo-p- dioxin(1,2 Mixture)		1.3E+0	7.7E-06
Hexachloroethane	67-72-1	4.0E-06	2.5E+00
Hydrazine	302-01-2	2.9E-03	3.4E-03
Hydrazine Sulfate	302-01-2	2.9E-03	3.4E-03
3-Methylcholanthrene	56-49-5	2.7E-03	3.7E-03
Methyl Hydrazine	60-34-4	3.1E-04	3.2E-02
Methylene Chloride	75-09-2	4.1E-06	2.4E+00
4,4'-Methylene-bis-2- chloroaniline	101-14-4	4.7E-05	2.1E-01
Nickel	7440-02-0	2.4E-04	4.2E-02



## Part 266, App. VI

Nickel Refinery Dust	7440-02-0	2.4E-04	4.2E-02
Nickel Subsulfide	12035-72-2	4.8E-04	2.1E-02
2-Nitropropane	79-46-9	2.7E-02	3.7E-04
N-Nitroso-n-butylamine	924-16-3	1.6E-03	6.3E-03
N-Nitroso-n-methylurea	684-93-5	8.6E-02	1.2E-04
N-Nitrosodiethylamine	55-18-5	4.3E-02	2.3E-04
N-Nitrosopyrrolidine	930-55-2	6.1E-04	1.6E-02
Pentachloronitrobenzene	82-68-8	7.3E-05	1.4E-01
PCBs	1336-36-3	1.2E-03	8.3E-03
Pronamide	23950-58-5	4.6E-06	2.2E+00
Reserpine	50-55-5	3.0E-03	3.3E-03
2,3,7,8-Tetrachloro-dibenzo-p-dioxin	1746-01-6	4.5E+01	2.2E-07
1,1,2,2-Tetrachloroethane	79-34-5	5.8E-05	1.7E-01
Tetrachloroethylene	127-18-4	4.8E-07	2.1E+01
Thiourea	62-56-6	5.5E-04	1.8E-02
1,1,2-Trichloroethane	79-00-5	1.6E-05	6.3E-01
Trichloroethylene	79-01-6	1.3E-06	7.7E+00
2,4,6-Trichlorophenol	88-06-2	5.7E-06	1.8E+00
Toxaphene	8001-35-2	3.2E-04	3.1E-02
Vinyl Chloride	75-01-4	7.1E-06	1.4E+00
(Amended July 26, 1994)			

## Appendix VI. - Stack Plume Rise

[Estimated Plume Rise (in Meters) Based on Stack Exit Flow Rate and Gas Temperature]

Exhaust Temperature (K°)											
Flow rate (m3/s)	<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

## Part 266, Appendix VII

50.0 - 12	21	26	31	34	36	39	41	42	44	46
59.9										
60.0 - 14	22	27	33	36	39	42	43	45	47	49
69.9										
70.0 - 16	23	29	35	38	41	44	46	47	49	51
79.9										
80.0 - 17	25	30	36	40	42	46	48	49	51	54
89.9										
90.0 - 19	26	31	38	42	44	48	50	51	53	56
99.9										
100.0 - 21	26	32	39	43	46	49	52	53	55	58
119.9										
120.0 - 22	28	35	42	46	49	52	55	56	59	61
139.9										
140.0 - 23	30	36	44	48	51	55	58	59	62	65
159.9										
160.0 - 25	31	38	46	50	54	58	60	62	65	67
179.9										
180.0 - 26	32	40	48	52	56	60	63	65	67	70
199.9										
>199.9 26	33	41	49	54	58	62	65	67	69	73

(Amended July 26, 1994)

## Appendix VII. - Health-Based Limits for Exclusion of Waste-Derived Residues\*

## Metals - TCLP Extract Concentration Limits

Constituent	CAS No.	Concentration limits (mg/L)
Antimony	7440-36-0	1xE+00
Arsenic	7440-38-2	5xE+00
Barium	7440-39-3	1xE+02
Beryllium	7440-41-7	7xE-03
Cadmium	7440-43-9	1xE+00
Chromium	7440-47-3	5xE+00
Lead	7439-92-1	5xE+00
Mercury	7439-97-6	2xE-01
Nickel	7440-02-0	7xE+01
Selenium	7782-49-2	1xE+00
Silver	7440-22-4	5xE+00
Thallium	7440-28-0	7xE+00

## Nonmetals - Residue Concentration Limits

Constituent	CAS No.	Concentration limits for residues (mg/kg)
Acetonitrile	75-05-8	2xE-01
Acetophenone	98-86-2	4xE+00
Acrolein	107-02-8	5xE-01
Acrylamide	79-06-1	2xE-04
Acrylonitrile	107-13-1	7xE-04
Aldrin	309-00-2	2xE-05
Allyl alcohol	107-18-6	2xE-01
Aluminum phosphide	20859-73-8	1xE-02
Aniline	62-53-3	6xE-02
Barium cyanide	542-62-1	1xE+00
Benz(a)anthracene	56-55-3	1xE-04
Benzene	71-43-2	5xE-03
Benzidine	92-87-5	1xE-06
Bis(2-chloroethyl) ether	111-44-4	3xE-04
Bis(chloromethyl) ether	542-88-1	2xE-06
Bis(2-ethylhexyl) phthalate	117-81-7	3xE+01
Bromoform	75-25-2	7xE-01
Calcium cyanide	592-01-8	1xE-06

Carbon disulfide	75-15-0	4xE+00
Carbon tetrachloride	56-23-5	5xE-03
Chlordane	57-74-9	3xE-04
Chlorobenzene	108-90-7	1xE+00
Chloroform	67-66-3	6xE-02
Copper cyanide	544-92-3	2xE-01
Cresols (Cresylic acid)	1319-77-3	2xE+00
Cyanogen	460-19-5	1xE+00
DDT	50-29-3	1xE-03
Dibenz(a, h)-anthracene	53-70-3	7xE-06
1,2-Dibromo-3-chloropropane	96-12-8	2xE-05
p-Dichlorobenzene	106-46-7	7.5xE-02
Dichlorodifluoromethane	75-71-8	7xE+00
1,1-Dichloroethylene	75-35-4	5xE-03
2,4-Dichlorophenol	120-83-2	1xE-01
1,3-Dichloropropene	542-75-6	1xE-03
Dieldrin	60-57-1	2xE-05
Diethyl phthalate	84-66-2	3xE+01
Diethylstilbesterol	56-53-1	7xE-07
Dimethoate	60-51-5	3xE-02
2,4-Dinitrotoluene	121-14-2	5xE-04
Diphenylamine	122-39-4	9xE-01
1,2-Diphenylhydrazine	122-66-7	5xE-04
Endosulfan	115-29-7	2xE-03
Endrin	72-20-8	2xE-04
Epichlorohydrin	106-89-8	4xE-02
Ethylene dibromide	106-93-4	4xE-07
Ethylene oxide	75-21-8	3xE-04
Fluorine	7782-41-4	4xE+00
Formic acid	64-18-6	7xE+01
Heptachlor	76-44-8	8xE-05
Heptachlor epoxide	1024-57-3	4xE-05
Hexachlorobenzene	118-74-1	2xE-04
Hexachlorobutadiene	87-68-3	5xE-03
Hexachlorocyclopentadiene	77-47-4	2xE-01
Hexachlorodibenzo-p-dioxins	19408-74-3	6xE-08
Hexachloroethane	67-72-1	3xE-02
Hydrazine	302-01-1	1xE-04
Hydrogen cyanide	74-90-8	7xE-05
Hydrogen sulfide	7783-06-4	1xE-06
Isobutyl alcohol	78-83-1	1xE+01
Methomyl	16752-77-5	1xE+00
Methoxychlor	72-43-5	1xE-01
3-Methylcholanthrene	56-49-5	4xE-05
4,4'-Methylenebis (2-chloroaniline)	101-14-4	2xE-03
Methylene chloride	75-09-2	5xE-02
Methyl ethyl ketone (MEK)	78-93-3	2xE+00
Methyl hydrazine	60-34-4	3xE-04
Methyl parathion	298-00-0	2xE-02
Naphthalene	91-20-3	1xE+01
Nickel cyanide	557-19-7	7xE-01
Nitric oxide	10102-43-9	4xE+00
Nitrobenzene	98-95-3	2xE-02
N-Nitrosodi-n-butylamine	924-16-3	6xE-05
N-Nitrosodiethylamine	55-18-5	2xE-06
N-Nitroso-N-methylurea	684-93-5	1xE-07
N-Nitrosopyrrolidine	930-55-2	2xE-04
Pentachlorobenzene	608-93-5	3xE-02
Pentachloronitrobenzene (PCNB)	82-68-8	1xE-01
Pentachlorophenol	87-86-5	1xE+00
Phenol	108-95-2	1xE+00
Phenylmercury acetate	62-38-4	3xE-03
Phosphine	7803-51-2	1xE-02
Polychlorinated biphenyls, N.O.S	1336-36-3	5xE-05
Potassium cyanide	151-50-8	2xE+00
Potassium silver cyanide	506-61-6	7xE+00
Pronamide	23950-58-5	3xE+00
Pyridine	110-86-1	4xE-02
Reserpine	50-55-5	3xE-05

Selenourea	630-10-4	2xE-01
Silver cyanide	506-64-9	4xE+00
Sodium cyanide	143-33-9	1xE+00
Strychnine	57-24-9	1xE-02
1,2,4,5-Tetrachlorobenzene	95-94-3	1xE-02
1,1,2,2-tetrachloroethane	79-34-5	2xE-03
Tetrachloroethylene	127-18-4	7xE-01
2,3,4,6-Tetrachlorophenol	58-90-2	1xE-02
Tetraethyl lead	78-00-2	4xE-06
Thiourea	62-56-6	2xE-04
Toluene	108-88-3	1xE+01
Toxaphene	8001-35-2	5xE-03
1,1,2-Trichloroethane	79-00-5	6xE-03
Trichloroethylene	79-01-6	5xE-03
Trichloromonofluoromethane	75-69-4	1xE+01
2,4,5-Trichlorophenol	95-95-4	4xE+00
2,4,6-Trichlorophenol	88-06-2	4xE+00
Vanadium pentoxide	1314-62-1	7xE-01
Vinyl chloride	75-01-4	2xE-03

\* Note 1: The health-based concentration limits for Appendix VIII Part 261 constituents for which a health-based concentration is not provided below is 2xE-06 mg/kg.

Note 2: The levels specified in this appendix and the default level of 0.002 micrograms per kilogram or the level of detection for constituents as identified in Note 1 of this appendix are administratively stayed under the condition, for those constituents specified in §266.112(b)(1), that the owner or operator complies with alternative levels defined as the land disposal restriction limits specified in §268.43 of these regulations for F039 nonwastewaters. See §266.112(b)(2)(i).

(Amended July 26, 1994, July 23, 1996)

## Appendix VIII. - Potential PICs for Determination of Exclusion of Waste-Derived Residues

### PICs Found in Stack Effluents

#### Volatiles

Benzene  
Toluene  
Carbon tetrachloride  
Chloroform  
Methylene chloride  
Trichloroethylene  
Tetrachloroethylene  
1,1,1-Trichloroethane  
Chlorobenzene  
cis-1,4-Dichloro-2-butene  
Bromochloromethane  
Bromodichloromethane  
Bromoform  
Bromomethane  
Methylene bromide  
Methyl ethyl ketone

#### Semivolatiles

Bis(2-ethylhexyl)phthalate  
Naphthalene  
Phenol  
Diethyl phthalate  
Butyl benzyl phthalate  
2,4-Dimethylphenol  
o-Dichlorobenzene  
m-Dichlorobenzene  
p-Dichlorobenzene  
Hexachlorobenzene  
2,4,6-Trichlorophenol  
Fluoranthene  
o-Nitrophenol  
1,2,4-Trichlorobenzene  
o-Chlorophenol  
Pentachlorophenol  
Pyrene  
Dimethyl phthalate  
Mononitrobenzene  
2,6-Toluene diisocyanate

(Amended July 26, 1994)

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

### Burning Hazardous Waste in Boilers and Industrial Furnaces

#### Table of Contents

- 1.0 Introduction
- 2.0 Performance Specifications for Continuous Emission Monitoring Systems



**Part 266, Appendix IX**

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

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

**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**

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

**3.3 Measurement of HCl and Cl<sub>2</sub>**

**3.3.1 Isokinetic HCl/Cl<sub>2</sub> Emission Sampling Train (Method 0050)**

**3.3.2 Midget Impinger HCl/Cl<sub>2</sub> Emission Sampling Train (Method 0051)**

**3.3.3 Protocol for Analysis of Samples from HCl/Cl<sub>2</sub> Emission Sampling Train (Method 9057)**

**3.4 Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) from Stationary Sources (Method 23)**

**3.5 Sampling for Aldehyde and Ketone Emissions from Stationary Sources (Method 0011)**

**3.6 Analysis for Aldehydes and Ketones by High Performance Liquid Chromatography (HPLC) (Method 0011A)**

**4.0 Procedure for Estimating Toxicity Equipment or Chlorinated Dibenzo-P-Dioxin and Dibenzofuran Congeners**

**5.0 Hazardous Waste Combustion Air Quality Screening Procedure**

**6.0 Simplified Land Use Classification Procedure for Compliance With Tier I and Tier II Limits**

**7.0 Statistical Methodology for Bevill Residue Determinations**

**8.0 Procedures for Determining Default Values for Air Pollution Control System Removal Efficiencies**

**8.1 APCS RE Default Values for Metals**

**8.2 APCS RE Default Values for HCl and Cl<sub>2</sub>**

**8.3 APCS RE Default Values for Ash**

**8.4 References**

**9.0 Procedures for Determining Default Values for Partitioning of Metals, Ash, and Total Chloride/Chlorine**

- 9.1 Partitioning Default Value for Metals
- 9.2 Special Procedures for Chlorine, HCl, and Cl
- 9.3 Special Procedures for Ash
- 9.4 Use of Engineering Judgement to Estimate Partitioning and APCS RE Values
- 9.5 Restrictions on Use of Test Data
- 10.0 Alternate Methodology for Implementing Metals Controls
- 10.1 Applicability
- 10.2 Introduction
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- 10.6 Precompliance Procedures

## Appendix A - Statistics

### Section 1.0 INTRODUCTION

This document presents required methods for demonstrating compliance with Delaware Regulations Governing Hazardous Waste (DRGHW) for boilers and industrial furnaces (BIFs) burning hazardous waste (see 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 with 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 (O<sub>2</sub>) 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<sub>2</sub>). 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<sub>2</sub> 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<sub>2</sub> 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 Part 266, Subpart H.

**Table 2.1-1 - Performance Specifications of CO and O<sub>2</sub> Monitors**

Parameter	CO monitors		O <sub>2</sub> monitors
	Low range	High range	
Calibration drift 24 hours.	≤6 ppm <sup>1</sup>	≤90 ppm	≤0.5% O <sub>2</sub>
Calibration error.	≤10 ppm <sup>1</sup>	≤150 ppm	≤0.5% O <sub>2</sub>
Response time.	≤2 min	≤2 min	≤2 min
Relative accuracy <sup>2</sup> .	( <sup>3</sup> )	( <sup>3</sup> )	(incorporated in CO RA calculation)

<sup>1</sup>For Tier II, CD and CE are ≤3% and ≤5% of twice the permit limit, respectively.

<sup>2</sup>Expressed as the sum of the mean absolute value plus the 95% confidence interval of a series of measurements.

<sup>3</sup>The greater of 10% of PTM or 10 ppm.

Table 2.1-2 - CEMS Span Values for CO and O<sub>2</sub> Monitors

	CO monitors		O <sub>2</sub> monitors (percent)
	Low range (ppm)	High range (ppm)	
Tier I rolling average 200 format.		3,000	25
Tier II rolling average 2 X permit limit. format.		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<sub>2</sub> 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<sub>2</sub> analyzer (for Tier I).

2.1.4.2.2 The high-level concentration for the CO or O<sub>2</sub> 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<sub>2</sub> for the O<sub>2</sub> 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<sub>2</sub> for the O<sub>2</sub> analyzer.

2.1.4.4 Response Time. The response time for the CO or O<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> monitor calibration response must not drift or deviate from the reference value by more than 0.5 percent O<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> shall be conducted simultaneously so that the results can be calculated for CO corrected to 7 percent O<sub>2</sub>. 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<sub>2</sub>) 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 <sub>2</sub> percent
	Low range <sup>1</sup>	High range	
1	0-40	0-600	0-2
2	60-80	900-1200	8-10
3	140-160	2100-2400	14-16

<sup>1</sup>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.

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:  $\leq$  5% of span each day for seven days.

Figure 2.1-1 Calibration Drift Determination

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<sub>2</sub> 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.

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



#### 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<sub>2</sub> 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<sub>2</sub>, NO, and CO<sub>2</sub> 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<sub>2</sub> 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.

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

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.

$$S_d = \frac{\sqrt{\frac{\sum_{i=1}^n d_i^2 - \frac{(\sum_{i=1}^n d_i)^2}{n}}{n-1}}}{n-1} \quad (\text{Eq. 2})$$

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

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

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

<sup>a</sup>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.

$$RA = \frac{|\bar{d}| + |CC|}{PTM} \times 100 \quad (\text{Eq. 4})$$

where:

$|\bar{d}|$  = Absolute value of the mean of the differences (Equation 1).

$|CC|$  = Absolute value of the confidence coefficient (Equation 3).

$\overline{PTM}$  = Average reference value.

2.1.7.5 Calibration Error. Calculate CE using Equation 5.

$$CE = \left| \frac{\bar{d}}{FS} \right| \times 100 \quad (\text{Eq. 5})$$

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<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub>, O<sub>2</sub>, and TRS." U.S. Environmental Protection Agency OAQPS, ESED, Research Triangle Park, North Carolina 27711, EPA-450/3-82-026, October 1982.

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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  $\pm 2$  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  $\pm 3$  ppm ( $\pm 3$  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 ( $\pm 5$  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.



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:  $\leq 3\%$  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.

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

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<sup>®</sup> 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 ( $\mu\text{g/ml}$ ) range in the analytical finish solution can be analyzed using this technique. Samples containing greater than approximately 50  $\mu\text{g/ml}$  of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20  $\mu\text{g/ml}$  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 m<sup>3</sup>, 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,  $\mu\text{g/ml}$ .
- B = volume of sample prior to aliquot for analysis, ml.
- C = stack sample volume, dscm (dsm<sup>3</sup>).
- D = in-stack detection limit,  $\mu\text{g/m}^3$ .

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-1 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 m<sup>3</sup>. If the sampling time is increased and 5 m<sup>3</sup> are collected, the in-stack method detection limits would be one fourth of the values shown in Table A-1 (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 ( $\mu\text{g}/\text{m}^3$ ) 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 4-6	Total train
Antimony	7.7 (0.7) <sup>*</sup>	3.8 (0.4) <sup>*</sup>		11.5 (1.1) <sup>*</sup>
Arsenic	12.7 (0.3) <sup>*</sup>	6.4 (0.1) <sup>*</sup>		19.1 (0.4) <sup>*</sup>
Barium	0.5	0.3		0.8
Beryllium	0.07 (0.05) <sup>*</sup>	0.04 (0.03) <sup>*</sup>		0.11 (0.08) <sup>*</sup>
Cadmium	1.0 (0.02) <sup>*</sup>	0.5 (0.01) <sup>*</sup>		1.5 (0.03) <sup>*</sup>
Chromium	1.7 (0.2) <sup>*</sup>	0.8 (0.1) <sup>*</sup>		2.5 (0.3) <sup>*</sup>
Copper	1.4	0.7		2.1
Lead	10.1 (0.2) <sup>*</sup>	5.0 (0.1) <sup>*</sup>		15.1 (0.3) <sup>*</sup>
Manganese	0.5 (0.2) <sup>*</sup>	0.2 (0.1) <sup>*</sup>		0.7 (0.3) <sup>*</sup>
Mercury	0.6 <sup>**</sup>	3.0 <sup>**</sup>	2.0 <sup>**</sup>	5.6 <sup>**</sup>
Nickel	3.6	1.8		5.4
Phosphorus	18	9		27
Selenium	18 (0.5) <sup>*</sup>	9 (0.3) <sup>*</sup>		27 (0.8) <sup>*</sup>
Silver	1.7	0.9		2.6
Thallium	9.6 (0.2) <sup>*</sup>	4.8 (0.1) <sup>*</sup>		14.4 (0.3) <sup>*</sup>
Zinc	0.5	0.3		0.8

(<sup>\*</sup>) Detection limit when analyzed by GFAAS.

<sup>\*\*</sup> 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  $\text{HNO}_3/\text{H}_2\text{O}_2$  impinger) shall also be constructed as described for the first impinger in method 5. The third impinger (or the second  $\text{HNO}_3/\text{H}_2\text{O}_2$  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  $\text{HNO}_3/\text{H}_2\text{O}_2$  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,

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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.



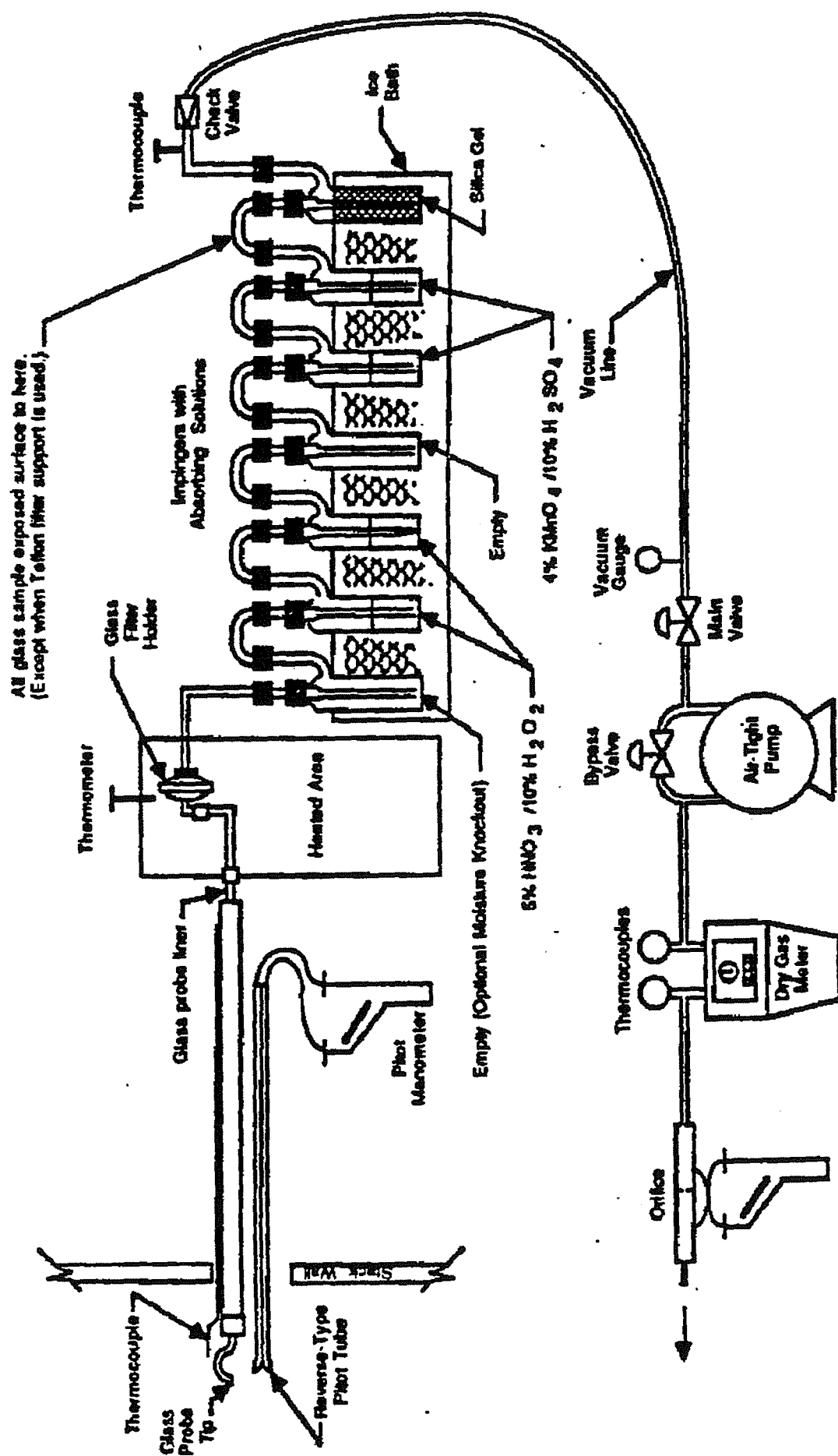


Figure 3.1-1 Schematic of multiple metals sampling train configuration

**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  $\text{KMnO}_4$ -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<sup>R</sup> 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  $\mu\text{g}/\text{in}^2$  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  $\mu\text{g}/\text{in}^2$  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  $\text{SO}_2$  or  $\text{SO}_3$ , the filter material must be of a type that is unreactive to  $\text{SO}_2$  or  $\text{SO}_3$ , 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 ( $\text{HNO}_3$ )/Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ ) Absorbing Solution, 5 Percent  $\text{HNO}_3$ /10 Percent  $\text{H}_2\text{O}_2$ . Carefully with stirring, add 50 ml of concentrated  $\text{HNO}_3$  to a 1000-ml volumetric flask containing approximately 500 ml of water, and then, carefully with stirring, add 333 ml of 30 percent  $\text{H}_2\text{O}_2$ . 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 ( $\text{KMnO}_4$ ) Absorbing Solution, 4 Percent  $\text{KMnO}_4$  (W/V), 10 Percent  $\text{H}_2\text{SO}_4$  (V/V). Prepare fresh daily. Mix carefully, with stirring, 100 ml of concentrated  $\text{H}_2\text{SO}_4$  into 800 ml of water, and add water with stirring to make a volume of 1 L: This solution is 10 percent  $\text{H}_2\text{SO}_4$  (V/V). Dissolve, with stirring, 40 g of  $\text{KMnO}_4$  into 10 percent  $\text{H}_2\text{SO}_4$  (V/V) and add 10 percent  $\text{H}_2\text{SO}_4$  (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  $\text{HNO}_3$  (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 ( $\text{HCl}$ ), 8 N. Make the desired volume of 8 N  $\text{HCl}$  in the following proportions. Carefully with stirring, add 690 ml of concentrated  $\text{HCl}$  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  $\text{HNO}_3$  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  $\text{HNO}_3$  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  $\text{HNO}_3$  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,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

3.1.4.4.14 Lanthanum, Oxide,  $\text{La}_2\text{O}_3$ .

3.1.4.4.15 AAS Grade Hg Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.16 AAS Grade Pb Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.17 AAS Grade As Standard, 1000  $\mu\text{g/ml}$ .



3.1.4.4.18 AAS Grade Cd Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.19 AAS Grade Cr Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.20 AAS Grade Sb Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.21 AAS Grade Ba Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.22 AAS Grade Be Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.23 AAS Grade Cu Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.24 AAS Grade Mn Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.25 AAS Grade Ni Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.26 AAS Grade P Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.27 AAS Grade Se Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.28 AAS Grade Ag Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.29 AAS Grade Tl Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.30 AAS Grade Zn Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.31 AAS Grade Al Standard, 1000  $\mu\text{g/ml}$ .

3.1.4.4.32 AAS Grade Fe Standard, 1000  $\mu\text{g/ml}$ .

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  $\mu\text{g/ml}$  intermediate mercury standard by adding 5 ml of 1000  $\mu\text{g/ml}$  mercury stock solution to a 500-ml volumetric flask; dilute with stirring to 500 ml by first carefully adding 20 ml of 15 percent  $\text{HNO}_3$  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  $\mu\text{g/ml}$  intermediate standard to a 250-ml volumetric flask and dilute to 250 ml with 5 ml of 4 percent  $\text{KMnO}_4$ , 5 ml of 15 percent  $\text{HNO}_3$ , 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  $\mu\text{g/ml}$  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  $\mu\text{g/ml}$  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  $\mu\text{g/ml}$  for Al, Cr, and Pb, 15  $\mu\text{g/ml}$  for Fe, and 10  $\mu\text{g/ml}$  for the remaining elements. Standards containing less than 1  $\mu\text{g/ml}$  of metal should be prepared daily. Standards containing greater than 1  $\mu\text{g/ml}$  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  $\mu\text{g/ml}$  standard by adding 1 ml of 1000  $\mu\text{g/ml}$  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  $\mu\text{g/ml}$  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  $\mu\text{g/ml}$  standard and diluting until it is in the range of the samples. Standards containing less than 1  $\mu\text{g/ml}$  of metal should be prepared daily. Standards containing greater than 1  $\mu\text{g/ml}$  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  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  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  $\text{La}_2\text{O}_3$  in 10 ml of concentrated  $\text{HNO}_3$  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  $\text{HNO}_3/\text{H}_2\text{O}_2$  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  $\text{KMnO}_4$  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.

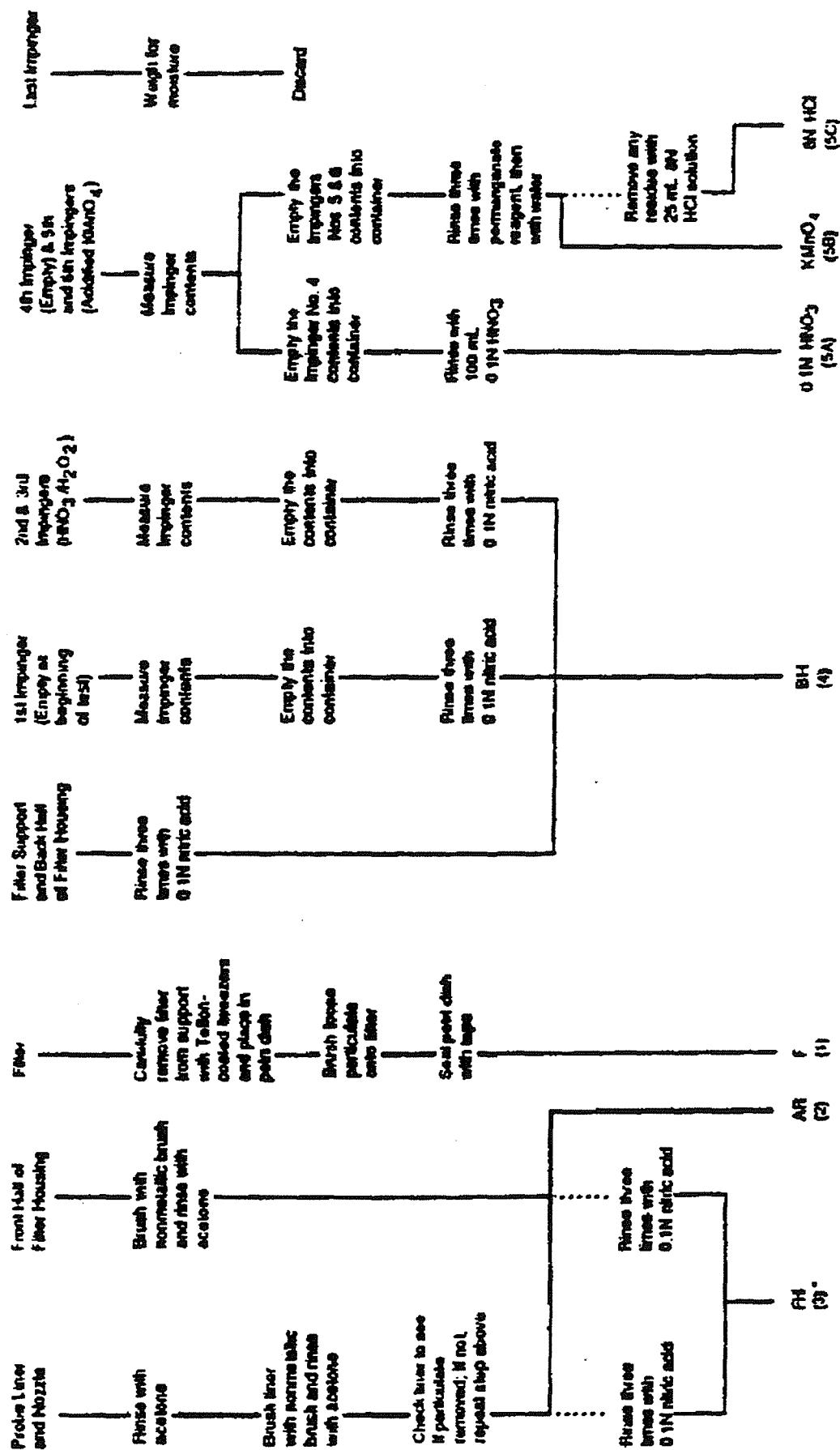
Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. 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 metal containing materials when recovering this train. Seal the labeled petri dish.





\* Number in parentheses indicates container number.

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 is 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,  $\text{HNO}_3/\text{H}_2\text{O}_2$  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  $\text{HNO}_3$ ), 5B ( $\text{KMnO}_4/\text{H}_2\text{SO}_4$  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  $\text{HNO}_3$  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  $\text{KMnO}_4$  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 permanent 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.

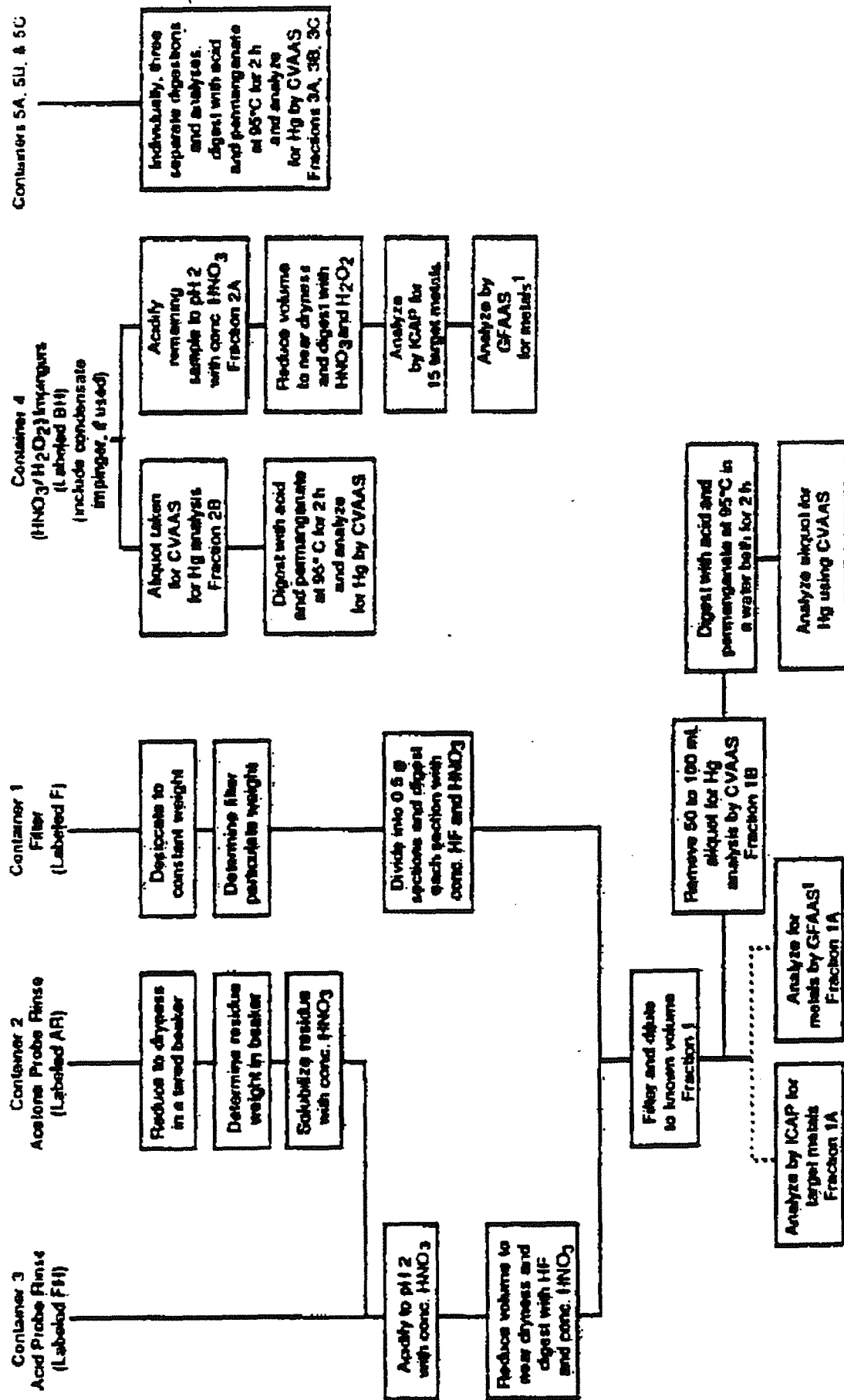
**3.1.5.2.11 Container No. 11 (8 N HCl Blank).** At least once during each field test, perform both of the following: Place 200 ml of water into a sample container. Pour 25 ml of 8N HCl carefully with stirring into the 200 ml of water in the container. Mix well and seal the container.

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.





<sup>1</sup> Analyze 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.

Figure 3.1-3 Sample preparation and analysis scheme.

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  $\pm 1$  ml or gravimetrically to  $\pm 0.5$  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  $\text{HNO}_3/\text{H}_2\text{O}_2$  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:

<u>Element</u>	<u>Wavelength (nm)</u>
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.

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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 volatilization	Spiked samples and add nickel nitrate solution to digestates prior to analysis.
Ba	Aspiration	7080	553.6	Aluminum	Use Zeeman background correction.
				Calcium	High hollow cathode current and narrow band set.
Be	Aspiration	7090	234.9	Barium ionization	2 mL of KCl per 100 mL of sample.
				500 ppm Al	Add 0.1% fluoride.
Be	Furnace	7091	234.9	High Mg and Si	Use method of standard additions.
				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.
Cr	Aspiration	7190	357.9	Pipet tips	Use cadmium-free tips.
				Alkali metal	KCl ionization suppressant in samples and standards.
				Absorption and scatter	Consult manufacturer's literature.



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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 $\mu$ L 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.
				AgCl insoluble	Avoid hydrochloric acid unless silver is in solution as a chloride complex.
				Viscosity	Sample and standards monitored for aspiration rate.

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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 volatilization by spiked samples or standard addition; Palladium is a suitable matrix modifier.
Zn	Aspiration	7950	213.9	High Si, Cu, & P Contamination	Strontium removes Cu and phosphate. 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  $\mu\text{g}$ , 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%  $\text{HNO}_3$  in water (1.5 ml concentrated  $\text{HNO}_3$  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  $M_{f_{nb}}$  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  $M_{f_{nb}}$  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  $Hg_{f_{nb}}$  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:

$$M_{fh} = C_{a1} F_d V_{soln,1} \quad \text{Eq. 1}^*$$

\* 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.

where:

$M_{fh}$  = total mass of each metal (except Hg) collected in the front half of the sampling train (Fraction 1),  $\mu\text{g}$ .  
 $C_{a1}$  = concentration of metal in sample Fraction 1A as read from the standard curve ( $\mu\text{g/ml}$ ).  
 $F_d$  = 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:

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

where:

$M_{bh}$  = total mass of each metal (except Hg) collected in the back half of the sampling train (Fraction 2),  $\mu\text{g}$ .  
 $C_{a2}$  = concentration of metal in sample concentrated Fraction 2A, as read from the standard curve ( $\mu\text{g/ml}$ ).  
 $F_a$  = 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 quantified metals collected in the sampling train as follows:

$$M_t = (M_{fh} - M_{fthb}) + (M_{bh} - M_{bthb}) \quad \text{Eq. 3}^*$$

where:

$M_t$  = total mass of each metal (separately stated for each metal) collected in the sampling train,  $\mu\text{g}$ .  
 $M_{fthb}$  = blank correction value for mass of metal detected in front-half field reagent blank,  $\mu\text{g}$ .  
 $M_{bthb}$  = blank correction value for mass of metal detected in back-half field reagent blank,  $\mu\text{g}$ .



Note: If the measured blank value for the front half ( $m_{fth}$ ) is in the range 0.0 to  $A \mu g$  (where  $A \mu g$  equals the value determined by multiplying  $1.4 \mu g$  per square inch ( $1.4 \mu g/in^2$ ) times the actual area in square inches ( $in^2$ ) of the filter used in the emission sample)  $m_{fth}$  may be used to correct the emission sample value ( $m_{fh}$ ); if  $m_{fth}$  exceeds  $A \mu g$ , the greater of the two following values (either I. or II.) may be used:

I.  $A \mu g$ , or

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

If the measured blank value for the back half ( $m_{bth}$ ) is in the range of 0.0 to  $1 \mu g$ ,  $m_{bth}$  may be used to correct the emission sample value ( $m_{bh}$ ); if  $m_{bth}$  exceeds  $1 \mu g$ , the greater of the two following values may be used:  $1 \mu g$  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:

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

where:

$Hg_{fh}$  = total mass of mercury collected in the front half of the sampling train (Fraction 1),  $\mu g$ .  
 $Q_{fh}$  = quantity of mercury in analyzed sample,  $\mu g$ .  
 $V_{soln,1}$  = 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 1B 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.

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

where:

$Hg_{bh2}$  = total mass of mercury collected in Fraction 2,  $\mu g$ .  
 $Q_{bh2}$  = quantity of mercury in analyzed sample,  $\mu g$ .  
 $V_{soln,2}$  = 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.

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

where:

$Hg_{bh3(A,B,C)}$  = total mass of mercury collected separately in Fraction 3A, 3B, or 3C,  $\mu g$ .  
 $Q_{bh3(A,B,C)}$  = quantity of mercury in separately analyzed samples,  $\mu g$ .  
 $V_{f3(A,B,C)}$  = 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.

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

where:

$Hg_{bh}$  = total mass of mercury collected in the back half of the sampling train,  $\mu g$ .

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

$$Hg_t = (Hg_{fh} - Hg_{fthb}) + (Hg_{bh} - Hg_{bthb}) \quad (\text{Eq. 8})$$

where:

$Hg_t$  = total mass of mercury collected in the sampling train,  $\mu g$ .  
 $Hg_{fthb}$  = blank correction value for mass of mercury detected in front-half field reagent blank,  $\mu g$ .  
 $Hg_{bthb}$  = blank correction value for mass of mercury detected in back-half field reagent blanks,  $\mu g$ .

Note: If the total of the measured blank values ( $Hg_{fthb} + Hg_{bthb}$ ) is in the range of 0 to 6  $\mu g$ , then the total may be used to correct the emission sample value ( $Hg_{fh} + Hg_{bh}$ ); if it exceeds 6  $\mu g$ , the greater of the following two values may be used; 6  $\mu g$  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:

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

where:

$C_s$  = concentration of each metal in the stack gas, mg/dscm.  
 $K_4$  =  $10^{-3}$ mg/ $\mu$ g.  
 $M_t$  = total mass of each metal collected in the sampling train,  $\mu$ g; (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 1988. 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  $\text{Cr}^{+6}$  emissions are collected isokinetically from the source. To eliminate the possibility of  $\text{Cr}^{+6}$  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  $\text{Cr}^{+6}$  by an ion chromatograph equipped with a post-column reactor and a visible wavelength detector. The IC/PCR separates the  $\text{Cr}^{+6}$  as chromate ( $\text{CrO}_4^{2-}$ ) from other components in the sample matrices that may interfere with the  $\text{Cr}^{+6}$ -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  $\text{Cr}^{+6}$  and 3.5  $\mu\text{g}$ /dscm of total chromium is 25% and 9% for  $\text{Cr}^{+6}$  and total chromium, respectively; for hazardous waste incinerators emitting 300 ng/dscm of  $\text{Cr}^{+6}$  it is 20 percent.

**3.2.2.4 Interference.** Components in the sample matrix may cause  $\text{Cr}^{+6}$  to convert to trivalent chromium ( $\text{Cr}^{+3}$ ) or cause  $\text{Cr}^{+3}$  to convert to  $\text{Cr}^{+6}$ . A post-sampling nitrogen purge and sample filtration are included to eliminate many of these interferences. The chromatographic separation of  $\text{Cr}^{+6}$  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  $\text{Cr}^{+6}$  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:

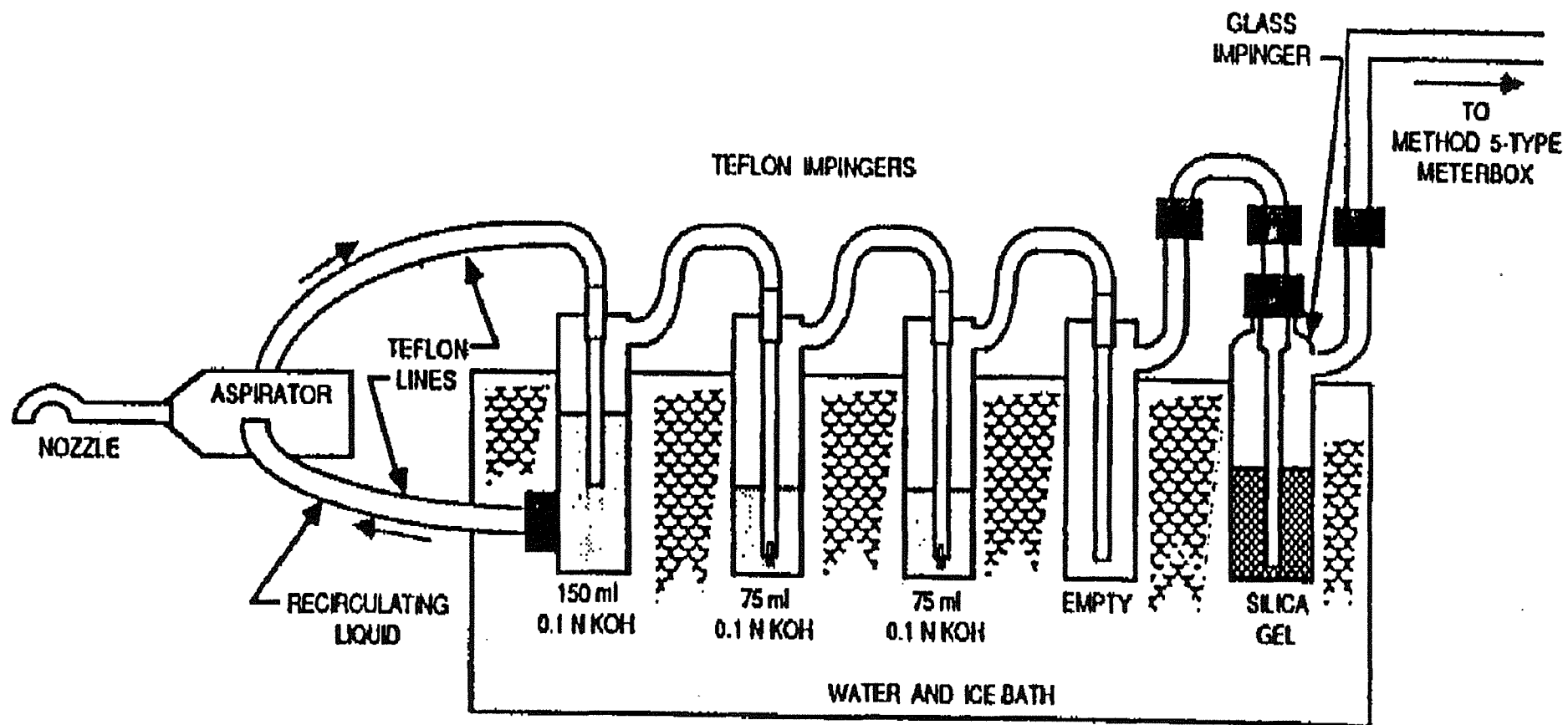


Figure 3.2-1 Schematic of recirculatory impinger train with aspirator assembly



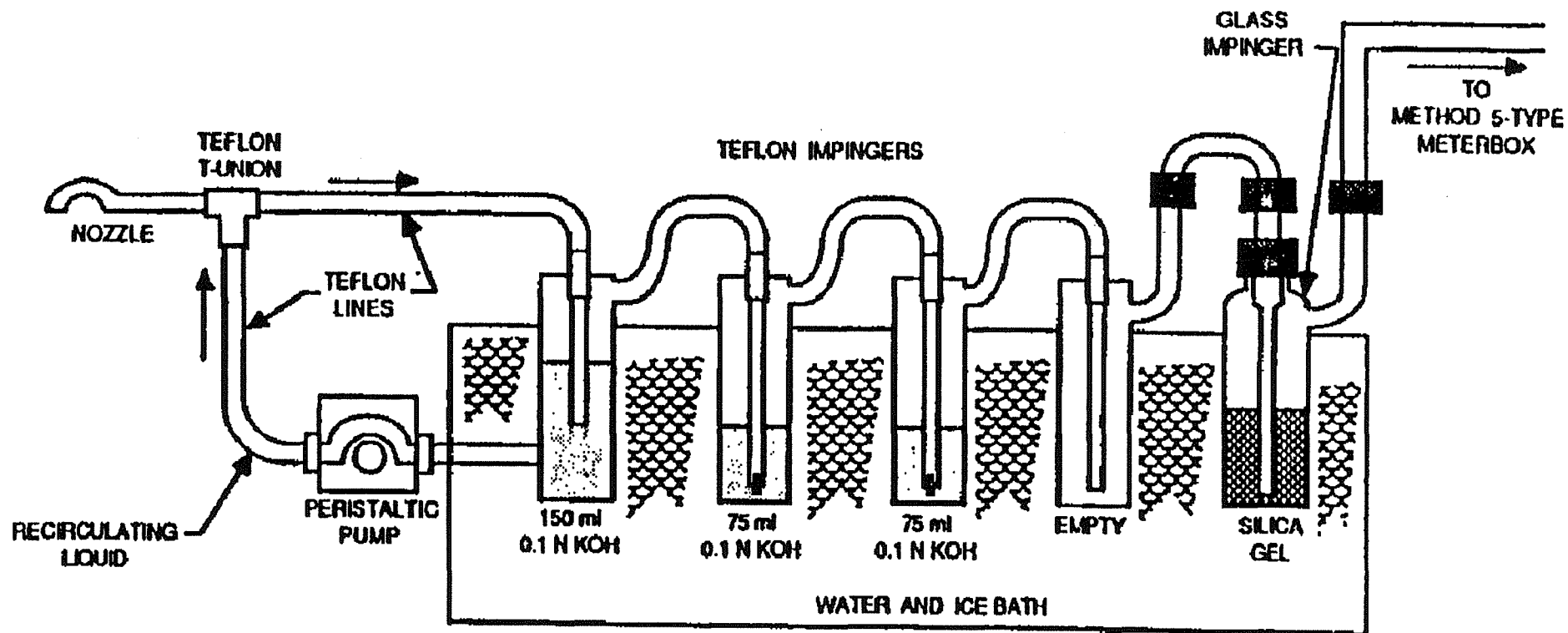


Figure 3.2-2 Schematic of recirculatory impinger train with pump/sprayer assembly

3.2.3.1.1 Probe Nozzle. Glass or Teflon with a sharp, tapered leading edge. The angle of taper shall be  $<30^\circ$  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 ( 1/8 to 1/2 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.

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

3.2.3.1.3 Teflon Sample Line. Teflon, 3/8" outside diameter (OD) and 1/4" inside diameter (ID), or 1/2" OD x 3/8" ID, of suitable length to connect aspirator (or T-union) to first Teflon impinger.

3.2.3.1.4 Teflon Recirculation Line. Teflon, 1/4" O.D. and 1/8" 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 3/8" 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 3/8" O.D. tubing as impinger stem. The second and third 3/8" OD Teflon stem has a 1/4" 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 from entering recirculating line; the second and third impinger stems should extend to 1/2" from impinger bottom. The first impinger should include a 1/4" 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 ( 1/2" 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 3/8-inch Teflon tubing and compression fittings in conjunction with an adjustable pressure regulator and needle valve may be used.

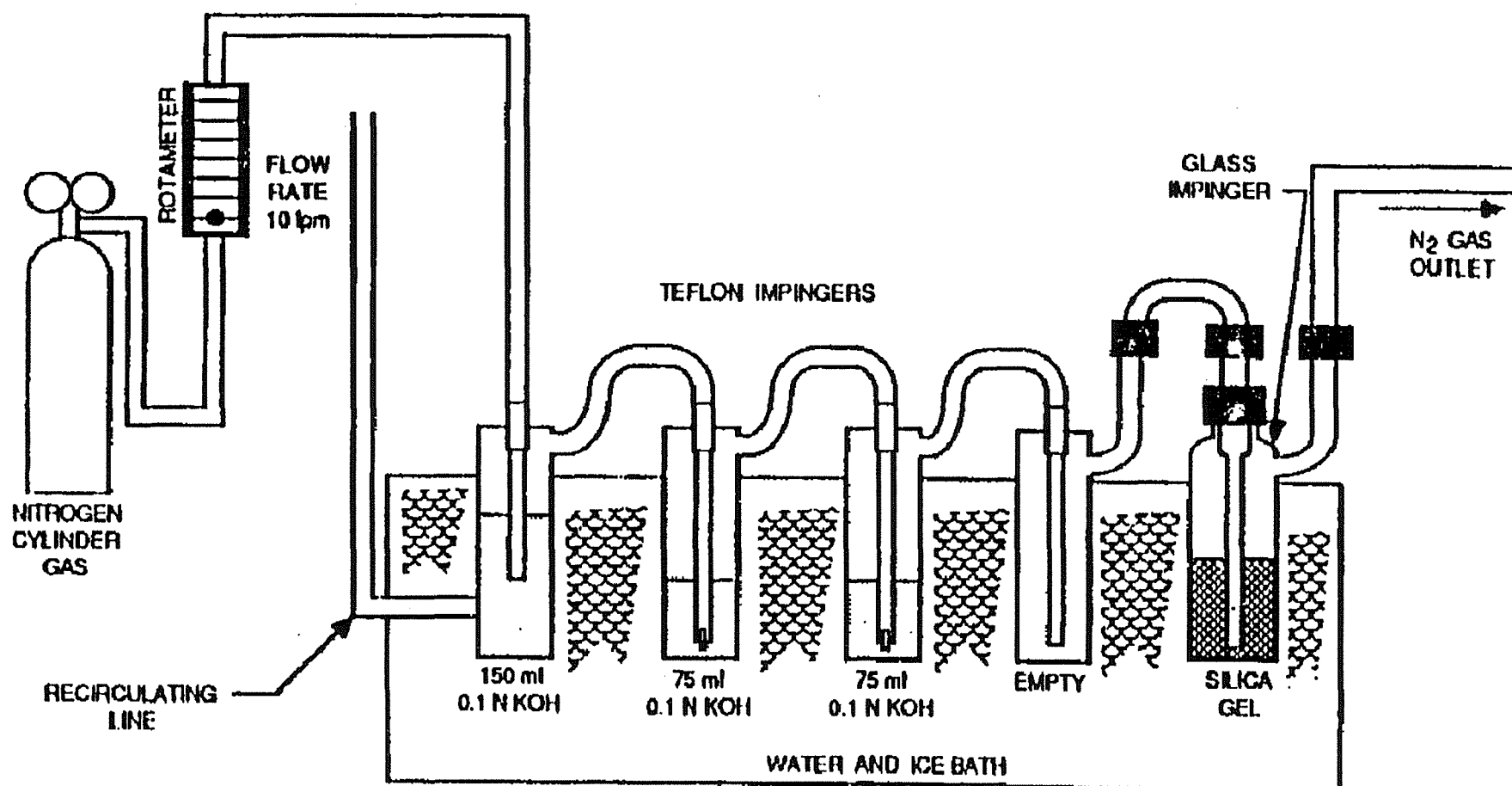


Figure 3.2-3 Schematic of post test nitrogen purge system.

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<sub>3</sub> 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  $\text{Cr}^{+6}$  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  $\text{Cr}^{+6}$  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  $\text{SO}_2$ , 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  $\text{HNO}_3$  (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 ( $\text{NH}_4\text{OH}$ ) and 33 grams of ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) 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<sup>+6</sup> Calibration Standard.** Prepare Cr<sup>+6</sup> standards from potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, FW 294.19). To prepare a 1000 µg/ml Cr<sup>+6</sup> stock solution, dissolve 2.829 g of dry K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 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 40 CFR, Part 60, Appendix A 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<sub>2</sub> 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 ( $\text{HNO}_3$  rinse optional for total chromium). With 0.1 N  $\text{HNO}_3$ , 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  $\text{HNO}_3$  Blank). Once during each field test if total chromium is to be determined, place a volume of 0.1 N  $\text{HNO}_3$  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  $\text{Cr}^{+6}$ , 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 3.2-4).

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  $\text{HNO}_3$  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.)

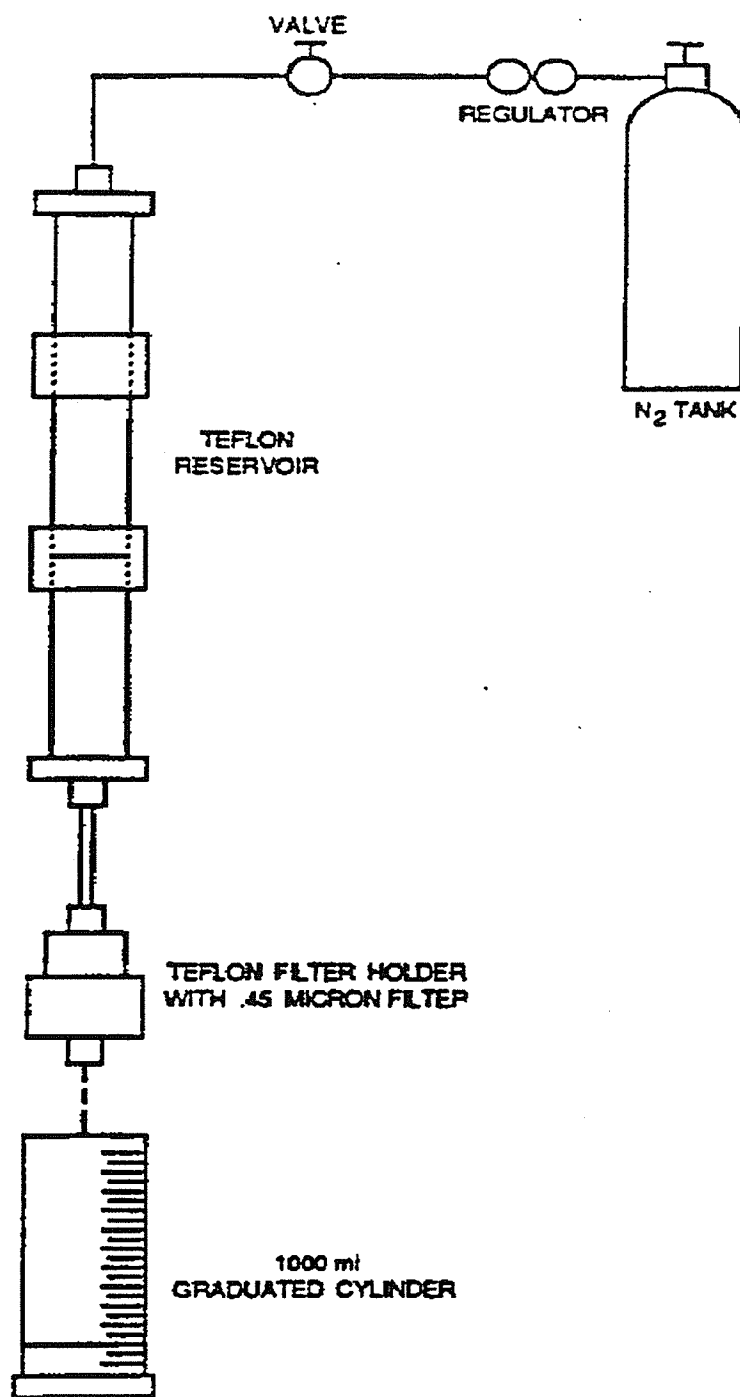


Figure 3.2-4 Schematic of sample filter system



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<sub>3</sub> 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<sup>+6</sup> 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- $\mu$  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<sup>+6</sup> is collected on the resin bed of the column. When the injection valve is switched, the eluent displaces the concentrated Cr<sup>+6</sup> sample moving it off the preconcentration column and onto the IC anion separation column. After separation from other sample components, Cr<sup>+6</sup> 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<sup>+6</sup> complex formed. The IC retention time and absorbance of the Cr<sup>+6</sup> complex is compared with known Cr<sup>+6</sup> 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<sup>+6</sup> 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<sup>+6</sup>/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  $\text{Cr}^{+6}$  concentration in  $\mu\text{g/L}$ . 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  $V_{m(\text{std})}$ , 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  $V_{w(\text{std})}$  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  $\mu\text{g Cr}^{+6}$  per Sample. Calculate as described below:

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

where:

- m = Mass of  $\text{Cr}^{+6}$  in the sample,  $\mu\text{g}$ .
- S = Concentration of sample,  $\mu\text{g Cr}^{+6}/\text{ml}$ .
- B = Concentration of blank,  $\mu\text{g Cr}^{+6}/\text{ml}$ .
- $V_{1s}$  = Volume of sample after filtration, ml.
- d = Dilution factor (1 if not diluted).

### 3.3 Measurement of HCl and Cl<sub>2</sub>

#### 3.3.1 Isokinetic HCl/Cl<sub>2</sub> 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<sub>2</sub>, 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 midjet impinger train sampling method designed for sampling sources of HCl/Cl<sub>2</sub> 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 40 CFR, Part 60, Appendix A 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<sub>2</sub>, respectively. Following sampling of emissions containing liquid droplets, any HCl/Cl<sub>2</sub> dissolved in the liquid in the cyclone and/or on the filter is vaporized and ultimately collected in the impingers by pulling Ascarite II<sup>®</sup> conditioned ambient air through the sampling train. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride (Cl<sup>-</sup>) ions. The Cl<sub>2</sub> 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<sup>+</sup>), Cl<sup>-</sup>, and hypochlorous acid (HClO). The Cl<sup>-</sup> 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<sub>2</sub>) gas which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water. Cl<sub>2</sub> 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 40 CFR, Part 60, Appendix A Method 5 procedures, and as such, the majority of the required equipment is identical to that used in 40 CFR, Part 60, Appendix A 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.

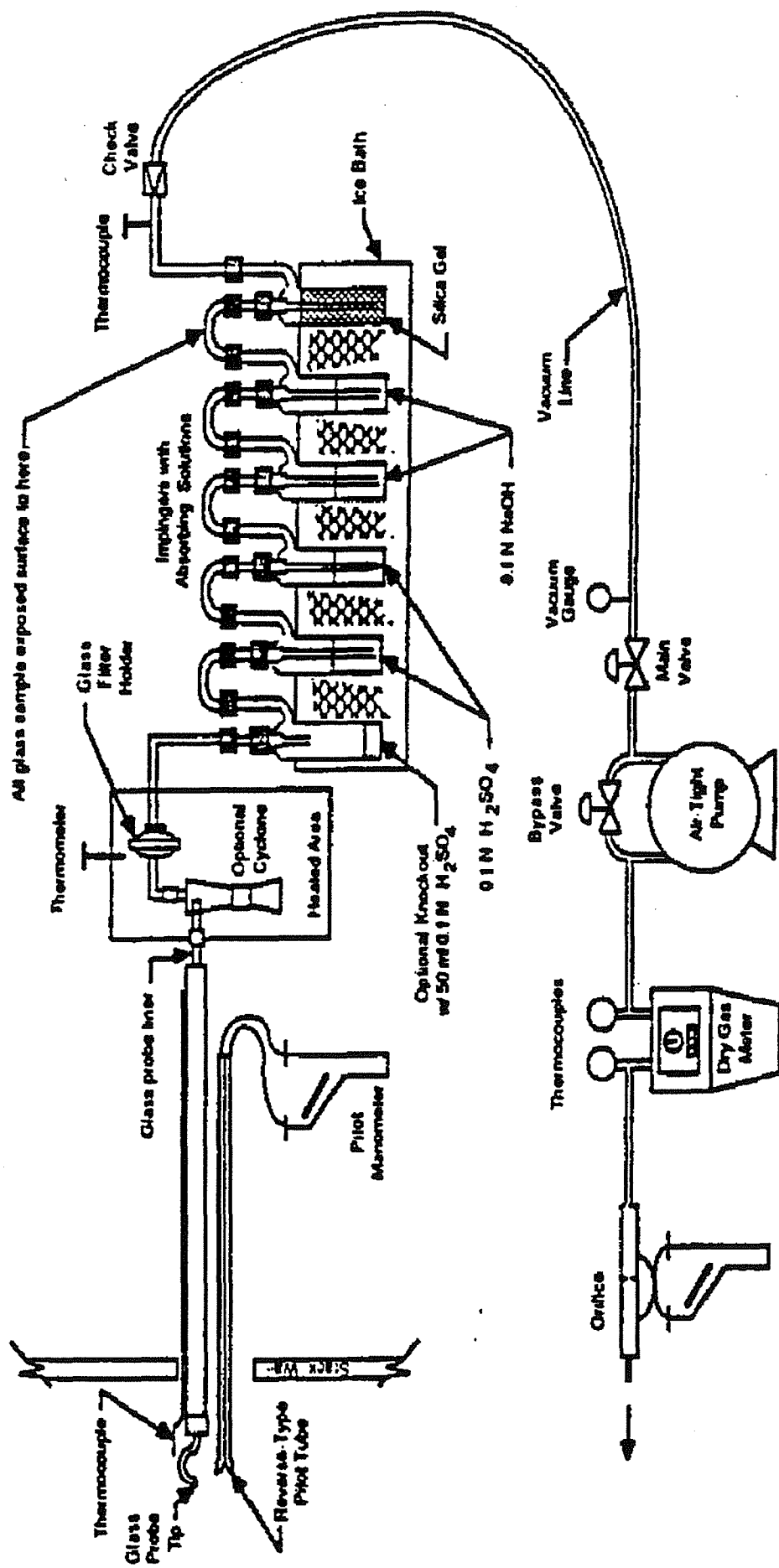


Figure 3.3-1 Isokinetic HCl/Cl<sub>2</sub> Sampling Train



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 40 CFR, Part 60, Appendix A 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  $120 \pm 14$  °C ( $248 \pm 25$  °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  $120 \pm 14$  °C ( $248 \pm 25$  °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 Cl<sub>2</sub>: 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  $\text{H}_2\text{SO}_4$ . The following two impingers (acid impingers which each contain 100 ml of 0.1 N  $\text{H}_2\text{SO}_4$ ) 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 ( 1/2-in) I.D. glass tube extending about 1.3 cm ( 1/2 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  $3^\circ\text{C}$  ( $5.4^\circ\text{F}$ ), 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<sup>®</sup> 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  $\pm 0.5$  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),  $\text{H}_2\text{SO}_4$ . Used as the  $\text{HCl}$  absorbing reagent in the impinger train. To prepare 1 L, slowly add 2.80 ml of concentrated  $\text{H}_2\text{SO}_4$  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).  $\text{NaOH}$ . Used as the  $\text{Cl}_2$  absorbing reagent in the impinger train. To prepare 1 L, dissolve 4.00 g of solid  $\text{NaOH}$  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 EPA 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<sub>2</sub> are described in method 9057 and for particulate matter in 40 CFR, Part 60, Appendix A 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  $20 \pm 5.6^{\circ}\text{C}$  ( $68 \pm 10^{\circ}\text{F}$ ) and ambient pressure for at least 24 hours, and weigh at intervals of at least 6 hours to a constant weight (i.e.,  $<0.5\text{-mg}$  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  $105^{\circ}\text{C}$  ( $220^{\circ}\text{F}$ ) 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  $\text{H}_2\text{SO}_4$  to the condensate impinger, if used. Place 100 ml of 0.1 N  $\text{H}_2\text{SO}_4$  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 tweezers 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  $<260^{\circ}\text{C}$  ( $500^{\circ}\text{F}$ ) 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  $0.00057\text{ m}^3/\text{min}$  (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  $0.00057 \text{ m}^3/\text{min}$  (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  $0.00057 \text{ m}^3/\text{min}$  (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  $120 \pm 14^\circ\text{C}$  ( $248 \pm 25^\circ\text{F}$ ).

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  $0.84 \pm 0.02$  and the stack gas equivalent density (dry molecular weight) is equal to  $29 \pm 4$ . 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.

### 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<sup>3</sup>/min. (cfm) \_\_\_\_\_  
 Probe Liner Material \_\_\_\_\_  
 Static Pressure, mm Hg (in Hg) \_\_\_\_\_  
 Filter No. \_\_\_\_\_

[illegible]

**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  $<20^{\circ}\text{C}$  ( $68^{\circ}\text{F}$ ) 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  $\text{H}_2\text{SO}_4$ , 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 EPA 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  $\text{Cl}_2$  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  $\text{Cl}_2$  impinger catches from the individual trains may be combined, and a single particulate analysis and single HCl and  $\text{Cl}_2$  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  $120 \pm 14^{\circ}\text{C}$  ( $248 \pm 25^{\circ}\text{F}$ ) 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<sup>®</sup>, 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<sub>2</sub>SO<sub>4</sub> 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  $\pm 1$  ml by using a graduated cylinder or by weighing it to within  $\pm 0.5$  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  $\text{Cl}_2$  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 $0.84 \pm 0.02$ ), 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, 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).
$T_m$ =	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.
$\Delta H$ =	Average pressure differential across the orifice meter, mm H <sub>2</sub> O (in H <sub>2</sub> O).
$\rho_a$ =	Density of acetone, mg/ $\mu$ l (see label on bottle).
$\rho_w$ =	Density of water, 0.9982 g/ml (0.002201 lb/ml).
$\Theta$ =	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:

$$K_1 = 0.3858 \text{ K/mm Hg for metric units, or}$$

$$K_1 = 17.64 \text{ °R/in. Hg for English units.}$$

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:

$$K_2 = 0.001333 \text{ m}^3/\text{ml for metric units, or}$$

$$K_2 = 0.04707 \text{ m}^3/\text{ml for English units.}$$

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  $B_w$  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  $\pm 1 \text{ °C}$  ( $2 \text{ °F}$ ).

3.3.1.7.7.6 Acetone blank concentration. For particulate determination.

$$C_a = \frac{m_a}{V_a P_a} \quad (4)$$

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.

$$I = \frac{100 T_s [K_3 F_{1c} + (V_m / T_m)(P_{bar} + H/13.6)]}{60 \theta V_s P_s A_n} \quad (7)$$

where:

$K_3 = 0.003454 \text{ mm Hg-m}^3/\text{ml-K}$  for metric units, or

$K_3 = 0.002669 \text{ in. Hg-ft}^3/\text{ml } ^\circ\text{R}$  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  $0.02 \mu\text{g}$  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/Cl<sub>2</sub> Emission Sampling Train (Method 0051)

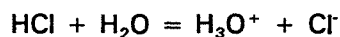
##### 3.3.2.1 Scope and Application.



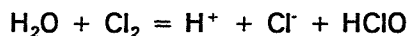
3.3.2.1.1 This method describes the collection of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chlorine (Cl<sub>2</sub>, CAS Registry Number 7782-50-5) in stack gas emission samples from hazardous waste incinerators, municipal waste combustors, and boilers and industrial furnaces. The collected samples are analyzed using method 9057. This method is designed to collect HCl/Cl<sub>2</sub> 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/Cl<sub>2</sub> 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<sup>-</sup>) as follows:



The Cl<sub>2</sub> 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<sup>+</sup>), Cl<sup>-</sup>, and hypochlorous acid (HClO) as follows:

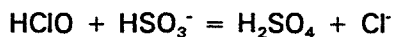


The Cl<sup>-</sup> ions in the separate solutions are measured by ion chromatography (Method 9057).

### 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 (Cl<sub>2</sub>) gas which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water. Cl<sub>2</sub> 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<sub>2</sub> with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl<sub>2</sub> results in a positive bias of 3.4 percent in the HCl measurement.

3.3.2.3.2 Reducing agents such as SO<sub>2</sub> may cause a positive bias in the Cl<sub>2</sub> measurement by the following reaction:



### 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 3/8-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 3/8-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 3/8-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),  $\text{H}_2\text{SO}_4$ . Used as the  $\text{HCl}$  absorbing reagent. To prepare 100 ml, slowly add 0.28 ml of concentrated  $\text{H}_2\text{SO}_4$  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),  $\text{NaOH}$ . Used as the  $\text{Cl}_2$  absorbing reagent. To prepare 100 ml, dissolve 0.40 g of solid  $\text{NaOH}$  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 midjet impingers should each be filled with 15 ml of 0.1 N  $\text{H}_2\text{SO}_4$ , 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  $\pm 0.5$  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.



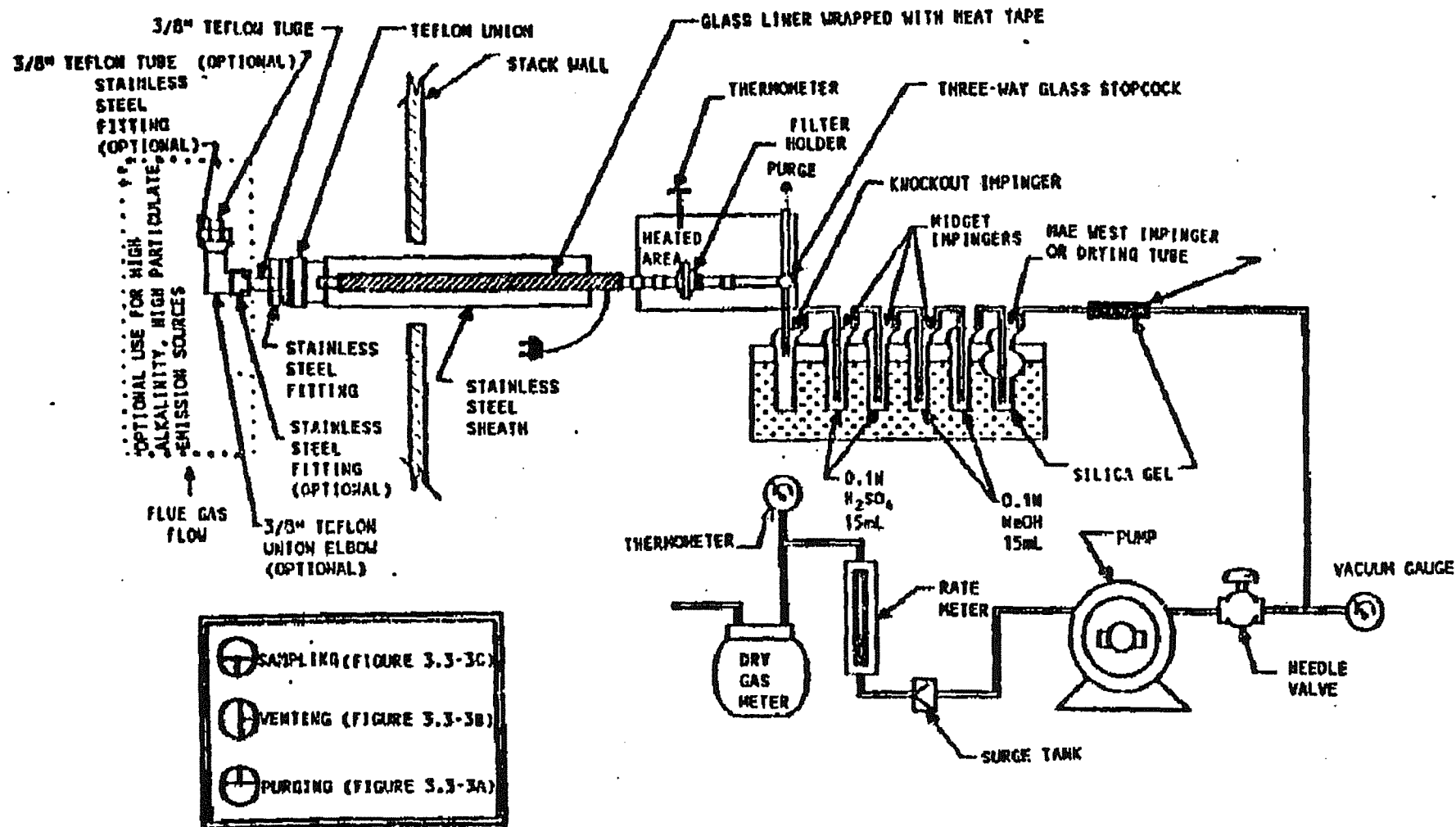


Figure 3.3-3 Midget Impinger HCl/Cl<sub>2</sub> Sampling Train

**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  $\text{H}_2\text{SO}_4$  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  $\text{Cl}_2$  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  $\text{H}_2\text{SO}_4$  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.

$B_{wa}$ =	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 <sup>3</sup> /°K-g-mole (21.85 in. Hg-ft <sup>3</sup> /°R-lb-mole).
$T_m$ =	Average dry gas meter absolute temperature, °K (°R).
$T_{std}$ =	Standard absolute temperature, 293 °K (528 °R).
$V_{1c}$ =	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.  
 $\rho_w$  = 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:

$$V_{m(std)} = V_m Y \frac{\left[ \frac{T_{std}}{T_m} \right]}{\left[ \frac{P_{bar}}{P_{std}} \right]}$$

$$= K_1 Y \frac{V_m P_{bar}}{T_m} \quad (1)$$

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.

$$V_{w(std)} = V_{lc} \frac{P_w}{M_w} \frac{RT_{std}}{P_{std}}$$

$$= K_2 V_{lc} \quad (2)$$

where:

$K_2$  = 0.0013333 m<sup>3</sup>/ml for metric units.

$K_2$  = 0.04707 ft<sup>3</sup>/ml for English units.

3.3.2.7.4.4 Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \quad (3)$$

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  $\mu\text{g}$  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  $\text{Cl}_2$  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/ $\text{Cl}_2$ Emission Sampling Train (Method 9057)

#### 3.3.3.1 Scope and Application.

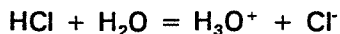
3.3.3.1.1 This method describes the analytical protocol for determination of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chloride ( $\text{Cl}_2$ , CAS Registry Number 7782-50-5) in stack gas emission samples collected from hazardous waste and municipal waste incinerators using the midjet impinger HCl/ $\text{Cl}_2$  sampling train (method 0051) or the isokinetic HCl/ $\text{Cl}_2$  sampling train (method 0050).

3.3.3.1.2 The lower detection limit is 0.1  $\mu\text{g}$  of chloride ( $\text{Cl}^-$ ) per ml of sample solution. Samples with concentrations which exceed the linear range of the analytical instrumentation may be diluted.

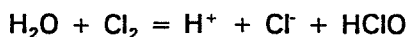
3.3.3.1.3 This method is recommended for use only by analysts experienced in the use of ion chromatography and in the interpretation of ion chromatograms.

### 3.3.3.2 Summary of Method.

3.3.3.2.1 The stoichiometry of HCl and Cl<sub>2</sub> 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<sup>-</sup>) according to the following formula:



The Cl<sub>2</sub> 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<sup>+</sup>), Cl<sup>-</sup>, and hypochlorous acid (HClO) as shown:

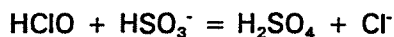


Non-suppressed or suppressed ion chromatography (IC) is used for analysis of the Cl<sup>-</sup>.

### 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<sub>2</sub>) gas which disproportionates to HCl and hypochlorous acid (HOCl) upon dissolution in water. Cl<sub>2</sub> 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<sub>2</sub> with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl<sub>2</sub> 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<sub>2</sub> may cause a positive bias in the Cl<sub>2</sub> measurement by the following reaction:



### 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),  $\text{H}_2\text{SO}_4$ . To prepare 100 ml, slowly add 0.28 ml of concentrated  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$  and 0.1 N NaOH) should be prepared for analysis with the field samples. For midjet 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  $\text{Cl}^-$  concentration can be calculated using the equation:

$$\mu\text{g Cl}^-/\text{ml} = \text{g of NaCl} \times 10^3 \times 35.453/58.44$$

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 midjet impinger  $\text{HCl}/\text{Cl}_2$  train or the isokinetic  $\text{HCl}/\text{Cl}_2$  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 midjet 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  $\text{Cl}^-$  appears in the chromatogram. If  $\text{Cl}^-$  is present, repeat the load/injection procedure until no  $\text{Cl}^-$  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  $\text{H}_2\text{SO}_4$  or 0.1  $\text{NaOH}$  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  $\text{Cl}^-$  concentrations in  $\mu\text{g}/\text{ml}$ . 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  $\text{Cl}^-$  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 $\mu\text{g}$ $\text{HCl}$ per sample. Calculate as described below:

$$^m\text{HCl} = (S - B) \times V_s \times 36.46/35.453 \quad (1)$$

where:

$^m\text{HCl}$  = Mass of  $\text{HCl}$  in sample,  $\mu\text{g}$ ,  
 $S$  = Analysis of sample,  $\mu\text{g}$   $\text{Cl}^-/\text{ml}$ ,  
 $B$  = Analysis of reagent blank,  $\mu\text{g}$   $\text{Cl}^-/\text{ml}$ ,  
 $V_s$  = Volume of filtered and diluted sample,  $\text{ml}$ ,  
 $36.46$  = Molecular weight of  $\text{HCl}$ ,  $\mu\text{g}/\mu\text{g-mole}$ , and  
 $35.45$  = Atomic weight of  $\text{Cl}^-$ ,  $\mu\text{g}/\mu\text{g-mole}$ .

3.3.3.7.4.2 Total  $\mu\text{g Cl}_2$  per sample. Calculate as described below:

$$^m\text{Cl}_2 = (S - B) \times V_2 \times 70.91/35.45 \quad (2)$$

where:

$^m\text{Cl}_2$  = Mass of  $\text{Cl}_2$  in sample,  $\mu\text{g}$ ,  
 70.91 = Molecular weight of  $\text{Cl}_2$ ,  $\mu\text{g}/\mu\text{g-mole}$ , and  
 35.45 = Atomic weight of  $\text{Cl}$ ,  $\mu\text{g}/\mu\text{g-mole}$ .

3.3.3.7.4.3 Concentration of HCl in the flue gas. Calculate as described below:

$$C = K \times m/V_{m(\text{std})} \quad (3)$$

where:

$C$  = Concentration of HCl or  $\text{Cl}_2$ , dry basis,  $\text{mg/dscm}$ ,  
 $K$  =  $10^{-3}\text{mg}/\mu\text{g}$ ,  
 $m$  = Mass of HCl or  $\text{Cl}_2$  in sample,  $\mu\text{g}$ , and  
 $V_{m(\text{std})}$  = Dry gas volume measured by the dry gas meter, corrected to standard conditions,  $\text{dscm}$  (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  $\text{Cl}^-$  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  $0.1 \mu\text{g}$  of  $\text{Cl}^-$  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 midjet impinger HCl/Cl<sub>2</sub> 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 Cl<sub>2</sub> 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.

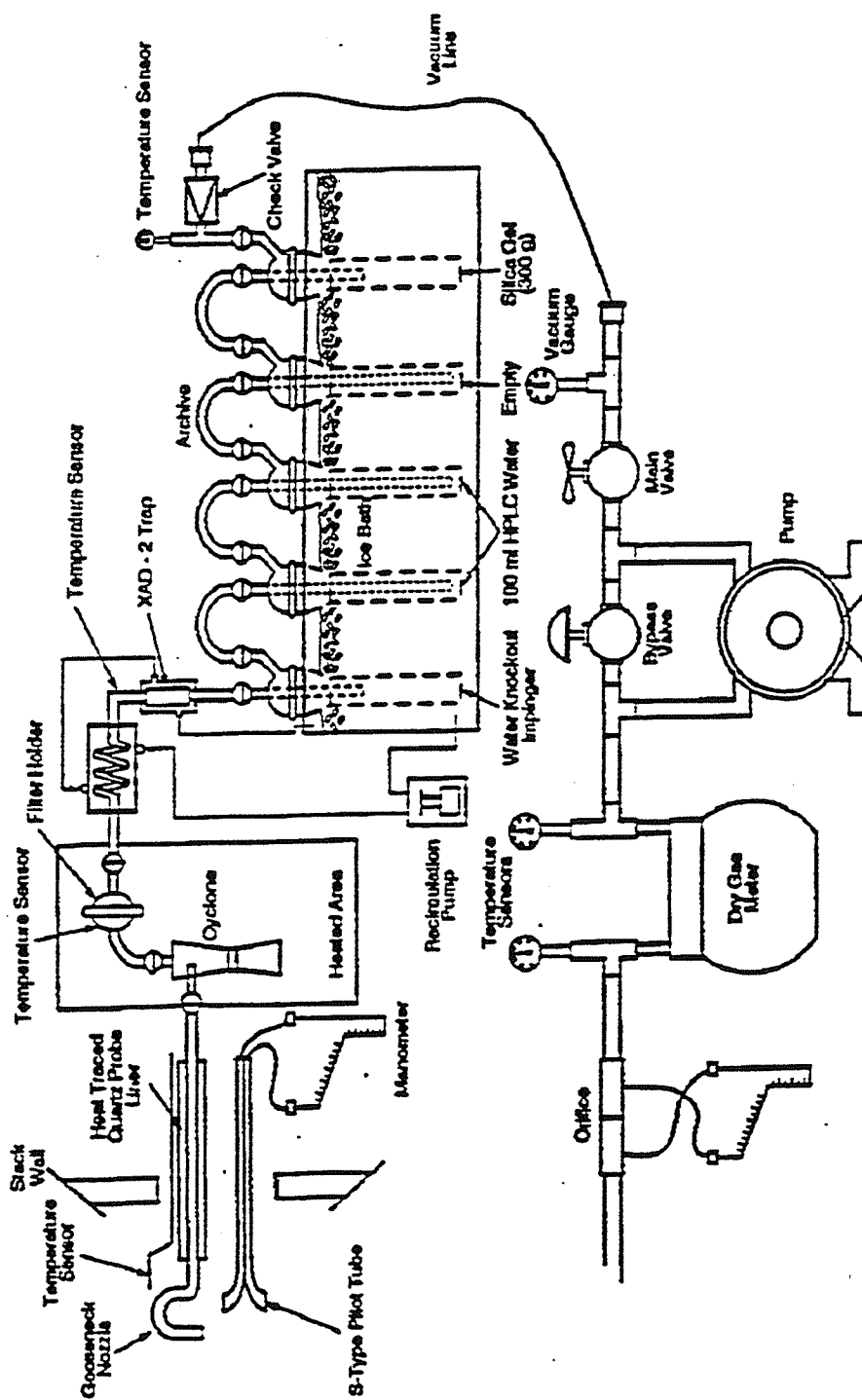
3.4.1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDDs and PCDFs are extracted from the sample, separated 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.



**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 ( 1/2 in. OD with 1/8 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.

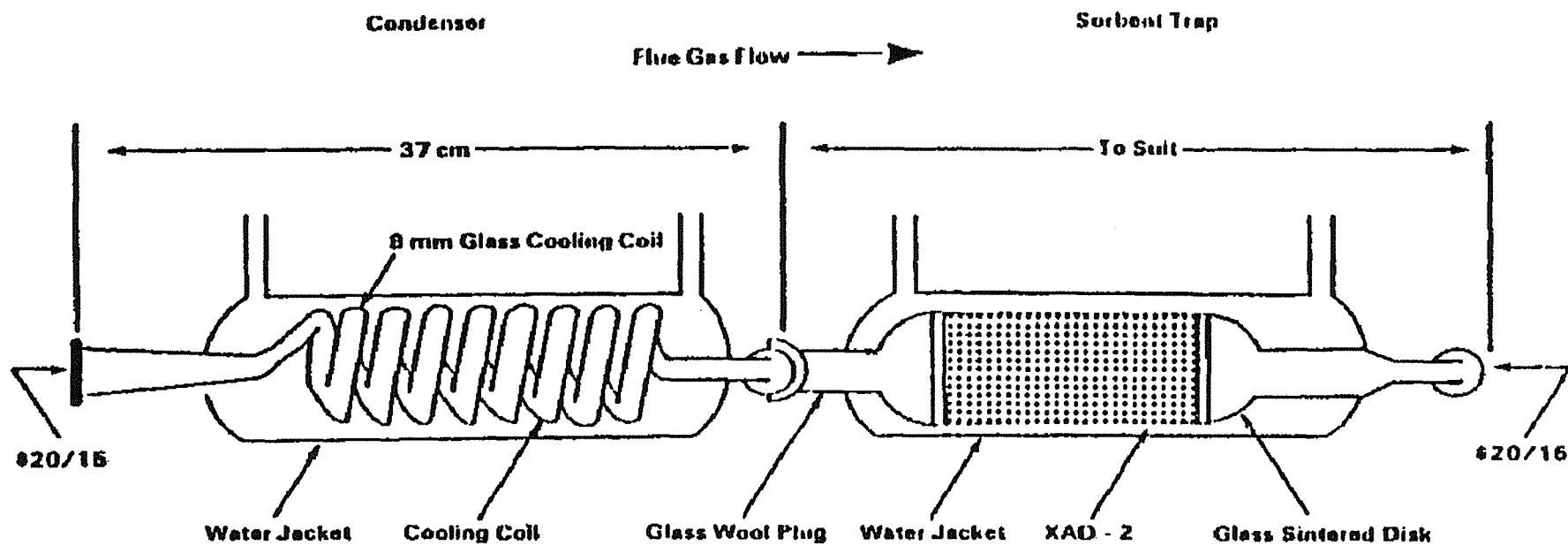


Figure 3.4-2 Condenser and adsorbent trap

### 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 X 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  $\pm 1$  °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  $\pm 1$  °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 X 0.25 mm inside diameter (ID), coated with DB.5 and a fused silica column, 30 m X 0.25 mm ID coated with DB-225. 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.

3.4.2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of  $\pm 5$  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 40 CFR, §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<sub>2</sub> 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 over-night, and discard. Extract with water for 8 hours.
Water	
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- $\mu$ l sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft X 1/8 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  $4 \times 10^{-11}$  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  $\mu$ l of methylene chloride into 100 ml of toluene. This corresponds to 100  $\mu$ g of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000  $\mu$ g/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 gel 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/ $\mu$ l)
<b>Internal Standards:</b>	
$^{13}\text{C}_{12}$ -2,3,7,8-TCDD	100
$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD	100
$^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD	100
$^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDD	100
$^{13}\text{C}_{12}$ -2,3,7,8-TCDF	100
$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF	100
$^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDF	100
$^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF	100
<b>Surrogate Standards:</b>	
$^{37}\text{C}_{14}$ -2,3,7,8-TCDD	100
$^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDD	100
$^{13}\text{C}_{12}$ -2,3,4,7,8-PeCDF	100
$^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF	100
$^{13}\text{C}_{12}$ -1,2,3,4,7,8,9-HpCDF	100
<b>Recovery Standards:</b>	
$^{13}\text{C}_{12}$ -1,2,3,4-TCDD	500
$^{13}\text{C}_{12}$ -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  $\mu$ l 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-0576.

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 within  $\pm 1$  ml by using a graduated cylinder or by weighing it to within  $\pm 0.5$  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  $\mu$ l 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 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  $\mu$ l 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 X 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  $\mu$ l using a stream of N<sub>2</sub>. 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- $\mu$ l aliquot of the Recovery Standard solution from Table 1 to each sample. A 2- $\mu$ l 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 <sup>a</sup>	Ion type	Elemental composition	Analyte
1	[Not used]			
2	292.9825	LOCK	C <sub>7</sub> F <sub>11</sub>	PFK
	303.9016	M	C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sub>4</sub> O	TCDF
	305.8987	M + 2	C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sup>37</sup> O	TCDF
	315.9419	M	<sup>13</sup> C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sub>4</sub> O	TCDF (S)
	317.9389	M + 2	<sup>13</sup> C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sup>37</sup> ClO	TCDF (S)
	319.8965	M	C <sub>12</sub> H <sub>4</sub> <sup>35</sup> ClO <sub>2</sub>	TCDD
	321.8936	M + 2	C <sub>12</sub> H <sub>4</sub> <sup>35</sup> Cl <sup>37</sup> ClO <sub>2</sub>	TCDD
	327.8847	M	C <sub>12</sub> H <sub>437</sub> Cl <sub>4</sub> O <sub>2</sub>	TCDD (S)
	330.9792	QC	C <sub>7</sub> F <sub>13</sub>	PFK
	331.9368	M	<sup>13</sup> C <sub>12</sub> H <sub>435</sub> Cl <sub>4</sub> O <sub>2</sub>	TCDD (S)
	333.9339	M + 2	<sup>13</sup> C <sub>12</sub> H <sub>435</sub> Cl <sup>37</sup> ClO <sub>2</sub>	TCDD (S)
	339.8597	M + 2	C <sub>12</sub> H <sub>335</sub> Cl <sub>437</sub> ClO	PCDF
	341.8567	M + 4	C <sub>12</sub> H <sub>435</sub> Cl <sub>3</sub> <sup>37</sup> Cl <sub>2</sub> O	PeCDF
	351.9000	M + 2	<sup>13</sup> C <sub>12</sub> H <sub>335</sub> Cl <sub>4</sub> <sup>37</sup> ClO	PeCDF (S)
	353.8970	M + 4	<sup>13</sup> C <sub>12</sub> H <sub>335</sub> Cl <sub>3</sub> <sup>37</sup> Cl <sub>2</sub> O	PeCDF (S)
	355.8546	M + 2	C <sub>12</sub> H <sub>335</sub> Cl <sub>337</sub> ClO <sub>2</sub>	PeCDD
	357.8516	M + 4	C <sub>12</sub> H <sub>335</sub> Cl <sub>337</sub> Cl <sub>2</sub> O <sub>2</sub>	PeCDD
	367.8949	M + 2	<sup>13</sup> C <sub>12</sub> H <sub>335</sub> Cl <sub>4</sub> <sup>37</sup> ClO <sub>2</sub>	PeCDD (S)
	369.8919	M + 4	<sup>13</sup> C <sub>12</sub> H <sub>335</sub> Cl <sub>3</sub> <sup>37</sup> ClO <sub>2</sub>	PeCDD (S)
	375.8364	M + 2	C <sub>12</sub> H <sub>435</sub> Cl <sub>5</sub> <sup>37</sup> ClO	HxCDF
	409.7974	M + 2	C <sub>12</sub> H <sub>335</sub> Cl <sub>6</sub> <sup>37</sup> ClO	HpCDF
3	373.8208	M + 2	C <sub>12</sub> H <sub>235</sub> Cl <sub>5</sub> <sup>37</sup> ClO	HxCDF
	375.8178	M + 4	C <sub>12</sub> H <sub>235</sub> Cl <sub>4</sub> <sup>37</sup> Cl <sub>2</sub> O	HxCDF
	383.8639	M	<sup>13</sup> C <sub>12</sub> H <sub>235</sub> Cl <sub>6</sub> O	HxCDF (S)
	385.8610	M + 2	<sup>13</sup> C <sub>12</sub> H <sub>235</sub> Cl <sub>5</sub> <sup>37</sup> ClO	HxCDF (S)
	389.8157	M + 2	C <sub>12</sub> H <sub>235</sub> Cl <sub>5</sub> <sup>37</sup> ClO <sub>2</sub>	HxCDD
	391.8127	M + 4	C <sub>12</sub> H <sub>235</sub> Cl <sub>4</sub> <sup>37</sup> Cl <sub>2</sub> O <sub>2</sub>	HxCDD
	392.9760	LOCK	C <sub>9</sub> F <sub>16</sub>	PFK
	401.8559	M + 2	<sup>13</sup> C <sub>12</sub> H <sub>235</sub> Cl <sub>5</sub> <sup>37</sup> ClO <sub>2</sub>	HxCDD (S)

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403.8529	M + 4	$^{13}\text{C}_{12}\text{H}_{236}\text{Cl}_4^{37}\text{Cl}_2\text{O}$	HxCDD (S)
445.7555	M + 4	$\text{C}_{12}\text{H}_{236}\text{Cl}_6^{37}\text{Cl}_2\text{O}$	OCDF
430.9729	QC	$\text{C}_9\text{F}_{17}$	PFK
407.7818	M + 2	$\text{C}_{12}\text{H}^{35}\text{Cl}_8^{37}\text{ClO}$	HpCDF
409.7789	M + 4	$\text{C}_{12}\text{H}^{35}\text{Cl}_5^{37}\text{Cl}_2\text{O}$	HpCDF
417.8253	M	$^{13}\text{C}_{12}\text{H}_{35}\text{Cl}_7\text{O}$	HpCDF (S)
419.8220	M + 2	$^{13}\text{C}_{12}\text{H}_{35}\text{Cl}_8^{37}\text{ClO}$	HpCDF (S)
423.7766	M + 2	$\text{C}_{12}\text{H}_{36}\text{Cl}_8^{37}\text{ClO}_2$	HpCDD
425.7737	M + 4	$\text{C}_{12}\text{H}_{36}\text{Cl}_6^{37}\text{Cl}_2\text{O}_2$	HpCDD
435.8169	M + 2	$^{13}\text{C}_{12}\text{H}_{36}\text{Cl}_8^{37}\text{ClO}_2$	HpCDD (S)
437.8140	M + 4	$^{13}\text{C}_{12}\text{H}_{36}\text{Cl}_5^{37}\text{Cl}_2\text{O}_2$	HpCDD (S)
479.7165	M + 4	$\text{C}_{12}\text{H}_{36}\text{Cl}_7^{37}\text{Cl}_2\text{O}$	NCPDE
430.9729	LOCK	$\text{C}_9\text{F}_{17}$	PFK
441.7428	M + 2	$\text{C}_{1235}\text{Cl}_7^{37}\text{ClO}$	OCDF
443.7399	M + 4	$\text{C}_{1235}\text{Cl}_6^{37}\text{Cl}_2\text{O}$	OCDF
457.7377	M + 2	$\text{C}_{1235}\text{Cl}_7^{37}\text{ClO}_2$	OCDD
459.7348	M + 4	$\text{C}_{1235}\text{Cl}_8^{37}\text{Cl}_2\text{O}_2$	OCDD
469.7779	M + 2	$^{13}\text{C}_{1235}\text{Cl}_7^{37}\text{ClO}_2$	OCDD (S)
471.7750	M + 4	$^{13}\text{C}_{1235}\text{Cl}_8^{37}\text{Cl}_2\text{O}_2$	OCDD (S)
513.6775	M + 4	$\text{C}_{1235}\text{Cl}_8^{37}\text{Cl}_2\text{O}_2$	DCDPE
442.9728	QC	$\text{C}_{10}\text{F}_{17}$	PFK

\*The following nuclidic masses were used: H = 1.007825, O = 15.994915, C = 12.000000,  $^{35}\text{Cl}$  = 34.968853,

$^{13}\text{C}$  = 13.003355,  $^{37}\text{Cl}$  = 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	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
6 <sup>a</sup>	M/M + 2	0.51	0.43	0.59
7 <sup>b</sup>	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

<sup>a</sup>Used only for <sup>13</sup>C-HxCDF<sup>b</sup>Used only for <sup>13</sup>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 <sup>13</sup>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 <sup>13</sup>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  $^{13}\text{C}_{12}$ -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  $^{13}\text{C}_{12}$ -1,2,3,4-TCDD. Recoveries of the hexa- through octa-internal standards are calculated using  $^{13}\text{C}_{12}$ -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  $\mu\text{L}$  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

		Concentrations (pg/μL)			
Compound	Solution No.	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

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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					
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDD	100	100	100	100	100
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDD	100	100	100	100	100
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8,-HxCDD	100	100	100	100	100
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
<sup>13</sup> C <sub>12</sub> -OCDD	200	200	200	200	200
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDF	100	100	100	100	100
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDF	100	100	100	100	100
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDF	100	100	100	100	100
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
Surrogate Standards					
<sup>37</sup> C <sub>14</sub> -2,3,7,8-TCDD	0.5	1	5	50	100
<sup>13</sup> C <sub>12</sub> -2,3,4,7,8-PeCDF	2.5	5	25	250	500
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
Alternative Standard					
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
Recovery Standards					
<sup>13</sup> C <sub>12</sub> -1,2,3,4-TCDD	100	100	100	100	100
<sup>13</sup> C <sub>12</sub> -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		
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDD	25	25
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDD	30	30
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDD	25	25
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDD	30	30
<sup>13</sup> C <sub>12</sub> -OCDD	30	30
<sup>13</sup> C <sub>12</sub> -2,3,7,8-TCDF	30	30
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-PeCDF	30	30
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-HxCDF	30	30
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-HpCDF	30	30

**Surrogate Standards**

<sup>37</sup> Cl <sub>4</sub> -2,3,7,8-TCDD	25	25
<sup>13</sup> C <sub>12</sub> -2,3,4,7,8-PeCDF	25	25
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDD	25	25
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-HxCDF	25	25
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8,9-HpCDF	25	25

**Alternate Standard**

<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-HxCDF	25	25
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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  $\mu$ l 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.

$A_{si}$ =	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 $j$ th calibration standard.
$A_{cij}^*$ =	Integrated ion current of the two ions characteristic of the internal standard $i$ in the $j$ th 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/M <sup>3</sup> .
$C_T$ =	Total concentration of PCDDs or PCDFs in the sample, pg/M <sup>3</sup> .
$m_{ci}$ =	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.

$$RRF_i = 1/n \sum_{j=1}^n [A_{cij} m_{ci}^* / (A_{cij}^* m_{ci})] \quad \text{Eq. 23-1}$$

## 3.4.9.3 Concentration of the PCDDs and PCDFs.

$$C_i = m_i^* A_i / (A_i^* RRF_i V_{m(std)}) \quad \text{Eq. 23-2}$$

## 3.4.9.4 Recovery Standard Response Factor.

$$RRF_{rs} = A_{ci}^* m_{rs} / (A_{rs} m_{ci}^*) \quad \text{Eq. 23-3}$$

3.4.9.5 Recovery of Internal Standards ( $R^*$ ).

$$R^* = (A_i^* m_{rs} / A_{rs} RRF_{rs} m_i^*) \times 100\% \quad \text{Eq. 23-4}$$

## 3.4.9.6 Surrogate Compound Response Factor.

$$RRFs = A_{ci}^* m_s / (A_{cis} m_{ci}^*) \quad \text{Eq. 23-5}$$

3.4.9.7 Recovery of Surrogate Compounds ( $R_s$ ).

$$R_s = (A_s m_i^* / A_i^* RRF_s m_s) \times 100\% \quad \text{Eq. 23-6}$$

## 3.4.9.8 Minimum Detectable Limit (MDL).

$$MDL = 2.5 A_{ci} m_i^* / (A_{ci}^* RRF_i) \quad \text{Eq. 23-7}$$

## 3.4.9.9 Total Concentration of PCDDs and PCDFs in the Sample.

$$C_T = \sum_{i=1}^n C_i \quad \text{Eq. 23-8}$$

## 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  $6.4 \times 10^{-8}$  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.

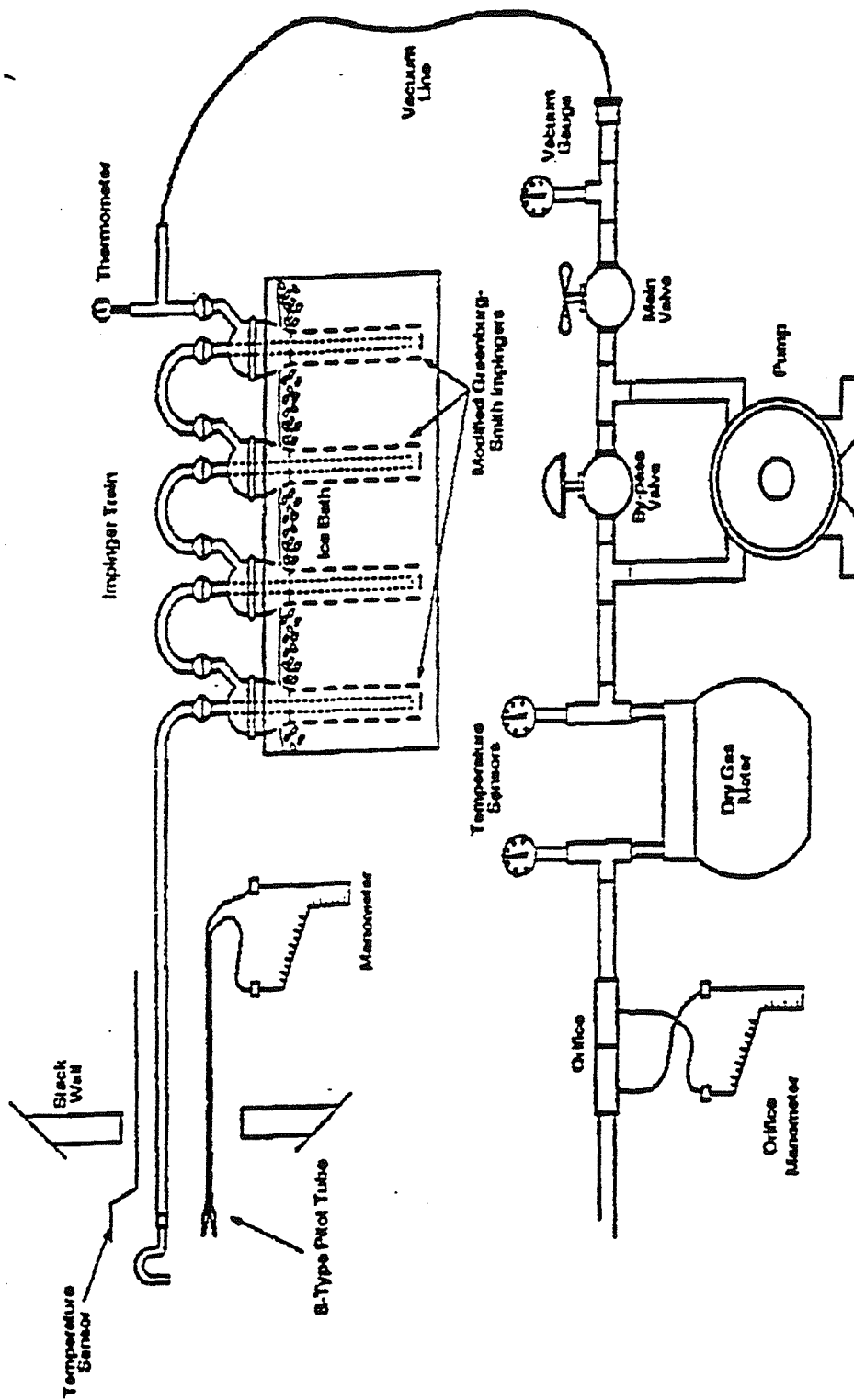
#### 3.5.4 Apparatus and Materials

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 ( 1/8 to 1/2 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  $120 \pm 14$  °C ( $248 \pm 25$ °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.



Formaldehyde Sampling Train

Figure 3.5-1



**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 impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm inside diameter ( 1/2 in) glass tube extending to 1.3 cm ( 1/2 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  $\pm 0.5$  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<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]NHNH<sub>2</sub>-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. Weigh 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<sup>1</sup>

Analyte	Detection limit, ppb <sup>2</sup>	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
o-/m-/p-Tolualdehyde	1.3	89
Dimethylbenzaldehyde	1.2	93

<sup>1</sup>Oxygenated compounds in addition to formaldehyde are included for comparison with formaldehyde; extension of the methodology to other compounds is possible.

<sup>2</sup>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,  $\mu\text{g/ml}$ ) 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):

$$\text{AIC} = 0.1 \times [\text{EAC} \times \text{SVOL} \times \text{FW} / 22.4 \times (\text{FW} + 180) / \text{FW}] (\text{RVOL} \times 1,000)$$

where:

0.1 is the acceptable contaminant concentration,  
 22.4 is a factor relating ppbv to g/L,  
 180 is a factor 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  $\mu\text{l}$  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,  $\text{CH}_2\text{Cl}_2$ : 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,  $\text{C}_6\text{H}_{12}$ : 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<sub>3</sub>OH: Methanol (HPLC grade or equivalent) is required for rinsing glassware.

3.5.5.10 Acetonitrile, CH<sub>3</sub>CN: 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 ft<sup>3</sup> of sample volume is required for the determination of the Destruction and Removal Efficiency (DRE) of formaldehyde from incineration systems (45 ft<sup>3</sup> 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  $<260^{\circ}\text{C}$  ( $500^{\circ}\text{F}$ ) 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 may 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)  $>0.00057 \text{ m}^3/\text{min}$  (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 it 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  $0.00057 \text{ m}^3/\text{min}$  (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 m<sup>3</sup>/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  $0.84 \pm 0.02$  and the stack gas equivalent density (dry molecular weight) is equal to  $29 \pm 4$ . 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.

Ambient Temperature \_\_\_\_\_  
 Barometric Pressure \_\_\_\_\_  
 Assumed Moisture % \_\_\_\_\_  
 Probe Length, m(ft) \_\_\_\_\_  
 Nozzle Identification No. \_\_\_\_\_  
 Average Calibrated Nozzle Diameter, cm (in) \_\_\_\_\_  
 Probe Heating Setting \_\_\_\_\_  
 Leak Rate, m<sup>3</sup>/min. (cfm) \_\_\_\_\_  
 Probe Liner Material \_\_\_\_\_  
 Static Pressure, mm Hg (in. Hg) \_\_\_\_\_  
 Filler No. \_\_\_\_\_

[illegible]

**Figure 3.5-2 Field Data Sheet**



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  $>20^{\circ}\text{C}$  ( $68^{\circ}\text{F}$ ) 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  $0.00057 \text{ m}^3/\text{min}$  (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  $0.00057 \text{ m}^3/\text{min}$  (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  $\pm 2^\circ\text{C}$  ( $3.60^\circ\text{F}$ ) 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  $\pm 2.5$  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  $\pm 0.5\%$  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:

$$\text{Total mg formaldehyde} = C_d \times V \times \text{DF} \times \frac{\text{[g/mole aldehyde]}}{\text{[g/mole DNPH derivative]}} \times 10^3 \frac{\text{mg}}{\mu\text{g}}$$

where:

$C_d$  = measured concentration of DNPH-formaldehyde derivative,  $\mu\text{g/ml}$ .

$V$  = organic extract volume ml.

$\text{DF}$  = dilution factor.

### 3.5.9.2 Formaldehyde concentration in stack gas.

Determine the formaldehyde concentration in the stack gas using the following equation:

$$C_f = K [\text{total formaldehyde, mg}] V_{m(\text{std})}$$



where:

$K =$  35.31 ft<sup>3</sup>/m<sup>3</sup> if  $V_{m(std)}$  is expressed in English units  
 $=$  1.00 m<sup>3</sup>/m<sup>3</sup> if  $V_{m(std)}$  is expressed in metric units.  
 $V_{m(std)}$  volume of gas sample as 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:

$$\text{Max FORM Mass} = [(WF) (\text{FORM conc}) (100 - \%DRE)] / 100$$

where:

$WF =$  mass flow rate of waste feed per h, g/h (lb/h).  
 $\text{FORM} =$  concentration of FORM (wt %) introduced into the combustion process.  
 $DRE =$  percent Destruction and Removal Efficiency required.  
 $\text{Max FORM} =$  mass flow rate (g/h [lb/l]) 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:

$$\text{Max FORM conc} = [\text{Max FORM Mass}] / DV_{\text{eff}(std)}$$

where:

$DV_{\text{eff}(std)} =$  volumetric flow rate of exhaust gas, dscm (dscf).  
 $\text{FORM conc} =$  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.

$$[\text{LDL}_{\text{FORM}} \times 10 / \text{FORM conc}] V_{\text{tbc}}$$

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  $\mu$ L 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  $\mu\text{m}$  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<sup>2</sup> 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	Precision <sup>1</sup>	Accuracy <sup>2</sup>	Detection limits <sup>3</sup>
Matrix: Dual trains	$\pm 15\%$ RPD	$\pm 20\%$	$1.5 \times 10^{-7}$ lb/ft <sup>3</sup> (1.8 ppbv).

<sup>1</sup>Relative percent difference limit for dual trains.

<sup>2</sup>Limit for field spike recoveries.

<sup>3</sup>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. <sup>1</sup>
Formaldehyde	50-00-0
Acetaldehyde	75-07-0

<sup>1</sup>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 ( $\mu\text{g/L}$ ) <sup>1</sup>
Formaldehyde	7.1	7.2

HPLC conditions: Reverse phase C18 column, 4.6 X 250 mm; isocratic elution using methanol/water (75:25, v/v); flow rates 1.0 mL/min.; detector 360 nm.

<sup>1</sup>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 ( $\mu\text{g/L}$ ) <sup>1</sup>
Formaldehyde	7.1	7.2
Acetaldehyde	8.6	171 <sup>1</sup>

HPLC conditions: Reverse phase C18 column, 4.6 X 250 mm; isocratic elution using methanol/water (75:25, v/v); flow rates 1.0 mL/min.; detector 360 nm.

<sup>1</sup>These values include reagent blank concentrations of approximately 13  $\mu\text{g/L}$  formaldehyde and 130  $\mu\text{g/L}$  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  $\mu\text{m}$  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- 1/2 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  $\mu$ L loop.

3.6.4.8.3 Column-250 mm X 4.6 mm ID, 5  $\mu$ m 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,  $\text{CH}_2\text{Cl}_2$ -HPLC grade or equivalent.

3.6.5.4 Methanol,  $\text{CH}_3\text{OH}$ -HPLC grade or equivalent.

3.6.5.5 Ethanol (absolute),  $\text{CH}_3\text{CH}_2\text{OH}$ -HPLC grade or equivalent.

3.6.5.6 2,4-Dinitrophenylhydrazine (DNPH) (70% (W/W)),  $[2,4-(\text{O}_2\text{N})_2\text{C}_6\text{H}_3]\text{NHNH}_2$ , 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),  $\text{CH}_3\text{CO}_2\text{H}$ .

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,  $\text{Na}_2\text{SO}_3$ , 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  $\mu\text{l}$  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  $\text{Na}_2\text{SO}_3$  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:

$$\text{Concentration (mg/ml)} = 30.03 \times (\text{N HCl}) \times (\text{ml HCl}) / 25.0$$

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  $\mu\text{L}$  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  $\mu\text{g/L}$ )-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 ( $\mu\text{g/L}$ )	No. of analyses
Formaldehyde	Reagent water	86	9.4	15-1430	39
	Final effluent	90	11.0	46.8-1430	16
	Phenol	93	12.0	457-1430	15
	formaldehyde sludge				

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  $5.0 \pm 0.1$  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 ml of acetate buffer and adjust the pH to  $5.0 \pm 0.5$  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 X 4.6 mm ID, 5 $\mu$ m particle size
Mobile Phase	methanol/water, 75:25 (v/v), isocratic
Flow Rate	1.0 ml/min
UV Detector	360 nm
Injection Volume	20 $\mu$ l

#### 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  $\mu$ g/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  $\mu$ g/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):

$$RF = \frac{\text{concentration of standard}}{\text{area of the signal}}$$

$$\text{mean} = RF = \overline{RF} = \frac{\sum_{i=1}^5 RF_i}{5}$$

3.6.7.8.2 Calculate the concentration of formaldehyde and acetaldehyde as follows:

$$\mu\text{g/ml} = (RF) (\text{area of signal}) (\text{concentration factor})$$

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  $\mu\text{g/ml}$  = (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 X MDL to 200 X 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

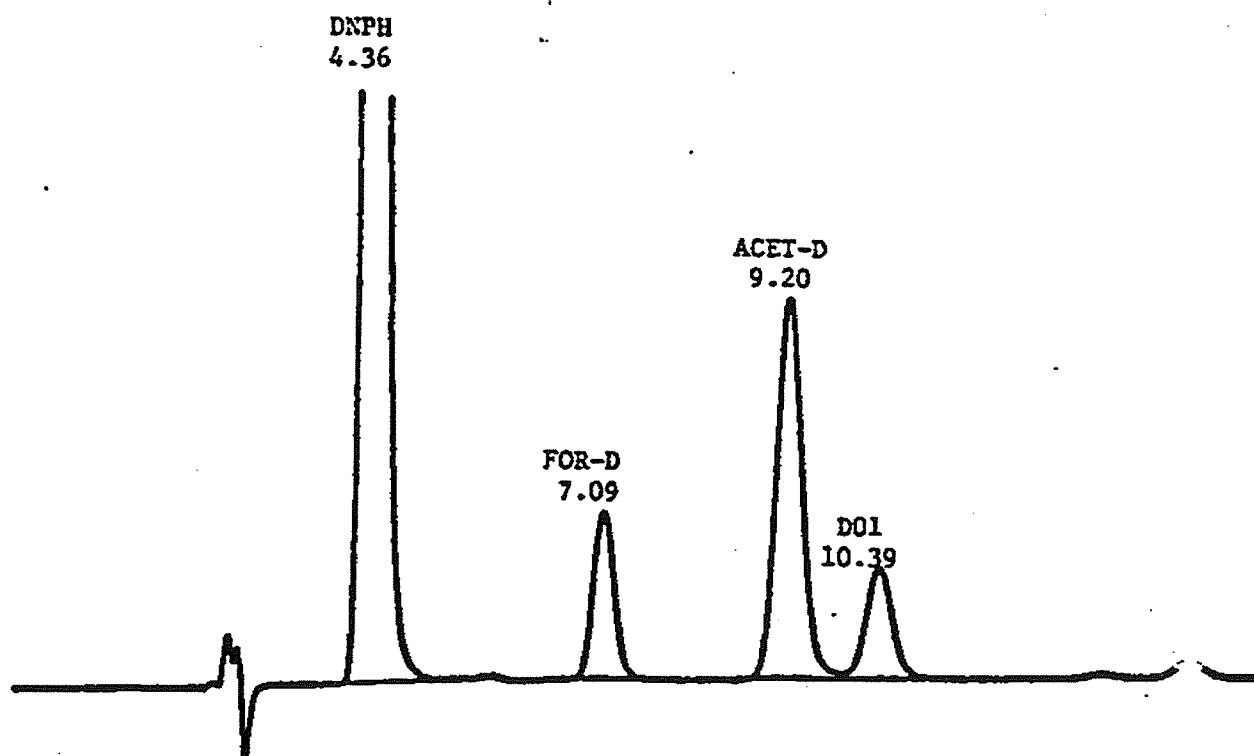
Analyte	Matrix type	Average percent recovery (x)	Standard deviation percent (p)	Spike range ( $\mu\text{g/L}$ )	No. of analyses
Formaldehyde	Reagent Water	91	2.5	50-1000	9
	Groundwater	92.5	8.2	50	6
	Liquids	69.6	16.3	250	12
Acetaldehyde	Reagent Water	60.3	3.2	50-1000	9
	Groundwater	63.6	10.9	50	12
	Liquids (2 types)	44.0	20.2	250	12
	Solids	58.4	2.7	0.10-1.0 <sup>a</sup>	12

<sup>a</sup>Spike range in units of mg/g.

x = Average recovery expected for this method.

p = Average standard deviation expected for this method.

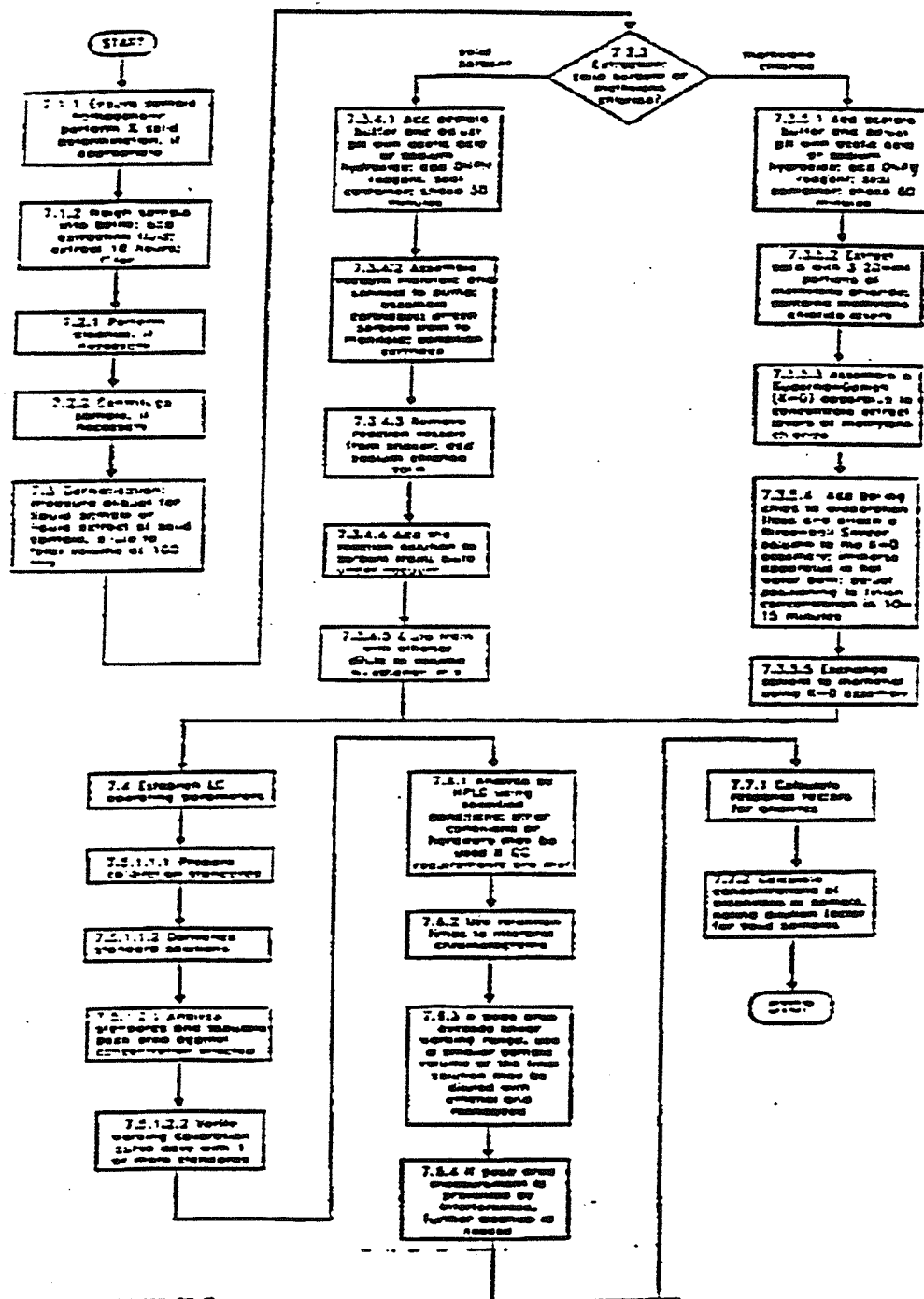
FIGURE 3.6-1  
REPRESENTATIVE CHROMATOGRAM OF A 50  $\mu\text{g/L}$  SOLUTION OF FORMALDEHYDE



FOR-D = Formaldehyde derivative  
ACET-D = Acetaldehyde derivative

FIGURE 3.6-2

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## 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<sup>1</sup> 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.

<sup>1</sup>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."

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)<sup>1</sup>

<u>Compound</u>	<u>1-TEFs, 89</u>
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
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.

<sup>1</sup>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<sup>1</sup> based on facility-specific information.

<sup>1</sup>The term dispersion coefficient refers to the change in ambient air concentration ( $\mu\text{g}/\text{m}^3$ ) resulting from a source with an emission rate of 1 g/sec.

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
- Step 9. Determine Compliance With Regulatory Limits
- Step 10. Multiple Stack Method

Step 1: Define Source Characteristics  
Provide the following source data:<sup>2</sup>

<sup>2</sup>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.

Stack Data:	Stack No. 1	Stack No. 2	Stack No. 3
Physical stack height (m)	-----	-----	-----
Exhaust temperature (°K)	-----	-----	-----
Flow rate (m <sup>3</sup> /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  $\geq 20$  meters in height)

Is the distance to the nearest shoreline <5 km? (Only applies to facilities with stacks  $\geq 20$  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 ( $\text{m}^3/\text{sec}$ )

T = Exhaust temperature ( $^{\circ}\text{K}$ )

Complete the following table to compute the "K" value for each stack:

Stack No.	Stack height X (m)	Flow rate X ( $\text{m}^3/\text{sec}$ )	Exit temp = ( $^{\circ}\text{K}$ )	K
1 _____	_____ X	_____ X	_____ =	_____
2 _____	_____ X	_____ X	_____ =	_____
3 _____	_____ X	_____ X	_____ =	_____

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:

$$\text{CEP (minimum)} = H + (1.5 \times L)$$

$$\text{GEP (maximum)} = \text{greater of 65 m or } H + (1.5 \times L)$$

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 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<sup>3</sup>, 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).

<sup>3</sup>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.

(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.<sup>4</sup>

<sup>4</sup>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

Exhaust Temperature (°K)

Flow rate (m <sup>3</sup> /s)	<325	325 - 349	350- 399	400- 449	450- 499	500- 599	600- 699	700- 799	800- 999	1 000 - 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



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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 <sup>1</sup>	Description	Urban or rural designation <sup>2</sup>
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)	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

<sup>1</sup>EPA, Guideline on Air Quality Models (Revised), EPA-450/2-78-027R, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, July, 1986.

<sup>2</sup>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.<sup>5</sup>

<sup>5</sup>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.

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 (check applicable space).	Urban	Rural
---	-------	-------

(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.

	Distance (m)	
Terrain adjusted effective stack height range (m)	Urban	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.<sup>6</sup> 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).

<sup>6</sup>For the distance range 6 to 20 kilometers, generic source number 1 is used to conservatively represent the maximum dispersion coefficient.

(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).<sup>7</sup> Record the maximum average hourly dispersion coefficient encountered.

<sup>7</sup>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.

#### Maximum Average Hourly Dispersion

Coefficient = \_\_\_\_\_ ( $\mu\text{g}/\text{m}^3/\text{g}/\text{sec}$ )

(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 ( $\mu\text{g}/\text{m}^3/\text{m}/\text{sec}$ )
0.0-0.5	----	----
>0.5-2.5	----	----
>2.5-5.0	----	----
>5.0-20.0	----	----

## Part 266, Appendix IX

Table 5.0-4.-ISCT Predicated Maximum Concentrations ( $\mu\text{G}/\text{M}^3$ )\* for Hazardous Waste Combustors Using Urban Conditions

D i s - t a n c e (KM)	Gener- ic Source #1 (<10M)	Gener- ic Source #2 (10M)	Gener- ic Source #3 (15M)	Gener- ic Source #4 (20M)	Gener- ic Source #5 (25M)	Gener- ic Source #6 (31M)	Gener- ic Source #7 (42M)	Gener- ic Source #8 (53M)	Gener- ic Source #9 (65M)	Gener- ic Source #10 (113M)	Gener- ic 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
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	86.5	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	6.5	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	84.1	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	26.5	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	69.6
2.00	66.9	66.9	48.8	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	3.6	49.3
4.00	40.2	40.2	29.3	22.8	17.4	14.7	7.6	7.6	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	27.8	27.8	27.8	27.8	27.8	27.8	27.8	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	23.8
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	17.6	17.6	17.6	17.6	17.6	17.6	17.6	17.6	17.6	17.6	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. - ISCST Predicted Maximum Concentrations ( $\mu\text{g}/\text{m}^3$ ) for Hazardous Waste Combustors Using Rural 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	28.0	10.1	3.5	0.0	1350.8
0.25	1310.6	678.4	316.9	183.6	104.6	71.8	38.0	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	0.8	1119.3
0.35	798.4	569.6	282.3	200.7	117.0	71.1	36.3	25.9	16.8	1.9	1023.8
0.40	656.9	516.5	278.7	194.4	125.2	82.7	25.3	24.6	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	851.8
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	263.8	168.0	121.6	93.3	38.6	22.1	13.6	6.5	730.6
0.60	616.6	370.4	254.0	169.1	116.2	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	85.8	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
0.80	520.9	286.8	212.1	157.7	98.8	78.5	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	491.8
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	426.8	234.2	176.8	138.1	96.3	72.6	44.4	29.8	18.2	4.0	415.8
1.10	387.5	214.7	162.5	128.2	91.9	71.1	41.8	29.5	19.3	3.9	375.0
1.20	353.5	198.4	150.3	119.3	87.4	69.1	39.1	28.6	19.8	4.1	340.3
1.30	323.0	189.6	139.9	111.5	82.9	66.7	36.6	27.5	19.8	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	92.8	71.0	59.1	31.8	23.6	18.4	4.2	242.2
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	218.3	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

\*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 Generic source stack (m)	No.	Maximum hourly dispersion coefficient ( $\mu\text{g}/\text{m}^3/\text{g}/\text{sec}$ )	Annual hourly ratio	Maximum annual dispersion coefficient ( $\mu\text{g}/\text{m}^3/\text{g}/\text{sec}$ ) <sup>1</sup>
Flat	0-20.0 0-0.5 >0.5-2.5				
Rolling or Complex	>2.5-5.0 >5.0-20.0				

<sup>1</sup>Maximum hourly dispersion coefficient times annual/hourly ratio.

- Step 8: Estimate Maximum Ambient Air Concentrations-see procedures prescribed in Subpart H of Part 266.
- Step 9: Determine Compliance with Regulatory Limits-see procedures prescribed in Subpart H of 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.<sup>8</sup>

<sup>8</sup>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 ( $\text{m}^3/\text{sec}$ )	Exit temp ( $^{\circ}\text{K}$ )	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:

$$\frac{\text{Maximum Effective Stack Height}}{\text{Minimum Effective Stack Height}} = \underline{\hspace{2cm}}$$

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 =                     

$$\frac{\text{Terrain Rise (m)}}{\text{Shortest Stack Height (m)}} \times 100 = \underline{\hspace{2cm}} \%$$

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<sup>9</sup>

Stack No.		
0-0.5	>0.5-2.5	>2.5-5.0

Distance Range (km)	HE	-	TR	=	TAE SH	HE	-	TR	=	TAE SH	HE	-	TR	=	TAE SH
1	-		=		-		=			-		=			
2	-		=		-		=			-		=			
3	-		=		-		=			-		=			

<sup>9</sup>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.<sup>10</sup> For the remaining stacks, proceed to Step 10(D)(2).

<sup>10</sup>This applies to all stacks less than or equal to 10 meters regardless of the terrain classification.

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).

Worksheet 5.0-1 Dispersion Coefficient by Downwind Distance<sup>1</sup>

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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			

<sup>1</sup> 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.

(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.<sup>11</sup> Record these data in the spaces provided below.<sup>12</sup>

<sup>11</sup>Recall that it is recommended that this analysis be performed for only one or two pollutants. The pollutants chosen for this analysis should be those that show the most significant exceedances of the risk threshold.

<sup>12</sup>Refer to Step 8 of the basic screening procedure. At this point in the screening procedure, annual emissions are used to represent hourly average emission rates. These values will be adjusted by the annual/hourly ratio to estimate annual average concentrations.

**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):

## Worksheet 5.0-2 Maximum 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
1.40	_____	_____	_____	_____
1.70	_____	_____	_____	_____
1.80	_____	_____	_____	_____
1.90	_____	_____	_____	_____
2.00	_____	_____	_____	_____
2.25	_____	_____	_____	_____
2.30	_____	_____	_____	_____
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 Hourly Ambient Air Concentration

Pollutant \_\_\_\_\_

Total Distance (km)	Stack 1 $ER \times DC = C$	Stack 2 $ER \times DC = C$	Stack 3 $ER \times DC = C$	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



(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:<sup>13</sup>

<sup>13</sup>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,<sup>14</sup> and then estimate the maximum annual average ambient air concentrations for each pollutant by completing the following table, where:

<sup>14</sup>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 ( $\mu\text{g}/\text{m}^3$ ) for pollutant "N" from Step 10(F),  
 C<sub>a</sub> = Maximum annual average air concentration for pollutant "N" ( $\mu\text{g}/\text{m}^3$ ),  
 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	$C_a (\mu\text{g}/\text{m}^3) \times R = C_a (\mu\text{g}/\text{m}^3)$		
-----	-----	X	-----
-----	-----	X	-----

(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 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)<sup>1</sup> 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.

<sup>1</sup>EPA, Guideline on Air Quality Models (Revised), EPA-450/2-78-027R, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, July, 1986.

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 1978), 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 <sup>1</sup>	Description	Urban or rural designation <sup>2</sup>
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.

<sup>1</sup>EPA, Guideline on Air Quality Models (Revised), EPA-450/2-78-027R, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, July, 1986.

<sup>2</sup>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:

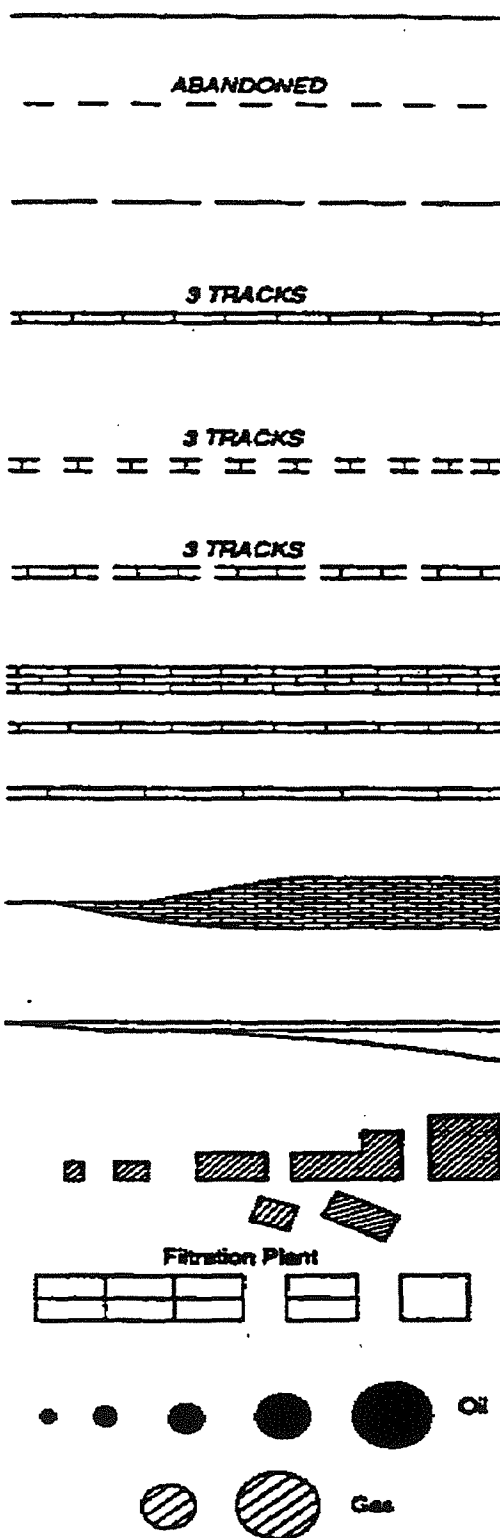
Green Wooded areas (rural).

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.

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.*



BILLING CODE 4880-S6-C

## 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 §266.112.

#### 7.1 Comparison of Waste-Derived Residue to Normal Residue

To be eligible for the Bevill exclusion from the definition of hazardous waste under 266.112(b)(1), waste-derived residue must not contain Appendix VIII, Part 261, constituents that could reasonably be attributable to the hazardous waste (toxic constituents) at concentrations significantly higher than in residue generated without burning or processing hazardous waste (normal residue). Concentrations of toxic constituents in normal residue are determined based on analysis of a minimum of 10 samples representing a minimum of 10 days of operation. The statistically-derived concentrations in normal residue are determined as the upper tolerance limit (95% confidence with a 95% proportion of the sample distribution) of the normal residue concentrations. The upper tolerance limit is to be determined as described in Section 7.2 below. If changes in raw materials or fuels could lower the statistically-derived concentrations of toxic constituents of concern, the statistically-derived baseline must be re-established for any such mode of operation with the new raw material or fuel.

Concentrations of toxic constituents in waste-derived residue are determined based on the analysis of one or more samples collected over a compositing period of not more than 24 hours. Multiple samples of the waste-derived residue may be analyzed or subsamples may be composited for analysis, provided that the sampling period does not exceed 24 hours. If more than one sample is analyzed to characterize the waste-derived residue generated over a 24-hour period, the arithmetic mean of the concentrations must be used as the waste-derived concentration for each constituent.

The concentration of a toxic constituent in the waste-derived residue is not considered to be significantly higher than in the normal residue (i.e., the residue passes the Bevill test for that constituent) if the concentration in the waste-derived residue does not exceed the statistically-derived concentration.

#### 7.2 Calculation of the Upper Tolerance Limit

The 95% confidence with 95% proportion of the sample distribution (upper tolerance limit) is calculated for a set of values assuming that the values are normally distributed. The upper tolerance limit is a one-sided calculation and is an appropriate statistical test for cases in which a single value (the waste-derived residue concentration) is compared to the distribution of a range of values (the minimum of 10 measurements of normal residue concentrations). The upper tolerance limit value is determined as follows:

$$UTL = X + (K)(S)$$

where  $X$  = mean of the normal residue concentrations,  $X = X_i/n$ ,

$K$  = coefficient for sample size  $n$ , 95% confidence and 95% proportion,

$S$  = standard deviation of the normal residue concentrations,

$S = (\sum (X_i - X)^2 / (n - 1))^{0.5}$ , and



$n$  = sample size.

The values of  $K$  at the 95% confidence and 95% proportion, and sample size  $n$  are given in Table 7.0-1.

For example, a normal residue test results in 10 samples with the following analytical results for toxic constituent A:

Sample No.	Concentration of constituent 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 the standard deviation of these measurements, calculated using the above equations, are 11.5 and 2.9, respectively. Assuming that the values are normally distributed, the upper tolerance limit (UTL) is given by:

$$UTL = 11.5 + (2.911)(2.9) = 19.9 \text{ ppm}$$

Thus, if the concentration of constituent A in the waste-derived residue is below 19.9 ppm, then the waste-derived residue is eligible for the Bevill exclusion for constituent A.

### 7.3 Normal Distribution Assumption

As noted in Section 7.2 above, this statistical approach (use of the upper tolerance limit) 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 always 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 (References 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 upper tolerance limit using the procedures in Section 7.2 above.

In all cases where the owner or operator 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, he/she must provide supporting rationale in the operating record that demonstrates 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 determination 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 Secretary.

Table 7.0-1. - K Values for 95% Confidence and 95% Proportion

Sample size (n)	K
10	2.911
11	2.815
12	2.736
13	2.670
14	2.614
15	2.566
16	2.523
17	2.486
18	2.458
19	2.423
20	2.396
21	2.371
22	2.350
23	2.329
24	2.303
25	2.292

#### 7.5 References

1. Shapiro, S.S. and Wilk, M.B. (1965), "An Analysis of Variance Test for Normality (complete samples)," *Biometrika*, 52,591-611.
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 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 chlorine, metals, or PM and the air pollution control system removal efficiency (APCS RE) for these pollutants. The SRE is defined as:

$$\text{SRE} = (\text{species input} - \text{species emitted}) / \text{species input}$$

The SRE can be calculated from the partitioning factor (PF) and APCS RE by the following formula:

$$\text{SRE} = 1 - [(PF/100) \times (1 - \text{APCS RE}/100)]$$

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<sub>2</sub>, 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.  $\Delta p$   
 VS.60 = Venturi Scrubber, ca. >60 in W.G.  $\Delta p$   
 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) <sup>1</sup>				
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

<sup>1</sup>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) <sup>1</sup>				
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
Silver	Ag	1080	940	840	740	660
Thallium	Tl	900	800	700	620	540

<sup>1</sup>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 Cl<sub>2</sub>

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  $\text{Cl}_2$  for most types of APCS is generally minimal. Therefore, the default assumption for APCS RE for  $\text{Cl}_2$  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. $\Delta p$
VS-60 =	Venturi Scrubber, ca. > 60 in W.G. $\Delta p$
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, Cl<sub>2</sub>, 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 Cl<sub>2</sub>

The Agency has established the special procedures presented below for chlorine because the emission limits are based on the pollutants HCl and Cl<sub>2</sub> formed from chlorine fed to the combustor. Therefore, the owner/operator must estimate the controlled emission rate of both HCl and Cl<sub>2</sub> 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 Cl<sub>2</sub>, 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  $\leq 0.95$ , the default partitioning factor is 20 percent Cl<sub>2</sub>, 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 Cl<sub>2</sub>.

3. To determine the uncontrolled (i.e., prior to acid gas APCS) emission rate of HCl and Cl<sub>2</sub>, 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 HCl to the molecular weight of Cl (i.e., 36.5/36.5). No conversion is needed for Cl<sub>2</sub>.

### 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<sub>2</sub>, 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<sub>2</sub>, 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<sub>2</sub> 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  $[(21 - O_2 \text{ concentration from step 1}) / (21 - 7)]$ .

### 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 §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:

$$ME \left( \frac{\text{lb Emitted Metal}}{\text{hr}} \right) = \frac{PME \left( \frac{\text{lb PM}}{\text{hr}} \right) \cdot DMC \left( \frac{\text{lb Dust Metal}}{\text{lb Dust}} \right) \cdot EF \left( \frac{\text{lb Emitted Metal/lb PM}}{\text{lb Dust Metal/lb Dust}} \right)}{1} \quad (1)$$

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 266.106), and that particulate emissions are at the particulate matter limit (PML):

$$DMCL \left( \frac{\text{lb Dust Metal}}{\text{lb Dust}} \right) = \frac{\text{Tier III Limit} \left( \frac{\text{lb Emitted Metal}}{\text{hr}} \right)}{PML \left( \frac{\text{lb PM}}{\text{hr}} \right) EF \left( \frac{\text{lb Emitted Metal} / \text{lb PM}}{\text{lb Dust Metal} / \text{lb Dust}} \right)} \quad (2)$$

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 ( $DMCL_v$ ):

$$DMCL_v \left( \frac{\text{lb Dust Metal}}{\text{lb Dust}} \right) = \frac{\text{Tier III Limit} \left( \frac{\text{lb Emitted Metal}}{\text{hr}} \right)}{PML \left( \frac{\text{lb PM}}{\text{hr}} \right) EF_{95\%} \left( \frac{\text{lb Emitted Metal} / \text{lb PM}}{\text{lb Dust Metal} / \text{lb Dust}} \right)} \quad (3)$$

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:

$$SEF \geq 2 EF_{95\%} \quad (4a)$$

If  $EF_{99\%}$  is not greater than two times the value of  $EF_{95\%}$ , the "safe" enrichment factor can be calculated using Equation 4b:

$$SEF \geq EF_{99\%} \quad (4b)$$

In cases where the enrichment factor cannot be determined because the kiln dust metal concentration is nondetectable, the "safe" enrichment factor is as follows:

$$SEF = 100 \quad (4c)$$

For all cases, the "conservative" dust metal concentration limit is calculated using the following equation:

$$DMCL_c \left( \frac{\text{lb Dust Metal}}{\text{lb Dust}} \right) = \frac{\text{Tier III Limit} \left( \frac{\text{lb Emitted Metal}}{\text{hr}} \right)}{PML \left( \frac{\text{lb PM}}{\text{hr}} \right) SEF \left( \frac{\text{lb Emitted Metal} / \text{lb PM}}{\text{lb Dust Metal} / \text{lb Dust}} \right)} \quad (5)$$

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  $EF_{95\%}$  exists, the "violation" dust metal concentration limit is set at ten times the "conservative" limit:

$$DMCL_v = 10 \times DMCL_c \quad (6)$$

#### 10.4 Overview

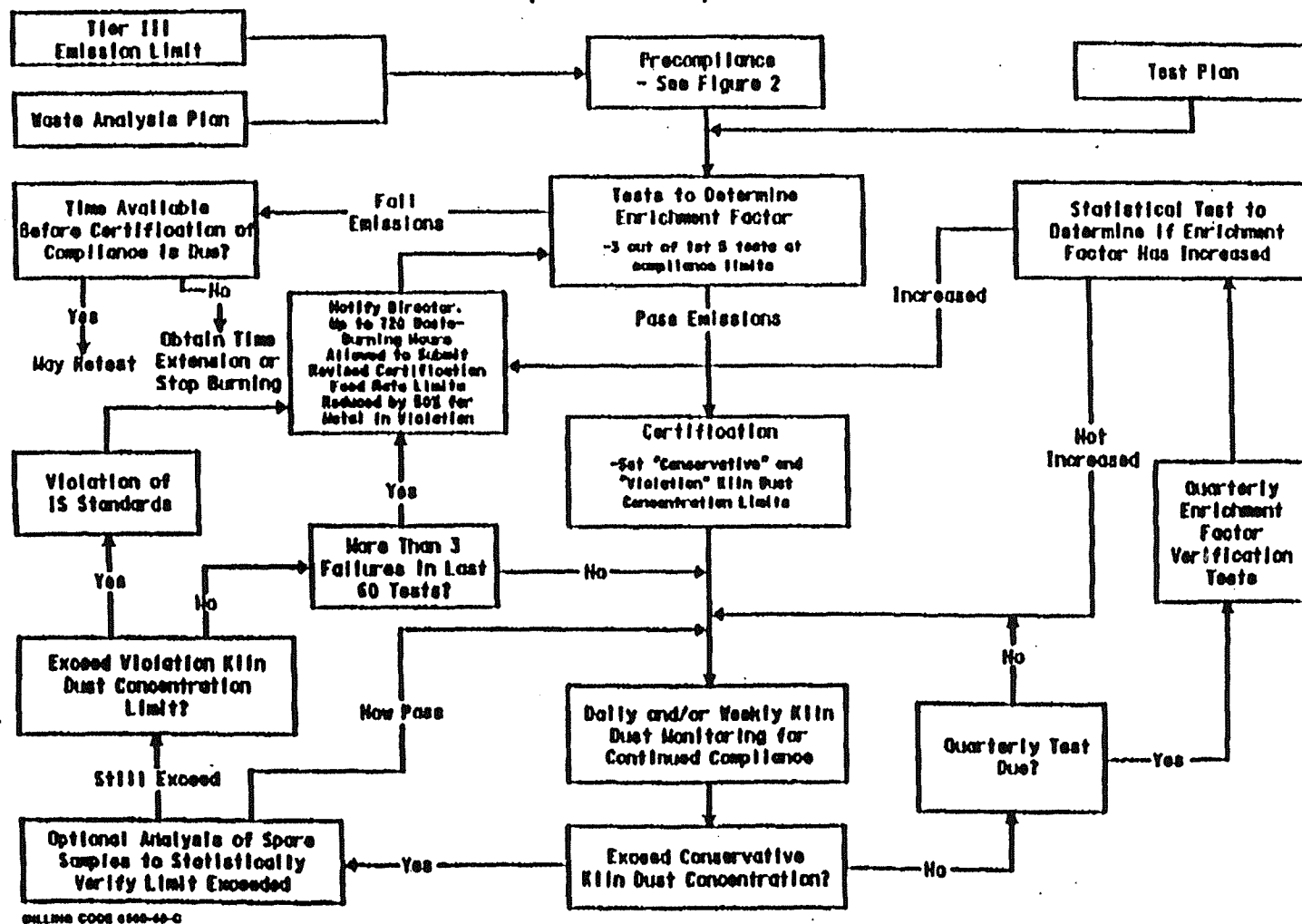
The flowchart for implementing the method is shown in Figure 10.4-1. The general procedure is as follows:

- Follow the certification of precompliance procedures described in subsection 10.6 (to comply with §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 266.103(c).



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Figure 10.4-1  
Compliance Implementation Flow Chart



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- 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 §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 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 §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  $EF_{95\%}$  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  $EF_{95\%}$  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  $EF_{95\%}$ .

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<sub>2</sub> 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 §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).

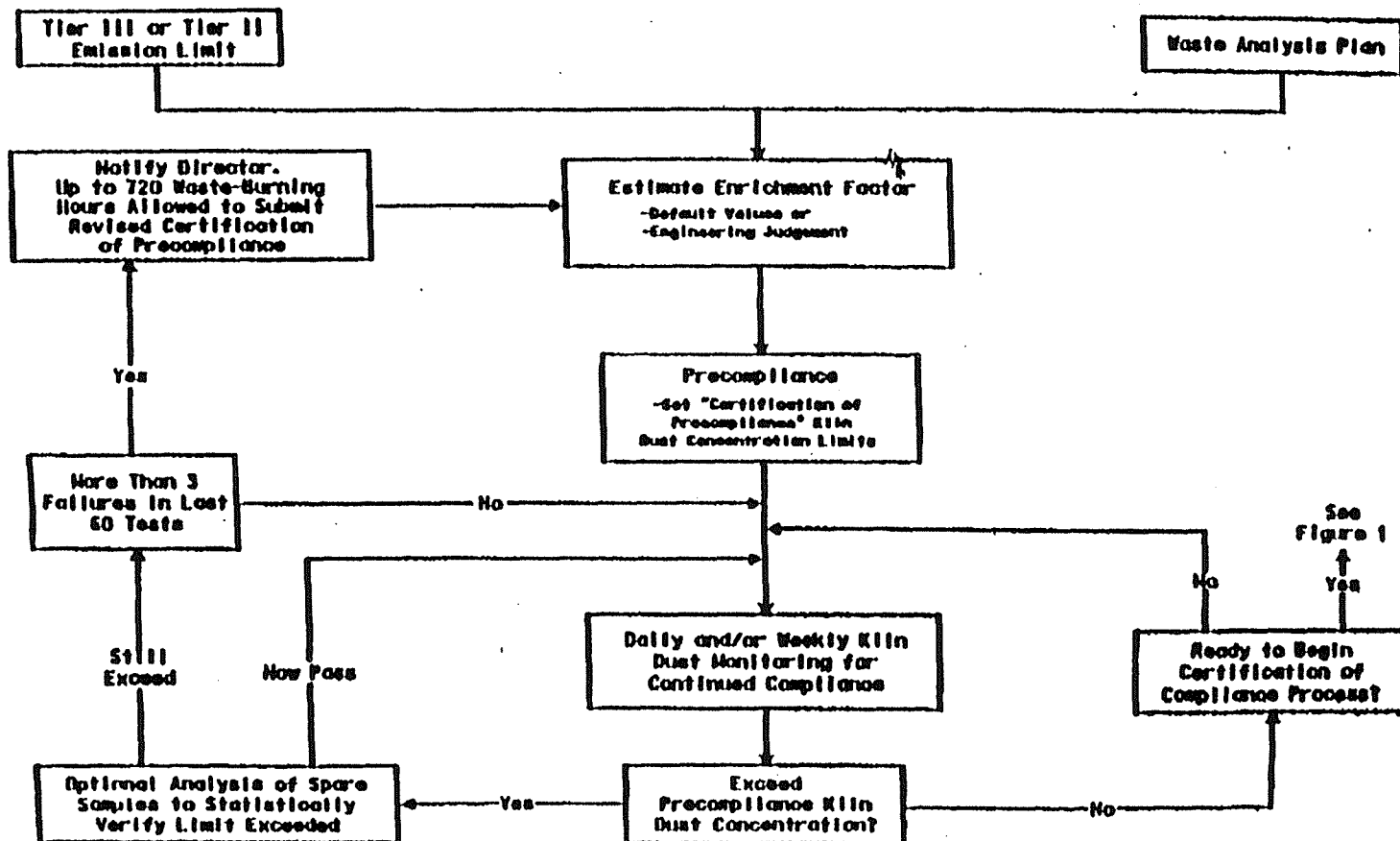
- Follow the procedures described in SW-846 for preparing waste analysis plans for the following tasks:

- 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.

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<sub>e</sub>) 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 8 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 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.
    - 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:

$$EF_{95\%} = EF + z_c \sigma \quad (1)$$

where:

$$\overline{EF} = \frac{\sum_{i=1}^n EF_i}{n} \quad (2),$$

$$\sigma = \left[ \frac{\sum_{i=1}^n (EF_i - \overline{EF})^2}{n} \right]^{1/2} \quad (3)$$

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:

$$EF_{95\%} = EF + t_c S \quad (4)$$

where the standard deviation,  $S$ , is defined as:

$$S = \left[ \frac{\sum_{i=1}^n (EF_i - \overline{EF})^2}{n-1} \right]^{1/2} \quad (5)$$

$t_c$  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  $t_{\text{meas}}$ :

$$t_{\text{meas}} = \frac{\overline{EF}_1 - \overline{EF}_2}{\sigma_t \left( \frac{1}{n_1} + \frac{1}{n_2} \right)^{1/2}} \quad (6)$$

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	2.76
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
$\infty$	1.645	2.33

$$\sigma_t = \left( \frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2} \right)^{1/2} \quad (7)$$

is compared to  $t_{\text{crit}}$  at the desired confidence level. The 95% confidence level is used in this method. Values of  $t_{\text{crit}}$  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  $t_{\text{meas}}$  is greater than  $t_{\text{crit}}$ , 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,  $Q_{\text{meas}}$ , is then compared with rejection values that are critical for a particular degree of confidence, where  $Q_{\text{meas}}$  is:

$$Q_{\text{meas}} = \frac{\text{DMC}_{\text{highest}} - \text{DMC}_{\text{next highest}}}{\text{DMC}_{\text{highest}} - \text{DMC}_{\text{lowest}}} \quad (8)$$

The 90% confidence level for data rejection is used in this method. Table A-2 provides the values of  $Q_{\text{crit}}$  at the 90% confidence level. If  $Q_{\text{meas}}$  is larger than  $Q_{\text{crit}}$ , 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	$Q_{\text{crit}}$
3	0.94
4	0.76
5	0.64
6	0.56
7	0.51
8	0.47
9	0.44
10	0.41

(Amended July 26, 1994, August 21, 1997)

Appendix X. - [Reserved]

**Appendix XI. - Lead-Bearing Materials That May be Processed in Exempt Lead Smelters**

**A. Exempt Lead-Bearing Materials When Generated or Originally Produced By Lead-Associated Industries<sup>1</sup>**

<sup>1</sup>Lead-associated industries are lead smelters, lead-acid battery manufacturing, and lead chemical manufacturing (e.g., manufacturing of lead oxide or other lead compounds).

Acid dump/fill solids

Sump mud

Materials from laboratory analyses

Acid filters

Baghouse bags

Clothing (e.g., coveralls, aprons, shoes, hats, gloves)

Sweepings

Air filter bags and cartridges

Respiratory cartridge filters

Shop abrasives

Stacking boards

Waste shipping containers (e.g., cartons, bags, drums, cardboard)

Paper hand towels

Wiping rags and sponges

Contaminated pallets

Water treatment sludges, filter cakes, residues, and solids

Emission control dusts, sludges, filter cakes, residues, and solids from lead-associated industries (e.g., K069 and D008 wastes)

Spent grids, posts, and separators

Spent batteries

Lead oxide and lead oxide residues



Lead plates and groups

Spent battery cases, covers, and vents

Pasting belts

Water filter media

Cheesecloth from pasting rollers

Pasting additive bags

Asphalt paving materials

**B. Exempt Lead-Bearing Materials When Generated or Originally Produced By Any Industry**

Charging jumpers and clips

Platen abrasive

Fluff from lead wire and cable casings

Lead-based pigments and compounding pigment dust  
(Amended July 26, 1994)

**Appendix XII. - Nickel or Chromium-Bearing Materials that may be Processed in Exempt Nickel-Chromium Recovery Furnaces**

**A. Exempt Nickel or Chromium-Bearing Materials when Generated by Manufacturers or Users of Nickel, Chromium, or Iron**

Baghouse bags

Raney nickel catalyst

Floor sweepings

Air filters

Electroplating bath filters

Wastewater filter media

Wood pallets

Disposable clothing (coveralls, aprons, hats, and gloves)

Laboratory samples and spent chemicals

Shipping containers and plastic liners from containers or  
vehicles used to transport nickel or chromium-containing wastes

Respirator cartridge filters

Paper hand towels

**B. Exempt Nickel or Chromium-Bearing Materials when Generated by Any Industry**

Electroplating wastewater treatment sludges (F006)

Nickel and/or chromium-containing solutions

Nickel, chromium, and iron catalysts

Nickel-cadmium and nickel-iron batteries

Filter cake from wet scrubber system water treatment plants  
in the specialty steel industry

(Amended July 26, 1994, August 21, 1997)

**Appendix XIII - Mercury Bearing Wastes That May Be Processed in Exempt Mercury Recovery Units**

These are exempt mercury-bearing materials with less than 500 ppm of Part 261, Appendix VIII organic constituents when generated by manufacturers or users of mercury or mercury products.

1. Activated carbon
2. Decomposer graphite
3. Wood
4. Paper
5. Protective clothing
6. Sweepings
7. Respiratory cartridge filters
8. Cleanup articles
9. Plastic bags and other contaminated containers
10. Laboratory and process control samples
11. K106 and other wastewater treatment plant sludge and filter cake
12. Mercury cell sump and tank sludge
13. Mercury cell process solids
14. Recoverable levels of mercury contained in soil