APPENDIX B

SAMPLING AND ANALYSIS

(139 pages)

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TABLES

FIGURES

ACRONYM LIST

µg	Microgram
µm	Micron
µg/m^3	Microgram per cubic meter
µg/mL	Microgram per milliliter
AED	Atomic emission detection
A/K	Aldehyde/ketone
AMS	Alkaline mercury speciation
BaP	Benzo(a)pyrene
BIF	Boiler and industrial furnace
BP	Boiling point
CARB	California Air Resources Board
CAS	Chemical Abstract Services
CB	Chlorobenzene
CEM	Continuous emissions monitor
CFR	Code of Federal Regulations
Cl_2	Chlorine
COPC	Chemical of potential concern
CP	Chlorophenol
dscm	Dry standard cubic meters
D/F	Dioxin and furan
DQO	Data quality objective
DNPH	2,4-dinitrophenylhydrazine
ECD	Electron capture detector
EDL	Estimated detection limit
EDO	Environmental data operation
EER	Energy and Environmental Research Corporation
EMPC	Estimated maximum possible concentration
EMTIC	Emissions Measurement Technical Information Center
EPA	U.S. Environmental Protection Agency
FGC	Field gas chromatography
FID	Flame ionization detector
FTIR	Fourier transform infrared
g	Gram

ACRONYM LIST (Continued)

GC	Gas chromatography
GC/MS	Gas chromatography/mass spectrometry
GFC	Gas filter correlation
GRAV	Gravimetric
HCl	Hydrogen chloride
HPLC	High performance liquid chromatography
HRGC	High resolution gas chromatography
HRMS	High resolution mass spectrometry
ICP	Inductively coupled plasma
IDL	Instrument detection limit
IR	Infrared
L	Liters
LC	Liquid chromatography
LOL	Limit of linearity
LOQ	Limit of quantitation
LRMS	Low resolution mass spectrometry
m^3	Cubic meter
MDL	Method detection limit
MDGC	Multi-dimensional gas chromatography
mg	Milligram
mL	Milliliters
MRI	Midwest Research Institute
MS	Mass spectrometry
ng	Nanogram
OSW	Office of Solid Waste
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofurans
pg	Picogram
POHC	Principal organic hazardous constituent
ppb	Parts-per-billion
ppm	Parts-per-million
ppq	Parts-per-quadrillion

ACRONYM LIST (Continued)

QAPP	Quality assurance project plan
RCRA	Resource Conservation and Recovery Act
RDL	Reliable detection limit
RSD	Relative standard deviation
SEM	Scanning electron microscope
SMVOC	Sampling method for volatile organic compounds
SOP	Standard operating procedure
SSSADIR	Stationary Source Sampling and Analysis Directory
SVOC	Semivolatile organic compound
TCO	Total chromatographable organic
TEF	Toxicity equivalence factor
TEQ	Toxic equivalent
THC	Total hydrocarbon
TIC	Tentatively identified compound
TOE	Total organic emissions
VOC	Volatile organic compound
VOST	Volatile organic sampling train

B.1 OVERVIEW OF SAMPLING AND ANALYSIS PROCEDURES

This appendix discusses procedures that are recommended by the U.S. Environmental Protection Agency (EPA) Office of Solid Waste (OSW) for collection of stationary source stack emissions data for evaluation in site-specific risk assessments. Site-specific risk assessment emissions data needs can generally be categorized as follows:

- Dioxins and furans (D/Fs);
- Organics other than dioxins and furans;
- Metals;
- Particle-size distribution; and
- Hydrogen chloride and chlorine.

In Chapter 2 of *Risk Burn Guidance for Hazardous Waste Combustion Facilities*, the importance of characterizing the stack emissions as completely as possible, regardless of the availability of toxicological data for the compounds of potential concern, is stressed. EPA OSW recommends that all compounds initially be identified and quantified to the maximum extent achievable by currently available sampling and analytical methods.

This appendix is intended to be a tool to assist permit writers and facility managers in making informed decisions regarding the emissions measurements necessary to meet their risk assessment data needs. This appendix identifies recommended methodologies for stack sampling and analysis, as well as considerations which have an impact upon the usability of the analytical data. Where data are available from 40 Code of Federal Regulations (CFR) Part 63 Appendix A Method 301 field validation tests with dynamic spiking, the data are summarized in this appendix to assist in the selection of an appropriate sampling and analytical methodology. This appendix also provides clarifications and “lessons learned” for the stack sampling and analytical methods that have not been widely published elsewhere.

In addition to the stack determinations to be performed as part of a risk burn, EPA OSW recommends that a comprehensive characterization of waste feeds, auxiliary fuels, and raw materials be performed to establish the basis for the risk burn and risk assessment. Characterization of process samples is discussed briefly in this appendix.

B.1.1 EMISSIONS TESTING OBJECTIVES

EPA OSW recommends that the sampling and analytical procedures used to generate emissions data for site-specific risk assessments be chosen to accomplish three primary objectives:

- ***Achieve the most comprehensive emissions characterization possible for toxic constituents;***

  A comprehensive emissions characterization identifies and quantifies as many individual toxic constituents as possible to assess their contribution to the total risk posed by the facility.

- ***Identify and quantify as many other constituents as possible, regardless of toxicity;***

  This recommended objective involves determinations for constituents that are not typically included on target analyte lists, such as tentatively identified compounds (TICs) and simple hydrocarbons, to reduce the uncertainty associated with the risk assessment.

- ***Evaluate the completeness of the organic emissions characterization.***

  The uncertainty of the risk assessment process depends upon the completeness of the characterization of the source. EPA OSW has recommended (EPA 1998a) that completeness be determined based on the difference between a Total Organic Emissions (TOE) measurement (EPA 1996a) and the total quantity of identified organics.

The first recommended objective, comprehensive characterization of emissions, is achieved by analyses for specific target analytes. The target list for an analytical method addresses known toxic compounds and, in most cases, the target list for a method includes compounds for which the applicability of the method has been demonstrated. EPA OSW recommends that analysis for the complete method target list for each method generally be performed. Deletion of individual compounds *a priori* (e.g., because they are not found in the waste feed stream, or because the compounds are not expected to be risk drivers) is not recommended. Organic stack emissions cannot be predicted with certainty based upon waste feed characteristics. Analyses performed for a modified method target list (a list generated by the deletion of certain compounds) generally do not cost significantly less than analyses performed for the complete target list because the laboratory needs the same amount of time to prepare the samples and perform the analysis for a modified method target list as for a complete method target list. Therefore, the *a priori* deletion of individual compounds is not likely to significantly reduce analytical costs and could jeopardize the chances of identifying the greatest possible percentage of organic compounds.

To support the second recommended objective, a comprehensive characterization of additional analytes (regardless of toxicity) to reduce uncertainty for the risk assessment, EPA OSW recommends that measurements for non-target compounds such as tentatively identified compounds and simple hydrocarbons be performed. These measurements, especially for simple hydrocarbons, can significantly improve the completeness of the overall emissions characterization.

For methods employing a mass spectrometric analysis, non-target compounds can be identified by means of on-line library search or interpretation of mass spectra, and a quantitative estimate can be provided for these additional compounds. Constituents identified in this manner are called tentatively identified compounds, since there is no reference standard analyzed at the same time as the tentative identification. Studies performed by Lemieux, Ryan, and Midwest Research Institute (MRI) have relied on comprehensive evaluations for TICs to expand compound identifications beyond standard method target analyte lists (Lemieux and Ryan 1997 and 1998; EPA 1997a; MRI 1997). Identification of TICs has also played a key role in full-scale research (Energy and Environmental Research Corporation [EER] 1997).

Uncertainty in the risk assessment can also be reduced by identifying and quantifying simple hydrocarbons, such as methane. Determinations that specifically identify methane and other aliphatic compounds add little cost to the analysis of emissions samples and can potentially alleviate concerns about the percentage of organic mass that might represent toxic compounds. In studies emphasizing complete characterization of emissions regardless of toxicity, MRI (MRI 1997) and EER (EER 1997) performed screening for C_1 through C_4 straight-chain alkanes, alkenes, and alkynes using an on-line gas chromatograph/flame ionization detector (GC/FID) and specific analyses of SW-846 (EPA 1996b) Method 0040 bag samples for C_1 - C_4 compounds. Simple hydrocarbons, especially methane, have been found to comprise a significant percentage of the total stack organic compounds (MRI 1997; Johnson 1996a).

The third recommended objective, equally as important as the first two, involves an assessment of the completeness of the organic emissions characterization. Organic compounds that cannot be identified by laboratory analysis will not be not addressed quantitatively in risk assessment calculations, and studies (EPA 1976; Pellizzari and others 1980) have shown that analyses based strictly on target analyte lists may account for less than 20 percent of the organic material in an environmental sample. However, the unidentified organic mass still may contribute to the overall risk, and EPA OSW has therefore recommended that the unidentified mass be considered in the uncertainty analysis for the risk assessment (DeCicco 1995; EPA 1998a). An assessment of the completeness of an organic emissions characterization can be made by performing a mass balance for the organic stack emissions. In particular, EPA OSW has recommended that a Total Organic Emissions analysis (EPA 1996a) be performed to quantify the total recoverable organic mass emitted from the source, and that the quantity of unidentified organic compounds be estimated based on the difference between the TOE mass and the total quantity of identified organic compounds (EPA 1998a). Research has recently been performed to evaluate and clarify the analytical procedures for the TOE determination, and revised technical details for TOE analysis are included in this guidance. The revised technical details will be incorporated into an updated TOE guidance expected to be released later in 2001.

EPA developed the TOE measurement to measure total recoverable organics (and therefore to provide an accounting of the total mass of unidentified organic compounds) because existing methods such as total hydrocarbon (THC) analyzers and analytical method target lists do not fully determine the total mass of organics present in stack gas emissions (Johnson 1996a). Several research studies have indicated that total hydrocarbon measurements may not be adequate or appropriate for supporting a mass balance of organic compounds (Ryan and others 1997a; MRI 1997). Total hydrocarbon monitors measure only gas phase organic compounds. Particulate material, including an indeterminate but sometimes significant fraction of the organic material, is filtered from the gas stream entering the THC analyzer and is discarded. This potential loss of non-volatile organic material is clearly unacceptable when a determination for total recoverable organic mass is desired (Johnson 1996a). The TOE analysis has been repeatedly cited as the preferred starting point for mass balance measurements (Lemieux and Ryan 1997 and 1998; EPA 1997a; Johnson 1996a; EPA 1996a). EPA OSW has recommended that the TOE result be used in conjunction with the total mass of identified organic compounds to calculate a TOE factor, which is then used to support an evaluation of uncertainty associated with the risk assessment (EPA 1998a). Permitting authorities can then evaluate the TOE factor and assess to what extent actual risks may be greater than estimated risks (EPA 1998a).

The methods and target analyte lists described in this appendix are generally commercially available, but recently developed methods for which limited actual field test data are available are also included when published EPA or other methods are limited. For the specific methods discussed in this appendix, available information is provided on method development and field evaluation studies for Clean Air Act analytes performed by EPA under contracts 68-D1-0010 and 68-D4-0022 where both laboratory data and field data were generated at stationary sources using dynamic spiking procedures.

Research by Ryan and others (Ryan and others 1997a and 1997b), Lemieux and Ryan (Lemieux and Ryan 1997 and 1998; EPA 1997a**)**, and Midwest Research Institute and A. T. Kearney (MRI 1997) provides valuable insight into the limitations of standard methods for identifying and quantifying organics. Innovative techniques suggested by Lemieux and Ryan (e.g., multi-dimensional gas chromatography/mass spectrometry (MDGC/MS), gas chromatography/atomic emission detection (GC/AED), and liquid chromatography/mass spectrometry (LC/MS) are currently research methodologies and not generally available in the commercial laboratories performing analyses for risk burns. However, as alternative options for performing measurements become available, facilities may prefer to apply these new methods upon demonstration of acceptable performance. Until further method development and evaluation have been performed, EPA OSW recommends that comprehensive characterization of organic emissions rely on correct application of the best available methods for specific target analytes and tentatively identified compounds, coupled with a TOE determination to indicate the portion of the organic mass that cannot be identified.

B.1.2 GENERATION OF USABLE DATA FOR RISK ASSESSMENTS

In selecting the specific sampling and analysis procedures to be used, EPA OSW recommends that each facility carefully consider the data quality objectives that need to be met to demonstrate an acceptable level of risk. Risk burn data quality objectives may necessitate analyses near or below analytical detection or quantitation levels. Because measurements made below analytical detection and quantitation levels are associated with increased measurement uncertainty, an understanding of these levels is important to the comprehension of the effect they may have when applied.

Compounds included on a target list that are not detected in the environmental sample present two questions:

- Is the compound really present?, and
- If the compound is present, at what concentration is the compound present?

Table B.1-1, reproduced from *Guidance for Data Useability in Risk Assessment* (EPA 1992) for the convenience of the reader, summarizes recommended requirements for confident identification and quantitation.

TABLE B.1-1

REQUIREMENTS FOR CONFIDENT IDENTIFICATION AND QUANTITATION

Identification	Analyte present above the instrument detection limit (IDL).
	Organic – Retention time and/or mass spectra matches authentic standards.
	Inorganic – Spectral absorptions compared to authentic standards.
	Knowledge of blank contamination (if any).
Quantitation	Instrument response known from analysis of an authentic standard.
	Detected concentration above the limit of quantitation and within the limit of linearity (instrument response not saturated).

As indicated by the information in Table B.1.1, the first objective of any analysis is confidence in the identification of chemicals of potential concern (COPCs). Identification requires that the chemical be present in an environmental sample above the detection limit, although it is possible to identify a chemical at a level lower than the level necessary for accurate quantitative analysis. Identification of inorganic chemicals is performed by comparison of their unique spectral absorption characteristics to authentic standards, with the certainty of the identification a function of the absence of interferences.

To ensure the highest possible level of confidence in the identification of an organic chemical, an instrumental technique such as mass spectrometry is necessary to provide definitive results. Analytical techniques alternative to mass spectrometry are frequently available, but mass spectrometry coupled with gas chromatographic separation procedures provides the best option for confident identification to minimize the risk of error in the qualitative identification of organic analytes. Specific methods contain the criteria for compound identification. The two mass spectral methodologies that are used are full scan, in which the mass spectrometer is scanned repeatedly over a defined mass range, and selected ion monitoring, in which the mass spectrometer monitors only the masses specified in a given time window.

Full-scan methods such as SW-846 Method 8260 (Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)) and SW-846 Method 8270 (Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)) specify criteria for the qualitative identification of compounds by comparison of chromatographic retention times to authentic standards for which the analytical system is calibrated and by comparison to reference mass spectra. These methods also present guidelines for tentative identification of sample components not associated with the calibration standards (TICs) using library search coupled with interpretation by an experienced analyst. Positive identification of TICs is confirmed by re-analysis of the sample with an authentic standard.

Methods that use selected ion monitoring techniques such as SW-846 Method 8290 (Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)) rely upon correspondence of gas chromatographic retention times to authentic standards, high resolution mass measurements, and accurate ratios between specified isotopic peaks in the ion clusters. Because only specified masses are monitored in a retention time window, methods that use selected ion monitoring procedures cannot be used to identify compounds other than the specified compounds.

In addition to the identification of the chemicals, accurate quantitative data is typically desired. For quantitative analysis, an analytical instrument response has to be known from analysis of an authentic standard, and the concentration that is detected has to be above the limit of quantitation and within the limit of linearity (the instrument response cannot be saturated either chromatographically or in the detector). The existence of contamination in blanks and samples can impact both the identification of analytes and their quantitative analysis.

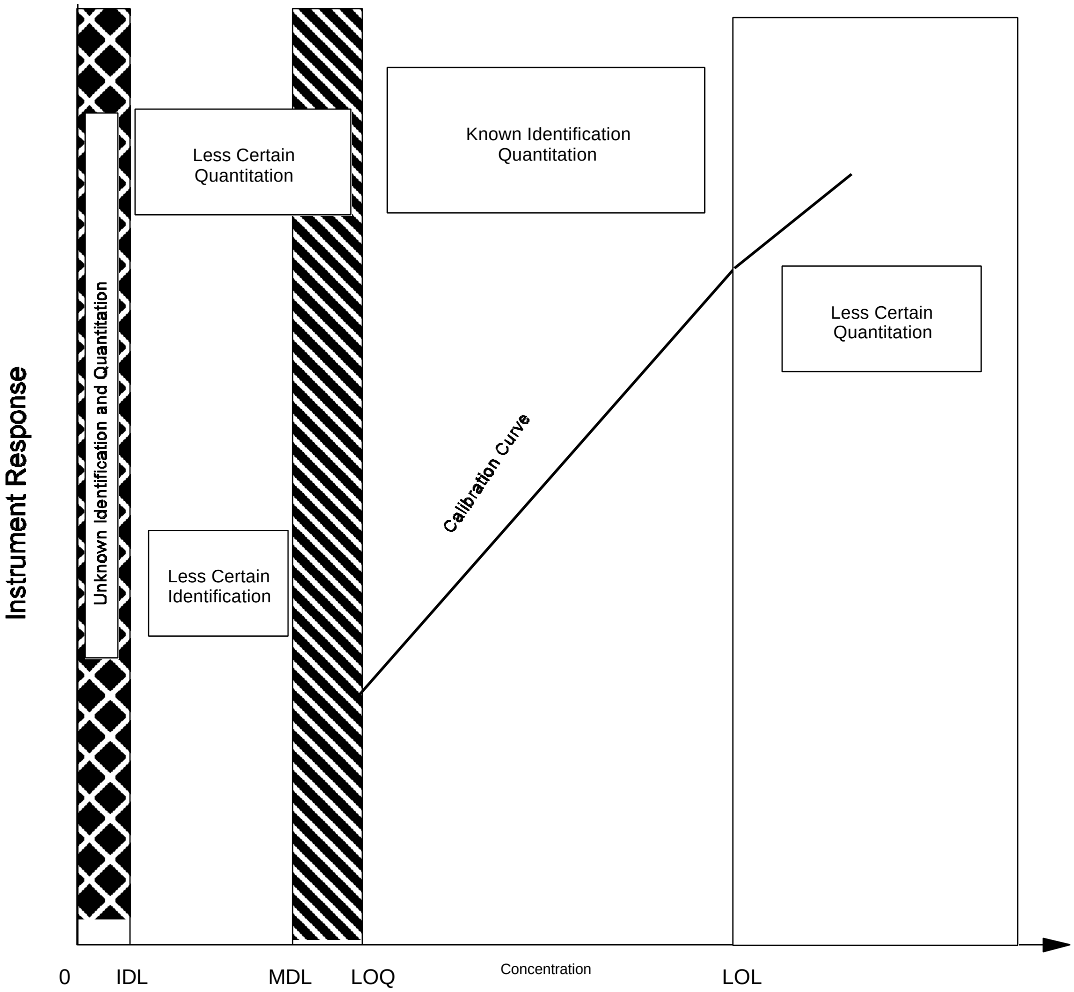
B.1.2.1 Detection Limits, Quantitation Limits, and the Range of Linearity

The relationship between analytical instrument response, detection limits, and a calibration curve is shown in Figure B.1-1, reproduced from *Guidance for Data Useability in Risk Assessment* (EPA 1992) for the convenience of the reader. The following information is also drawn from that guidance and is consistent with the approach discussed therein.

Numerous terms are used to describe detection limits and the level at which a compound of potential concern can be quantitatively measured with the desired degree of confidence. The terms “detection limit” and “quantitation limit” are usually considered to be generic unless the specific types are defined. The general terms depicted in Figure B.1-1 are described below. Additional terms specific to combustion risk assessment applications are discussed later in Section B.1.2.3.

- Instrument detection limit (IDL) is the smallest signal above background that can be reliably detected (but not quantified) by an analytical instrument. An IDL is generally described as a function of the signal-to-noise ratio. The IDL includes only the instrumental portion of detection, not sample preparation, concentration/dilution factors, or any method-specific parameters. Potentially significant matrix factors that may affect analyte recoveries are not addressed.

- The Method Detection Limit (MDL) is the minimum concentration of a material that can be routinely identified using a specific method. The MDL is determined based on analysis of replicate samples of a specific matrix type containing the compound of potential concern. The replicate samples are prepared and analyzed according to the complete



IDL = Instrument Detection Limit
MDL = Method Detection Limit
LOQ = Limit of Quantitation
LOL = Limit of Linearity

FIGURE B.1-1. RELATIONSHIP BETWEEN INSTRUMENT RESPONSE AND DETECTION LIMITS

method, and the MDL is based on statistical analysis of the data generated. Since the MDL includes sample preparation effects, the MDL is more representative than the IDL. However, since MDLs are typically determined by spiking clean matrices in the lab, potentially significant matrix effects from the actual environmental sample that may affect analyte recoveries are not addressed. For any given method, the MDL is laboratory- and compound-specific. Laboratories typically produce MDLs specific to each method performed by the laboratory on an annual basis.

- The Limit of Quantitation (LOQ) is the level above which quantitative results may be obtained with a specified degree of confidence. When analyte concentrations are close to but above the MDL, the uncertainty in the quantitative analysis is relatively high. Although the presence of the analyte is accepted, the quantitative results reported may be in the range of ± 30 percent.

- The Limit of Linearity (LOL) is the point at or above the upper end of the instrumental calibration curve where the relationship between the quantity present and instrumental response ceases to be linear (Taylor 1987). The instrument response is usually depressed at or above the LOL, and the concentration that is reported will be less than the amount actually present in the sample because the detector of the analytical instrument is saturated. When analyte concentrations are above the LOL, the sample should be diluted to perform a successful quantitative analysis. However, dilutions correspondingly increase the MDL for a given sample.

The area of known identification and quantitation is the area encompassed by the calibration curve. In the range above or below the calibration curve, either quantitation or identification or both become far less certain. The wide range of chemical concentrations that may be present in the environmental matrix of interest may require multiple analyses of dilutions to obtain usable data.

B.1.2.2 Site-Specific Data Quality Objectives for Detection and Quantitation Limits

Prior to a risk burn, EPA OSW recommends that site-specific data quality objectives (DQOs) for detection and quantitation limits be established. DQOs define the quality and quantity of data needed to support decisions, considering the purpose of collecting the data. It is highly recommended that a facility perform a preliminary risk evaluation to determine target detection and quantitation limits. This information can then be used to determine whether modifications to the sampling and analytical procedures may be needed to achieve lower detection or quantitation limits. Limits for D/Fs and bioaccumulative metals may be critical for the indirect risk pathway. Other organic compounds that may warrant particular attention because they could be important contributors to indirect risk include the compounds shown in Table B.1-2.

The relationship between an MDL and a specific concentration of concern is introduced in Figure B.1-2, reproduced from *Guidance for Data Useability in Risk Assessment* (EPA 1992) for the convenience of the reader. When the concentration of concern for an analyte is greater than the MDL, to the extent that the confidence limits of both the MDL and concentration of concern do not overlap, then both "non-detect" and "detect" results can be used with confidence. If the confidence limits of the MDL and concentration of concern overlap, there will be a possibility of false positives (i.e., the chemical may be misidentified as present at the concentration of concern) and false negatives (i.e., the chemical may be misidentified as being below the concentration of concern). When the concentration of concern is sufficiently less than the MDL that the confidence limits do not overlap, only "detect" results are useful. Reported "non-detect" values are not meaningful (because, at the MDL, the compound cannot be confirmed to be below the concentration of concern).

This guidance, as well as the references cited, provides limited information regarding detection limits that can generally be expected from the various combinations of sampling train and analytical methods. In some cases, for draft methods or modified methods, method detection limits may not be established.

TABLE B.1-2

ORGANIC COMPOUNDS THAT COULD BE IMPORTANT CONTRIBUTORS TO INDIRECT RISK

Dioxins/Furans (D/Fs)
2,3,7,8-tetrachlorodibenzodioxin
Total tetrachlorodibenzodioxins
1,2,3,7,8-pentachlorodibenzodioxin
Total pentachlorodibenzodioxins
1,2,3,6,7,8-hexachlorodibenzodioxin
1,2,3,4,7,8-hexachlorodibenzodioxin
1,2,3,7,8,9-hexachlorodibenzodioxin
Total hexachlorodibenzodioxins
1,2,3,4,6,7,8-heptachlorodibenzodioxin
Total heptachlorodibenzodixoins
Octachlorodibenzodioxin

2,3,7,8-tetrachlorodibenzofuran
Total tetrachlorodibenzofurans
1,2,3,7,8-pentachlorodibenzofuran
2,3,4,7,8-pentachlorodibenzofuran
Total pentachlorodibenzofurans
1,2,3,6,7,8-hexachlorodibenzofuran
1,2,3,7,8,9-hexachlorodibenzofuran
1,2,3,4,7,8-hexachlorodibenzofuran
2,3,4,6,7,8-hexachlorodibenzofuran
Total hexachlorodibenzofurans
1,2,3,4,6,7,8-heptachlorodibenzofuran
1,2,34,7,8,9-heptachlorodibenzofuran
Total heptachlorodibenzofurans
Octachlorodibenzofuran

Polycyclic Aromatic Hydrocarbons (PAHs)
benzo(a)pyrene
benz(a)anthracene
benzo(b)fluoranthene
benzo(k)fluoranthene
chrysene
dibenz(a,h)anthracene
indeno(1,2,3-cd)pyrene

Nitroaromatics
1,3-dinitrobenzene
2,4-dinitrotoluene
2,6-dinitrotoluene
nitrobenzene
pentachloronitrobenzene

Polychlorinated Biphenyls (PCBs)
Total PCBs
Dioxin-Like Coplanar PCBs (12 compounds):

IUPAC Number	Name
77	3,3',4,4'-tetrachlorobiphenyl
81	3,4,4',5-tetrachlorobiphenyl
105	2,3,3',4,4'-pentachlorobiphenyl
114	2,3,4,4',5-pentachlorobiphenyl
118	2,3',4,4',5-pentachlorobiphenyl
123	2',3,4,4',5-pentachlorobiphenyl
126	3,3',4,4',5-pentachlorobiphenyl
156	2,3,3',4,4',5-hexachlorobiphenyl
157	2,3,3',4,4',5'-hexachlorobiphenyl
167	2,3',4,4',5,5'-hexachlorobiphenyl
169	3,3',4,4',5,5'-hexachlorobiphenyl
189	2,3,3',4,4',5,5'-heptachlorobiphenyl

Other Chlorinated Organics
hexachlorobenzene
pentachlorophenol

Phthalate Esters
bis(2-ethylhexyl) phthalate
di-*n*-octyl phthalate

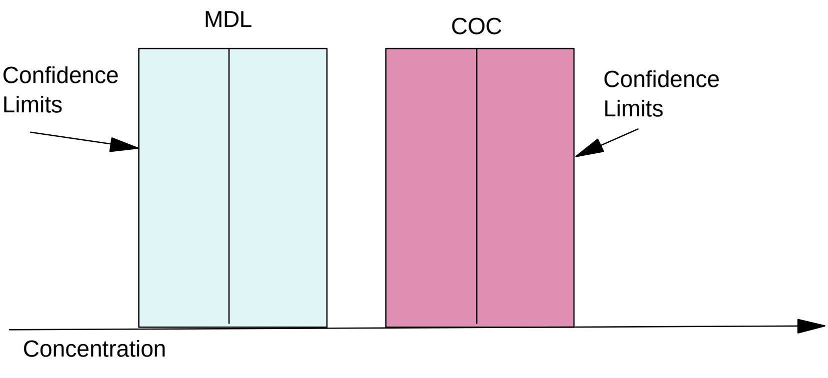
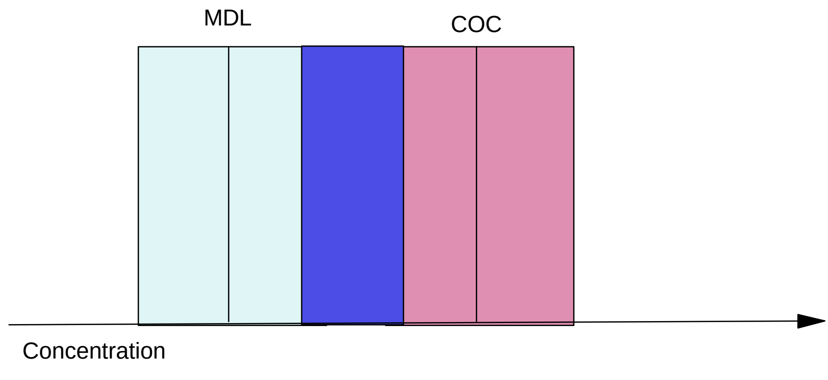
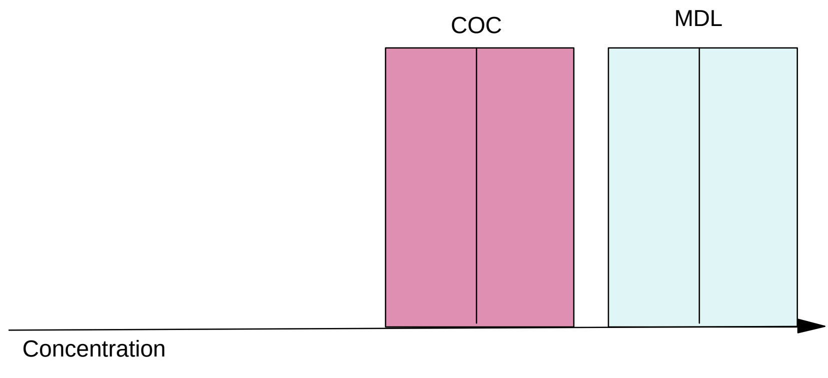
Relationship Between Method Detection Limit (MDL) and Concentration of Concern (COC)	**Result**
	Detects and Non-Detects Usable
	False Positives and False Negatives Possible
	Non-Detects Not Usable Detects Usable False Negatives Possible

FIGURE B.1-2. IMPACT OF DETECTION LIMIT AND CONCENTRATION OF CONCERN ON DATA PLANNING

Detection and quantitation limits are best assigned with input from the qualified analytical chemist who will oversee the analysis for the specific application. In conferring with the analytical chemist regarding detection and quantitation limits, EPA OSW recommends that the following issues be addressed:

- How does the laboratory define “detection limit” and “quantitation limit”?
- What medium or matrix (i.e., adsorbent resin, filter, condensate) is used to determine method detection limits? If the method provides options regarding volumetric treatments, which specific volumetric treatments are used?
- What final sample or extract volume corresponds to the reported detection or quantitation limit (in micrograms, µg)?
- Will anticipated detection/quantitation limits need to be adjusted to reflect sample-specific volumetric treatments, such as splits and dilutions, that may differ from the method?
- How will non-detects for individual sampling train fractions be treated in the summation to determine a total mass for the sampling train? (EPA OSW recommends the following data reporting convention for non-detects: If all of the train fractions are non-detect, then the non-detects should be summed and reported with a “less than” sign. If the analyte is detected in some of the train fractions but not in others, then the data should be reported as a range (i.e., “greater than” the total detected amount, but “less than” the total detected amount plus the non-detects)).
- In summary, what are the detection/quantitation limits (in µg) ***per sample train***?

With information on the anticipated detection/quantitation limits for a given sampling train (in µg) and information on the volume of stack gas to be sampled (in cubic meters, m^3), the facility can evaluate the limits in terms of analyte mass per volume of stack gas sampled (in $\mu g/m^3$). This value will be the detection/quantitation limit in the stack, and may or may not meet the data quality objectives for the risk burn and risk assessment.

If a stack or quantitation limit does not meet risk burn data quality objectives, it may be appropriate for a facility to evaluate modifications to the sampling/analytical methodology that will allow the risk burn data quality objectives to be met. When lower detection or quantitation limits are necessary, it may be possible to collect a larger sample (i.e., sample at a higher flow rate or for a longer period of time), or the final sample volume may be concentrated. However, either of these procedures has potential disadvantages.

Sampling for a longer period of time may saturate the collection medium or may saturate an analytical instrument in the presence of matrix interferences. Concentration of a sample may result in evaporative loss of more volatile analytes from the sample.

EPA OSW also recommends that the facility confer with the laboratory regarding the meaning of any data qualifiers that may accompany the final results. Examples of data qualifiers which are sometimes used and which may have particular relevance in the final risk calculations include:

U - This flag may indicate that the compound was analyzed for, but not detected.

J - This flag may indicate that the compound is present, but that the quantity is estimated. It is often used for an organic chemical where the spectral identification criteria have been met, but the concentration is less than the quantitation limit.

E - This flag may indicate that the quantity is estimated (e.g., for an organic compound where the concentration exceeds the upper level of the calibration range, or for an inorganic compound because matrix interferences are present). For organic compounds where the concentrations exceed the upper level of the calibration range, the sample should be diluted and re-analyzed if possible.

B - This flag may be used when the analyte is found in a blank associated with the sample to indicate possible blank contamination.

The types and definitions of data qualifiers are likely to vary among different laboratories and different applications. Thus, EPA OSW recommends that the specific definitions for data qualifiers be reported with each data set.

B.1.2.3 Use in the Risk Assessment of Data Reported as Non-Detect

EPA OSW's recommendations regarding treatment of non-detect results in risk assessment calculations are dependent upon the analytical method used to produce the data. To increase consistency and reproducibility in dealing with non-detects, EPA OSW has recommended application of the MDL-derived reliable detection limit (RDL) to quantify non-detects for COPCs analyzed with non-isotope dilution analytical methods, and application of the method-defined estimated detection limit (EDL) to quantify non-detects for COPCs analyzed with isotope dilution methods (EPA 1998a).

Non-Isotope Dilution Methods (SW-846 Methods 8260, 8270): To quantify non-detects for non-isotope dilution methods such as Methods 8260 and 8270, EPA OSW has recommended that an MDL-derived RDL for each COPC non-detect be calculated from the developmental test data used to generate the MDL (derived according to procedures consistent with 40 CFR Part 136, Appendix B). The RDL is a total of 8 times the standard deviation of the replicate measurements performed to generate the MDL for a given constituent.

The MDL procedure was promulgated in 1984 and is incorporated in more than 130 EPA analytical methods for the determination of several hundred analytes. To determine the MDL as specified in 40 CFR Part 136, Appendix B, at least seven replicate samples with the compound of interest spiked at a level near the estimated MDL are analyzed. The standard deviation among these analyses is calculated and multiplied by 3.14 (this factor is based on a t-test with six degrees of freedom and provides a 99 percent confidence that the analyte concentration is greater than zero). The result of the calculation becomes the MDL (EPA 1995). The RDL is a total of 8 times the standard deviation of the MDL developmental test data, or 2.55 times the MDL when the MDL is based on seven replicate samples (i.e., standard deviation x 3.14 x 2.55). It is appropriate to adjust the RDL as necessary to account for sample-specific volumetric treatments (such as splits and dilutions) that differ from those utilized in the Part 136 MDL determinations. The 40 CFR Part 136, Appendix B MDL procedure is specific to the Clean Water Act and therefore specifies the use of water as the matrix for MDL determination. Using spiked sorbent media, the methodology has been adapted to the determination of MDLs for stationary source methods that collect analytes on a sorbent matrix. For stationary source samples, MDLs have historically been determined by spiking a clean matrix that is representative of each sample train fraction (i.e., adsorbent resin, condensate) rather than the actual stationary source matrix. Unless the actual stationary source matrix is used, potentially significant matrix factors that may affect analyte recoveries are not addressed. For example, SW-846 Method 8260B notes that matrix effects in actual volatile organic sampling train (VOST) samples can cause MDLs to be larger than the MDLs determined on clean VOST sorbent tubes by a factor of 500-1000. Laboratories typically produce MDLs specific to each non-isotope dilution method performed by the laboratory on an annual basis.

Isotope Dilution Methods (SW-846 Methods 8290, Method 0023A; Office of Water Method 1668A; California Air Resources Board (CARB) Method 429, etc.): The Estimated Detection Limit (EDL) is a quantitation level defined in SW-846 (EPA 1996b) that is applied to isotope dilution analytical methods such as SW-846 Method 8290. The EDL is defined in various methods as the estimate made by the laboratory of the concentration of a given analyte necessary to produce a signal with a peak height of at least 2.5 times the background signal level. As generally reported by commercial laboratories, the EDL is the detection limit reported for a target analyte that is not detected, or presents an analyte response that is less than 2.5 times the background level. The EDL is specific to a particular analysis of the sample and will be affected by sample size, dilution, etc. EPA OSW has recommended that non-detects for COPCs analyzed using isotope dilution analytical methods be quantified for use in the risk assessment using the EDL as defined by the analytical method without the use of empirical factors or other mathematical manipulations specific to the laboratory (EPA 1998a).

For isotope dilution methods, there is also the issue of how to report Estimated Maximum Possible Concentrations (EMPCs). An EMPC, as defined in SW-846 Methods 8280A and 8290, may be calculated for D/F congeners that are characterized by an analytical instrument response with a signal-to-noise ratio of at least 2.5 for both the ions used in the quantitative analysis, and that meet all the relevant identification criteria specified in the method except the ion abundance ratio. The ion abundance ratio may be affected by chromatographically co-eluting interferences that contribute to the quantitative ion signals and produce a positive bias for one or both of the ion signals. The EMPC is a worst-case estimate of the concentration. EPA OSW (EPA 1998a) has recommended that EMPC values be used as full detections in the risk assessment without any further manipulations (such as dividing by 2). Because EMPCs are worst case estimates of stack gas concentrations, EPA OSW has recommended that permitting authorities and facilities consider techniques to minimize EMPCs when reporting trial and risk burn results, especially when EMPC values result in risk estimates above regulatory levels of concern (EPA 1998a). Some procedures that may be used to minimize EMPCs include additional cleanup procedures (as defined by the analytical method) for the sample or archived extract and/or re-analysis of the sample under different chromatographic conditions.

The EPA OSW risk assessment guidance (EPA 1998a) also notes that statistical distribution techniques are available for calculating a range of standard deviations to quantify non-detect concentrations of COPCs. These techniques include random replacement scenarios, such as the procedures found in journal articles by Cohen and Rao (Cohen 1989; Rao 1991) including:

- The uniform fill-in method, where each Limit of Detection value is replaced with a randomly generated data point by using a uniform distribution;
- The log fill-in method, where each Limit of Detection value is replaced with a randomly generated data point by using a logarithmic distribution;
- The normal fill-in method, where each Limit of Detection value is replaced with a randomly generated data point by using a log-normal distribution; and
- The maximum likelihood estimation techniques.

EPA OSW has explained that a Monte Carlo simulation may be used to determine a “statistical” value for each non-detect concentration if the permitting authority determines the methodology to be applicable (EPA 1998a). However, EPA OSW has recommended that, in most cases, emission rates for undetected COPCs be estimated by assuming that COPCs are present at a concentration equivalent to the MDL-derived RDL for non-isotope dilution methods, or the method-defined EDL for isotope dilution methods (EPA 1998a). EPA OSW has articulated the belief that these methods are reasonable and conservative, and that they represent a scientifically sound approach that supports maximum protection of human health and the environment while recognizing the uncertainty associated with analytical measurements at very low concentrations in an actual sample matrix (EPA 1998a). There are necessarily subjective components and limitations to each of the non-detect methodologies presented in the EPA OSW risk assessment guidance, including the recommended methods.

Some state permitting authorities have expressed the desire to obtain and use non-routine data (e.g., uncensored data) of defensible quality in risk assessment as a way to deal with non-detect issues.

EPA OSW has stated that the decision to use non-routine data in a risk assessment is not precluded just because the data are different: a permitting authority that chooses to use non-routine data should carefully identify and evaluate the limitations associated with non-routine data and clearly document this discussion in the uncertainty section of the risk assessment report (EPA 1998a).

B.1.2.4 Treatment of Blanks for Risk Assessment

Blanks are used to monitor the presence of contamination introduced into a sample during collection, transportation, or preparation and analysis. Blank samples are analyzed in the same manner as site samples. To prevent the inclusion of contaminants in the risk assessment process, EPA OSW has recommended that the identities and concentrations of compounds detected in the blanks be compared to the identities and concentrations of the compounds detected in the field samples (EPA 1998a). Four types of blanks are defined in the *Risk Assessment Guidance for Superfund* (EPA 1989) and discussed in *Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities* (EPA 1998a):

- ***Trip Blank*** **-** A trip blank is used to indicate potential contamination due to conditions occurring during transport of sampling media to the field and collected samples to the laboratory. The trip blank accompanies the sampling media to the field as well as the collected samples returning to the laboratory for analysis. The trip blank is not opened until it is prepared/analyzed in the laboratory.

- ***Field Blank*** **-** A field blank is used to determine if field sampling or cleaning procedures (e.g., insufficient cleaning of sampling equipment) result in contamination of field samples. Like the trip blank, the field blank is transported to the field with sampling media and analyzed in the laboratory together with the field samples. However, unlike the trip blank, a field blank consisting of sorbent, for example, is opened in the field and placed in a sampling train (which does not collect an actual sample) for the duration of a sampling run and recovered in the same manner as the field samples.

- ***Method Blank*** **-** A method blank results from the treatment of clean sampling media or distilled, deionized water with all of the reagents and manipulations (e.g., extractions, cleanups, extract concentration) to which field samples will be subjected. Positive results in the reagent blank may indicate either contamination of the chemical reagents or the glassware and implements used to store or prepare the sample and resulting solutions. Although a laboratory following Good Laboratory Practices will have its analytical processes under control, in some instances method blank contaminants cannot be entirely eliminated.

- **Reagent Blank -** A reagent blank consists of a separate analysis of any of the reagents used in the field recovery or laboratory preparation of the samples. In practice, aliquots of all solvents used in the field or laboratory are archived and analyzed individually in the event contamination is observed in one of the other blank samples in order to eliminate individual solvents as a source of contamination.

EPA OSW recommends that data generated in the analysis of blanks be compared to the specific analytical results with which the blanks are associated. However, even if the specific association between blanks and the field data cannot be made, blank data can be compared to the results from the entire sample data set. EPA OSW recommends that all data be reported without blank correction.

In the *Guidance for Data Useability in Risk Assessment* (EPA 1992), EPA makes a distinction between blanks containing common laboratory contaminants and blanks containing contaminants not frequently used in laboratories. Compounds considered to be common laboratory contaminants that frequently appear on method target lists include acetone, 2-butanone (methyl ethyl ketone), methylene chloride, toluene, and the phthalate esters. If compounds considered to be common laboratory contaminants are detected in the blanks, then the 1992 guidance recommends that sample results not be considered to be detected unless the concentrations in the sample are equal to or exceed ten times the maximum amount detected in the applicable blanks. If the concentration of a common laboratory contaminant in a sample is less than ten times the blank concentration, then the 1992 guidance recommends that the compound be treated as a non-detect in that particular sample. Common laboratory contaminants are summarized in Table B.1-3, which has been reproduced from the 1992 guidance for the convenience of the reader.

In some cases, blanks may contain compounds that are not considered by EPA to be common laboratory contaminants as identified above. In these cases, the 1992 guidance recommends that sample results not be considered to be detected unless the concentrations in the sample exceed five times the maximum amount detected in the applicable blanks. If the concentration in a sample is less than five times the blank concentration, then the 1992 guidance recommends that the compound be treated as a non-detect in that particular sample.

EPA OSW recommends that permitting authorities carefully consider the evaluation of blank data in the overall context of the risk assessment and permitting process. Risk burn data should be carefully evaluated

TABLE B.1-3

COMMON LABORATORY CONTAMINANTS, CONCENTRATION REQUIREMENTS, AND RISK ASSESSMENT IMPLICATIONS[a]

Common Laboratory Contaminants	**Concentration Requirements**	**Risk Assessment Implications**
Target Compounds		
methylene chloride	Sample concentrations < 10 x Blank are reported as non-detect or flagged (B)	– Include the analyte if concentration is > 10 x Blank – Include the analyte if concentration is < 10 x Blank and multiple volatile chlorinated analytes are detected; exclude analyte in all other situations
acetone	Sample concentrations < 10 x Blank are reported as non-detect or flagged (B)	– Include analyte if concentration is > 10 x Blank – Include analyte if concentration is < 10 x Blank and multiple ketones are detected; exclude analyte in all other situations
toluene	Sample concentrations < 10 x Blank are reported as non-detect or flagged (B)	– Include analyte if concentration is > 10 x Blank – Include analyte if concentration is < 10 x Blank and multiple aromatic or fuel hydrocarbons are detected; exclude analyte in all other situations.
2-butanone (methyl ethyl ketone)	Sample concentrations < 10 x Blank are reported as non-detect or flagged (B)	– Include analyte if concentration is > 10 x Blank – Include analyte if concentration is < 10 x Blank and multiple ketones are detected; exclude analyte in all other situations.
phthalate esters (i.e., dimethyl, diethyl, di-*n*-butyl, butylbenzyl, *bis* (2-ethylhexyl), and/or di-*n* octyl phthalate)	Sample concentrations < 10 x Blank are reported as non-detect or flagged (B)	– Include analyte if concentration is > 10 x Blank – Exclude analyte in all other situations.

TABLE B.1-3

COMMON LABORATORY CONTAMINANTS, CONCENTRATION REQUIREMENTS, AND RISK ASSESSMENT IMPLICATIONS[a] (Continued)

Common Laboratory Contaminants	**Concentration Requirements**	**Risk Assessment Implications**
Tentatively Identified Compounds		
carbon dioxide	Not reported if present in the Method Blank.	– Exclude analyte in all situations.
diethyl ether	Not reported if present in the Method Blank.	– Include analyte if concentration is > 10 x Method Blank. – Exclude analyte in all other situations.
hexanes	Not reported if present in the Method Blank.	– Exclude if analyte concentration is not 10 x Method Blank – Exclude if analyte is not 10 x Field Blank – Exclude if sample is not analyzed within 7 days
Freons (i.e., 1,1,2-trichloro-1,2,2-trifluoroethane, fluorotrichloromethane)	Not reported if present in the Method Blank.	– Exclude if analyte concentration is not 10 x Method Blank – Exclude if analyte concentration is not 10 x Field Blank – Exclude if sample is not analyzed within 7 days
solvent preservative (e.g., cyclohexanone, cyclohexenone, cyclohexanol, cyclohexanol, chlorocyclohexene, chlorocyclohexanol)	Not reported if present in the Method Blank.	– Exclude if artifact concentration is not 10 x Method Blank – Exclude if artifact concentration is not 10 x Field Blank – Exclude if sample is not analyzed within 7 days
Aldol reaction products of acetone (e.g., 4-hydroxy-4-methyl-2-pentanone, 4-methylpenten-2-one, 5,5-dimethyl-2(5H)-furanone)	Not reported if present in the Method Blank.	– Include analyte if concentration is > 10 x Blank – Include analyte if concentration is < 10 x Blank and multiple ketones are detected – Exclude analyte in all other situations

[a] Table is presented in *Guidance for Data Useability in Risk Assessment* (EPA 1992).

to ensure that the level of contamination present in the blanks does not compromise the integrity of the data for purposes of the risk assessment, or result in a need for re-testing in order to properly address data quality issues. When considering blank contamination in the selection of COPCs, EPA OSW recommends that permitting authorities ensure:

1. The facility or data generator has made every reasonable attempt to ensure good data quality and has rigorously implemented the quality assurance project plan (QAPP) and good industry/laboratory sampling and testing practices.
2. Trial and risk burn data have not been submitted to the permitting authority as “blank corrected.” The permitting authority should have the full opportunity to review the data without additional manipulation by the data generator.
3. The effect of the blank correction on the overall risk estimates, if such an effort is considered, is clearly described in the uncertainty section of the risk assessment report.
4. The risk assessment reports emission rates both as measured and as blank corrected in situations where there is a significant difference between the two values.

EPA OSW recommends that caution be exercised in applying blank results to correct or qualify sample results. Blanks are usually provided in minimal quantities, usually only one blank of any type per set of samples, due to cost considerations associated with collection and analysis of samples. The blank is therefore not statistically representative, and blank results are at best only qualitative indicators of the validity of a data set.

B.1.2.5 General Description of Emissions Calculations

This appendix is concerned with methods for collecting stationary source emissions samples, with subsequent analysis of those samples in the laboratory. Two sets of calculations will be performed:

1. One set of calculations involves the sampling train and the sampling parameters, ultimately resulting in a value (expressed as m^3) for volume of gaseous emissions sampled; and
2. A second set of calculations is performed in the laboratory for calibration of instruments and calculation of analytical results. The results generated in the laboratory are usually either a weight of material or a weight of material/volume of solvent. If the laboratory

results are weight of material per volume of solvent, the results need to be multiplied by the total volume of solvent in order to obtain a weight of material per sampling train.

Once laboratory results are available as weight of material per sampling train (usually µg) and the volume of gaseous emissions sampled (expressed as m^3) is known, the material collected can be related to the volume of emissions from which it was collected (µg/m^3). This ultimate calculation is usually not performed by the laboratory, because the laboratory is usually not associated with the sampling effort and does not know the volume of gaseous emissions sampled by a given sampling train.

For stationary source emissions testing, the units in which the results are reported have meaning only in the context of the stationary source at which the samples were taken and in relation to the specific sampling parameters. The following specific results may be reported:

- Volatile organic compound (VOC) results are typically obtained from the laboratory as a weight of material (nanograms, ng, for VOST, or µg/m^3 for SW-846 Method 0040). The VOST values need to be related to the actual volume sampled. Since VOST sampling volumes are usually measured in liters (L), the units will be ng/L. These units can readily be converted to µg/m^3, if desired, since 1000 L = 1 m^3 and 1 µg = 1000 ng. If tentatively identified compounds are identified in association with the VOST determination, a relative instrument response factor of 1 is assumed and the quantitative analysis is performed relative to the nearest-eluting internal standard to obtain an estimated quantity for the tentatively identified compounds. The same procedure for characterization of tentatively identified compounds can be followed for the SW-846 Method 0040 analysis when the analytical procedure involves mass spectrometry in the full scan mode.

- The results for the semivolatile organic compounds (SVOCs) are reported as µg/milliliter (mL) directly from the analytical instrument, with three sets of values typically generated for each sampling train. Since the volume of solvent used in each of the three fractions is known, the total µg per train fraction can be calculated and summed. The ultimate value reported by the laboratory is the total µg per sampling train. The volume of gaseous emissions sampled by each sampling train (expressed as m^3) is known, and the value of the total weight of material per sampling train is related to the total volume sampled and expressed as µg/m^3. Tentatively identified compounds, if characterized, can be quantified using an instrument response factor of 1, with the quantitative analysis performed relative to the nearest-eluting internal standard to obtain an estimated quantity for the tentatively identified compounds.

- Chlorobenzenes/chlorophenols (CBs/CPs) and polycyclic aromatic hydrocarbons (PAHs) are also semivolatile organic compounds, which are reported as total µg per sampling train, with µg/m^3 calculated using the actual volume sampled in the field.

- Polychlorinated biphenyls (PCBs) are likewise semivolatile organic compounds, with the quantity calculated by the laboratory as nanograms (or µg) per sampling train. The goal of the analysis is to report accurate quantitative values for the coplanar polychlorinated biphenyls, with the non-coplanar compounds reported as "Other PCBs" at a specific chlorination level. Calculations involving polychlorinated biphenyls are complicated by the consideration that the coplanar polychlorinated biphenyls are considered to exhibit dioxin-like toxic effects, and are assigned toxicity equivalence factors (TEFs) accordingly. Thus, for the coplanar PCBs, an additional step involving a toxic equivalence (TEQ) determination is involved in the calculation (Section B.5). The ultimate reported values for the polychlorinated biphenyls also have to be related to the volume of gaseous emissions sampled in the field (expressed as m^3). Polychlorinated biphenyls are analyzed using selected ion monitoring mass spectrometric procedures, so no information is available to determine tentatively identified compounds from this analysis.

- Polychlorinated dibenzodioxins and dibenzofurans are also semivolatile organic compounds, which are calculated by the laboratory as picograms (pg) or nanograms (ng) per sampling train. The goal of the analysis is to report accurate quantitative values for the 2,3,7,8-substituted dioxins and furans, with the non-2,3,7,8-substituted compounds reported as "Other Dioxins/Furans" at a specific chlorination level. Calculations involving dioxins and furans are complicated by the consideration that each 2,3,7,8-substituted congener is assigned a TEF which corresponds to its toxicity in relation to 2,3,7,8-tetrachlorodibenzodioxin (Section B.6). The ultimate values for the polychlorinated dibenzodioxins and dibenzofurans also have to be related to the volume sampled in the field (expressed as m^3). Polychlorinated dioxins and furans are analyzed using selected ion monitoring mass spectrometric procedures, so no information is available to determine tentatively identified compounds from this analysis.

- Combined measurement techniques likewise have the goal of determining the weight of analyzed material per sampling train, so that this quantity can be related to the volume sampled. Since no two laboratories follow exactly the same scheme of dividing/combining fractions, a very careful tracking of division/combination of extracted fractions should be performed in order to be sure that accurate values are obtained for the quantity of material collected by the sampling train. For example, if the standard method uses extraction of an entire fraction to perform the analysis but the combined method divides the fraction in half for different analyses, the chemist should be aware that the analytical values have to be multiplied by two to obtain the total weight of material per sampling train. The ultimate reported values for the compounds of interest also have to be related to the volume of gaseous emissions sampled in the field (expressed as m^3). Any fractions of a combined method that are analyzed using mass spectrometric procedures in the full scan mode can produce information for characterizing tentatively identified compounds, which can then be quantified using the procedures described above.

- In the application of SW-846 Method 0011 to the measurement of aldehydes and ketones (A/Ks), the final value reported by the laboratory should be total weight of material per sampling train. This value of total weight of material per sampling train can be related to the volume of gaseous emissions sampled (expressed as m^3).

- Facility-specific compounds may be either volatile or semivolatile organic compounds, which are treated as described above. If the analytical methodology involves full scan mass spectrometry, tentatively identified compounds can be characterized and quantified.

- Metals analysis frequently involves the summation of metals analyzed in several fractions of the sampling train to obtain a total weight of metal per sampling train. The scheme of combination of fractions to determine the total weight of a given metal is quite complicated and is described thoroughly in SW-846 Method 0060. The weight of metal per sampling train is related to the volume of gaseous emissions sampled in the field (expressed as m^3).

- Hydrogen chloride (HCl) and chlorine (Cl_2) determinations involve quantifying results from multiple impingers as described in the sampling/analytical method to obtain a total weight per sampling train. The weight of HCl/Cl_2 per sampling train is related to the volume of gaseous emissions sampled in the field (expressed as m^3).

In summary, all of the analytes are reported as a total weight of material collected by the sampling train, related to the volume of stack gas sampled in the field (expressed as m^3).

B.1.3 METHOD SUMMARY

Table B.1-4 provides a summary of source sampling and analysis procedures which are recommended for collection of stationary source emissions data for evaluation in site-specific risk assessments. Specific information regarding each determination is provided in subsequent sections.

The recommended determinations rely on methods from the SW-846 Compendium (EPA 1996b), where available. The most recent versions of the SW-846 methods are available at SW-846 On-line (http://www.epa.gov/sw-846/main.htm). When revisions are made to any of the SW-846 sampling or analytical methods, EPA OSW recommends that the facility use the latest revised method, as available on-line. Additional test methods are also available through the EPA Emission Measurement Center (http://www.epa.gov/ttn/emc/tmethods.html). Methods available through this site include Promulgated, Proposed, Approved Alternative, Conditional, and Preliminary stationary source test methods. The Emission Measurement Center has recently completed the development of a 24-hour automated telephone information hotline known as the “SOURCE.” The SOURCE, at (919) 541-0200, provides callers with a variety of technical emissions testing information. The SOURCE includes connections to technical

TABLE B.1-4

RISK-BASED STACK EMISSION DETERMINATIONS

Pollutant Category	Sampling Method [1]	Analysis Method [1]	Constituents To Be Determined	Applicability	Comments
Dioxins/Furans	M0023A	8290 HRGC/HRMS	2,3,7,8-tetrachlorodibenzodioxin Total tetrachlorodibenzodioxins 1,2,3,7,8-pentachlorodibenzodioxin Total pentachlorodibenzodioxins 1,2,3,6,7,8-hexachlorodibenzodioxin 1,2,3,4,7,8-hexachlorodibenzodioxin 1,2,3,7,8,9-hexachlorodibenzodioxin Total hexachlorodibenzodioxins 1,2,3,4,6,7,8-heptachlorodibenzodioxin Total heptachlorodibenzodixoins Octachlorodibenzodioxin 2,3,7,8-tetrachlorodibenzofuran Total tetrachlorodibenzofurans 1,2,3,7,8-pentachlorodibenzofuran 2,3,4,7,8-pentachlorodibenzofuran Total pentachlorodibenzofurans 1,2,3,6,7,8-hexachlorodibenzofuran 1,2,3,7,8,9-hexachlorodibenzofuran 1,2,3,4,7,8-hexachlorodibenzofuran 2,3,4,6,7,8-hexachlorodibenzofuran Total hexachlorodibenzofurans 1,2,3,4,6,7,8-heptachlorodibenzofuran 1,2,34,7,8,9-heptachlorodibenzofuran Total heptachlorodibenzofurans Octachlorodibenzofuran	Generally applicable	Method 0023A may be modified to allow simultaneous sampling and analysis of PCBs, PAHs, or SVOCs. However, specific approval should be obtained for this modification, a detailed description of the proposed methodology should be provided, and demonstration of method performance should be provided, including how the modification affects detection limits for all compounds in the combined method.

TABLE B.1-4

RISK-BASED STACK EMISSION DETERMINATIONS (Continued)

Pollutant Category	Sampling Method [1]	Analysis Method [1]	Constituents To Be Determined	Applicability	Comments
Non-D/F Organics:					
Volatile Organics	VOST M0030/0031 for Low Concentration Organics in Specified BP Ranges (<121 EC)	5041A/8260B GC/MS	C Volatile target analyte list, per Table B.2-1 C TICs, per Section B.11	Generally applicable	Condensate collected during Method 0030/0031 sampling is analyzed using Method 8260B. Section B.2 identifies BP ranges for each method.
	Tedlar® Bag M0040 for Very Volatile & High Concentration Organics	8260B GC/MS	C Volatile target analyte list, per Table B.2-1 C TICs, per Section B.11	Generally applicable	Condensate collected during Tedlar® bag sampling is analyzed using Method 8260B.
		GC/FID GC/ECD	Alkanes, alkenes, alkynes, volatile halogenated organics	Highly recommended	Examples: Methane, ethane, ethene, acetylene, propane, propene, and propyne may be identified and quantified by this method.
Semivolatile Organics	M0010 for Organics with BP >100 EC	3542/8270C GC/MS	C Semivolatile target analyte list, per Table B.3-1 C TICs, per Section B.11	Generally applicable	
Chlorobenzenes/ Chlorophenols	M0010	GC/MS	C CBs/CPs in Table B.4-1	Generally applicable	Analysis of the M0010 extract for CBs/CPs is recommended.
PAHs	M0010	CARB 429[2]	C PAHs in Table B.4-2	Generally applicable	Separate cleanup of the M0010 extract and analysis for PAHs by HRGC/HRMS is recommended.

TABLE B.1-4

RISK-BASED STACK EMISSION DETERMINATIONS (Continued)

Pollutant Category	Sampling Method [1]	Analysis Method [1]	Constituents To Be Determined	Applicability	Comments
PCBs	M0023A or CARB 428 [2]	CARB 428 [2] or Method 1668A[3] HRGC/HRMS	Total PCBs, based upon summation of homolog groups listed in Table B.5-1	Generally applicable	In order to determine PCBs from the M0023A sampling train, the condensate and impinger contents have to be retained and analyzed. Although HRMS is not specified for total PCBs in CARB 428, it is recommended in order to provide lower detection limits.
		Method 1668A[3] HRGC/HRMS	Twelve dioxin-like congeners listed in Table B.5-1		
Aldehydes/ Ketones	M0011	8315A HPLC	M0011 is written specifically for formaldehyde, but additional compounds can be determined	Site-specific determination as discussed in Section B.9	Method 0011 is severely affected by oxidizing agents, such as NO_2. See Section B.9.
Facility-Specific Compounds	Compound-specific, see Section B.10	Compound-specific, see Section B.10	Significant facility-specific compounds may need to be determined as appropriate: C Pesticides per Table B.10-1 C Herbicides per Table B.10-2 C Nitroaromatics C Cyanides	Site-specific determination as discussed in Section B.10	Additional compounds may need to be determined to represent the wastes burned at a particular facility.

TABLE B.1-4

RISK-BASED STACK EMISSION DETERMINATIONS (Continued)

Pollutant Category	Sampling Method [1]	Analysis Method [1]	Constituents To Be Determined	Applicability	Comments
Total Organic Mass [4]	Tedlar® Bag M0040	GC/FID	Total organic mass (µg) for organics boiling between (-)160 to 100 EC	Generally applicable	
	Tedlar® Bag M0040 (Condensate Fraction)	Purge and Trap GC/FID	Total organic mass (µg) for water soluble organics		The result for the condensate is combined with the result for the Tedlar® bag fraction to give total organic mass for organics boiling between (-)160 to 100 EC.
	M0010	GC/FID	Total organic mass (µg) for organics boiling between 100-300 EC		A separate M0010 train is generally necessary for the total organic mass determination unless procedures in Section B.8.9 are followed.
		Gravimetric	Total organic mass (µg) for organics boiling at temperatures > 300 EC		
THC/CO	CEMs - 40 CFR Part 266 Appendix IX Section 2.0		THC/CO, corrected to 7% oxygen, dry basis	Generally applicable	Baseline may be needed for continuous performance assurance.
Metals	M0060/ 0061	6010B/6020 7000-series	Al, Co, Cu, Mn, Ni, Se, V, and Zn, in addition to As, Be, Cd, Cr, Ag, Ba, Hg, Pb, Sb, Tl	Generally applicable	Metals may be excluded if the facility assumes that 100 percent of the metal which is fed is emitted (i.e., assumption of no partitioning/ removal).
Particle-Size Distribution	CARB 501[2]	Gravimetric	Site-specific particle-size distribution	See discussion in Section B.14	Particle density also needs to be determined.
Hydrogen Chloride and Chlorine	M0050/0051	M9057/9056	Hydrogen chloride and chlorine	Generally applicable	See Section B.15 for additional methods.

TABLE B.1-3

RISK-BASED STACK EMISSION DETERMINATIONS (Continued)

Notes:

[1] Sampling and analysis methods are from “Test Methods for Evaluating Solid Waste,” SW-846 or EPA’s Emission Measurement Center. The latest revision, available from SW-846 on-line (http://www.epa.gov/sw-846/main.htm) should be used. If detection limits are not low enough to achieve target risk levels, then modifications to the sampling and analytical procedures may need to be considered. Other methods may be considered provided that the user can demonstrate the methods meet the data quality objectives for the particular application.

[2] California Environmental Protection Agency, Air Resources Board, Sacramento, CA, (http://www.arb.ca.gov/testmeth/vol3/vol3.htm ***and*** http://arbis.arb.ca.gov/testmeth/vol1/vol1.htm).

[3] EPA “Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by High Resolution Gas Chromatography/High Resolution Mass Spectrometry,” EPA-821-R-00-002, Office of Science and Technology, Office of Water, December 1999.

[4] “Guidance for Total Organics - Final Report,” prepared for EPA by Radian Corporation, EPA/600/R-96/033, March 1996, as updated considering the technical recommendations discussed in Section B.7 of this document. See also “Determination of Total Organic Emissions from Hazardous Waste Combustors,” Larry D. Johnson, *Analytical Chemistry*, Vol. 68, No.1, January 1, 1996.

See the Appendix B Acronym List for acronym definitions.

material through an automatic facsimile link and with technical staff during working hours. Other locations for stationary source test methods are the California Air Resources Board sites, Test Methods for Determining Emissions of Toxic Air Contaminants from Stationary Sources (http://www.arb.ca.gov/testmeth/vol3/vol3.htm) and Stationary Source Criteria Pollutant Test Methods (http://arbis.arb.ca.gov/testmeth/vol1/vol1.htm). Additional information for selection and field evaluation of sampling and analytical methods is available through EPA's *Stationary Source Sampling and Analysis Directory, Version 2.1* (SSSADIR) (Jackson 1995a).

The numbered methods as written are intended as guidance, and EPA OSW recommends that the numbered methods generally be used as starting points for the preparation of standard operating procedures (SOPs) for the methods that will actually be used. The SW-846 Compendium provides guidance on individual method modifications. Methods other than the methods in the SW-846 Compendium may be appropriate for generation of risk burn emissions data, and EPA OSW recommends that all methods and method modifications proposed for a specific application be discussed in detail in the risk burn plan and QAPP. Detailed information regarding the actual methods should be described in the plans, and the plans should define data quality objectives (DQOs) for the particular application. For all test methods, EPA OSW recommends that the user demonstrate and document that the proposed methods meet the DQOs for the particular application. Additional modifications to standard methods may be appropriate in order to meet site-specific objectives (e.g., the need for reduced analytical detection limits or a desire to use a single sampling train for multiple pollutant determinations).

B.1.4 QUALITY ASSURANCE/QUALITY CONTROL

EPA OSW recommends establishing DQOs for risk burn measurements and defining detailed quality assurance objectives in a project-specific QAPP as a critical component of the risk burn planning process. Although a thorough treatment of the DQO process and specific quality assurance/quality control provisions is beyond the scope of this guidance, there are other sources of information that may be consulted. EPA QA/G-4: "Guidance for the Data Quality Objectives Process" provides a standard working tool for project managers and planners to develop DQOs for determining the type, quantity, and quality of data needed to reach defensible decisions. Since 1997, EPA has recommended that a QAPP be written for any activity that involves an environmental data operation (EDO), as documented in EPA QA/R-5: “EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations.” An additional source of information provided by the EPA Quality Assurance Division to assist with writing a QAPP is the document EPA QA/G-5: “EPA Guidance for Quality Assurance Project Plans.” All of these documents are available on the web (http://www.epa.gov/ncerqa/qa/qa_docs.html).

The documents available from the EPA Quality Assurance Division offer broad guidelines regarding the DQO planning process and QAPP development. Information specific to stationary source measurements is also available and should be consulted. Individual test methods, such as those in SW-846, outline quality assurance/quality control procedures to be followed to assure acceptable performance of the method. In addition, the following documents focus on quality assurance/quality control procedures for the source measurements commonly performed at hazardous waste combustion facilities:

C U.S. EPA Region 6. *Hazardous Waste Combustion Unit Permitting Manual. Component 2 - How to Review a Quality Assurance Project Plan.* Center for Combustion Science and Engineering, Multi Media Planning Division. January 1998.
(Includes a generic trial burn quality assurance project plan as Attachment A.)
http://www.epa.gov/earth1r6/6pd/rcra_c/manual/manual.htm#A.

C U.S. EPA. *Handbook: Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration*. Office of Research and Development. EPA/625/6-89/023. January 1990.

C U.S. EPA. *Handbook: Hazardous Waste Incineration Measurement Guidance Manual. Volume III of the Hazardous Waste Incineration Guidance Series.* Office of Solid Waste and Emergency Response. EPA/625/6-89/021. June 1989.

The Emission Measurement Center provides guidance on test plan and final report preparation on the web (http://www.epa.gov/ttn/emc/guidlnd.html). In addition, the Emission Measurement Center currently operates the Stationary Source Compliance Audit Program, through which compliance audit samples may be requested by Regional Offices, State Agencies, and Local Agencies for stack tests. Information on the Stationary Source Compliance Audit Program is available on the Emission Measurement Center web site: http://www.epa.gov/ttn/emc/email.html#audit.

B.2 VOLATILE ORGANIC COMPOUNDS (VOCs)

There are two EPA methods available for the determination of volatile organic compounds (VOCs), and numerous methods in draft stages for a variety of specific volatile organic analytes. The two EPA methods include:

C The Volatile Organic Sampling Train (VOST) is actually a combination of sampling and analytical methods from the SW-846 Compendium. Sample collection is performed using either Method 0030 or 0031, desorption of the sorbent cartridges is performed using Method 5041A, and analysis is achieved via GC/MS (Method 8260).

- Method 0030 (Volatile Organic Sampling Train)

  VOST describes the collection of volatile principal organic hazardous constituents (POHCs) from the stack gas effluents on paired sorbent resin and sorbent resin/charcoal cartridges. Method 0030 may be used to collect volatile POHCs with boiling points (BPs) between 30EC and 100EC, although performance may be adequate for compounds with boiling points up to 121EC. If the boiling point of a POHC of interest is less than 30EC, the POHC may break through the sorbent under the conditions of the sample collection procedure. Many compounds that boil above 100EC (such as chlorobenzene) may also be efficiently collected and analyzed using the VOST, but VOST collection and desorption efficiency for these compounds should be demonstrated.

- Method 0031 (Sampling Method for Volatile Organic Compounds (SMVOC))

  Method 0031 is a modified version of Method 0030 whereby two sorbent resin cartridges are employed prior to the sorbent resin/charcoal cartridge, for a total of three cartridges. Method 0031 may be used to collect VOCs that have a boiling point between -15EC and 121EC. Field application for VOCs with boiling points less than 0EC should be supported by data obtained from laboratory gaseous dynamic spiking of the sampling train with gas chromatography/mass spectrometry (GC/MS) analysis according to Methods 5041/8260 to demonstrate the efficiency of the sampling and analysis methods.

- Method 5041A (Analysis for Desorption of Sorbent Cartridges from Volatile Organic Sampling Train (VOST))

  Method 5041A describes the desorption of POHCs collected from stack gas effluents of hazardous waste incinerators using the VOST methodology with analysis by GC/MS (Method 8260).

C Method 0040 (Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar® Bags

> Method 0040 establishes standardized test conditions and sample handling procedures for the collection of VOCs from effluent gas samples from stationary sources using time-integrated evacuated Tedlar® bags. Method 0040 may generally be used to collect VOCs with boiling points less than 121EC, although actual performance will depend on analyte concentration and condensation point. Method 0040 is a sample collection method and does not directly address the analysis of these samples other than to recommend the application of GC/MS procedures because of the ability of GC/MS to provide positive identification of compounds in complex mixtures such as stack gas. In some cases, the samples may be analyzed in the field using GC/FID or GC with an electron capture detector (ECD).

Method 0030, the VOST sampling method, specifies the use of SKC Lot 104 charcoal in the sorbent tube used for sample collection. The specified sorbent has not been commercially available for many years, and EPA has done several studies to identify and specify a sorbent (Anasorb®-747) that is technically equivalent and commercially available (Johnson 1996b). Use of Anasorb®-747 is recommended for both Method 0030 and Method 0031.

In the application of the sampling methods, Methods 0030 and 0031 involve time-integrated collection of VOCs on sorbent and, therefore, typically can achieve lower detection limits than the Tedlar® bag method (Method 0040). However, the upper range of analyte concentrations for the sorbent sampling methods is limited by the capacity of the sorbent and the capacity of the chromatographic analytical column and the mass spectrometric detection system. Methods 0030/0031 were developed for the collection/analysis of trace levels of specific analytes at parts-per-billion (ppb) levels in the stack gas stream (or 500-1000 ng on the analytical column, depending upon the specific compound). Non-polar, relatively stable, hydrophobic compounds typically perform well in Methods 0030/0031. Because these methods involve purging the sorbent tubes through water, they are generally very poorly applicable (or not applicable at all) to volatile, polar water-soluble compounds.

Method 0040 is a whole-gas sampling technique developed initially to provide an alternative to Methods 0030/0031 for sources where the emission concentrations were higher than the Method 0030/0031 limits (i.e., levels ranging from parts-per-million (ppm) to hundreds of ppm in the emission stream). Method

0040 allows aliquots of the sample to be analyzed and the aliquot can be pre-concentrated. Non-polar, relatively stable, hydrophobic compounds that can be shown to be stable in a Tedlar® bag for at least 72 hours typically perform well in Method 0040. Attachment 1 of this appendix provides a memorandum clarifying certain aspects of the Method 0040 Tedlar® bag method.

EPA OSW recommends that project-specific measurement objectives for volatile organic compounds be established in the QAPP and used to select appropriate sampling and analytical methods for the range of volatile compounds that may be emitted. Pre-testing can provide valuable information. For example, pre-testing can reveal whether certain compounds are present at concentrations which exceed the operating range for Methods 0030/0031. If high concentration volatile organic compounds are present, a Method 0040 Tedlar® bag determination with GC/MS analysis may be needed to achieve accurate quantitative results for the higher concentration organics. Volatility of the organic compounds should also be considered. Although the Method 8260B analytical conditions can and do obtain quantitative measurements for the very volatile halogenated compounds (such as chloromethane, chloroethane, etc.), these compounds cannot be sampled reliably using Method 0030. Thus, either Method 0031 or Method 0040 would be needed to sample the very volatile compounds (with boiling points less than 30 EC), followed by GC/MS analysis. For trace levels of the very volatile halogenated compounds, analysis of a Method 0040 Tedlar® bag sample by GC/ECD may be considered in some cases to increase sensitivity. However, compound identification is less certain with GC/ECD.

To capture the complete range of constituent concentrations and volatility, it is likely that two sampling methods will be needed. Methods 0030/0031 can typically achieve lower detection limits than the Method 0040 Tedlar® bag (ppb versus ppm levels). However, Method 0030 will not reliably capture very volatile compounds (i.e., those boiling below 30 EC), and neither of the VOST/SMVOC methods (Methods 0030/0031) will reliably capture compounds present in high concentrations (i.e., ppm levels). Thus, a Method 0040 Tedlar® bag sample may be needed to augment the Method 0030/0031 results for very volatile and high concentration compounds. EPA OSW recommends that all samples (VOST, Tedlar® bag, and condensates) be analyzed by GC/MS for the target analytes appropriate to the sampling method as discussed in Section B.2.1, and for TICs as described in Section B.11. Analysis of Tedlar® bag samples for simple hydrocarbons is also recommended, as discussed in Section B.2.2. When both Method

0030/0031 and Method 0040 procedures are applied at a given source and a VOC is detected using both methods, EPA OSW recommends that the higher of the two results generally be used for the risk assessment and in the summation of total identified organics. If a compound is not detected, EPA OSW recommends that the lower of the two detection limits generally be used.

EPA OSW also recommends that condensate samples from both Methods 0030/0031 and Method 0040 be analyzed. These samples can be introduced into the analytical system by direct aqueous injection, or Method 8260 analytical procedures can be applied.

B.2.1 VOLATILE TARGET ANALYTE LISTS AND TENTATIVELY IDENTIFIED COMPOUNDS

Individual laboratories are very likely to use a target list for VOCs, in conjunction with both Methods 0030/0031 and Method 0040, that is the same as or derived from the Volatile Organic Compound Target List shown in Table B.2-1, based on analytical Method 8260B. However, all of the compounds listed in Table B.2-1 are not appropriate analytes for Methods 0030/0031 and Method 0040. Table B.2-2 lists VOCs for which field method evaluation data, using quadruple sampling trains with dynamic spiking according to the procedures of EPA Method 301 (Field Validation of Pollutant Measurement Methods from Various Waste Media, 40 CFR Part 63 Appendix A), are available. [If EPA currently recognizes an appropriate test method or considers the analyst's test method to be satisfactory for a particular analyte at a particular source, the Administrator may waive use of the method validation protocol or may specify a less rigorous validation procedure.] A list of validated methods may be obtained by contacting the Emissions Measurement Technical Information Center (EMTIC), U. S. Environmental Protection Agency, Research Triangle Park, NC 27711 (919)541-0200, or through the Emissions Measurement Center web site (http://www.epa.gov/ttn/emc). Table B.2-3 lists analytes for Method 0040, including compounds that met acceptance criteria in a field method evaluation study, compounds that failed to meet acceptance criteria, and appropriate candidates not tested. Table B.2-4 lists analytes which preliminary laboratory testing has demonstrated to be inappropriate candidates for VOST sampling and analytical methodology.

TABLE B.2-1

VOLATILE ORGANIC COMPOUND TARGET LIST DERIVED FROM METHOD 8260B

Volatile Organic Compound	CAS Number	Boiling Point, EC[1]
acetone[2]	67-64-1	56
acrylonitrile[2]	107-13-1	78
benzene	71-43-2	80
bromodichloromethane	75-27-4	87
bromoform[3]	75-25-2	149
bromomethane[1]	74-83-9	4
2-butanone (methyl ethyl ketone)[4]	78-93-3	80
carbon disulfide	75-15-0	46
carbon tetrachloride	56-23-5	77
chlorobenzene[3]	108-90-7	132
chlorodibromomethane[3]	124-48-1	119
chloroethane[1]	75-00-3	12
chloroform	67-66-3	62
chloromethane[1]	74-87-3	-24
dibromomethane	74-95-3	97
dichlorodifluoromethane[4]	75-34-3	57
1,1-dichloroethane	75-34-3	57
1,2-dichloroethane	107-06-2	83
1,1-dichloroethene	75-35-4	32
cis-1,2-dichloroethene	156-59-2	48
trans-1,2-dichloroethene	156-60-5	48
1,2-dichloropropane	78-87-5	95
cis-1,3-dichloropropene[3]	10061-01-5	108
trans-1,3-dichloropropene[3]	10061-02-6	107
ethylbenzene[3]	100-41-4	136
iodomethane[2]	74-88-4	43
methylene chloride	75-09-2	40
styrene[3]	100-42-5	145
1,1,2,2-tetrachloroethane[3]	79-34-5	146

TABLE B.2-1

VOLATILE ORGANIC COMPOUND TARGET LIST DERIVED FROM METHOD 8260B (Continued)

Volatile Organic Compound	CAS Number	Boiling Point, EC[1]
tetrachloroethene[3]	127-18-4	121
toluene[3]	108-88-3	110
1,1,1-trichloroethane	71-55-6	74
1,1,2-trichloroethane[3]	79-00-5	114
trichloroethene	79-01-6	87
trichlorofluoromethane[1]	75-69-4	24
1,2,3-trichloropropane[3]	96-18-4	157
vinyl chloride[1]	75-01-4	-13
xylenes (total)[3]	1330-02-7	137

Notes:

[1] Existing sampling methods for VOCs are boiling-point specific. The appropriate sampling methods should be considered to achieve results for the entire VOC target analyte list. For example, compounds with boiling points less than 30EC cannot be reliably sampled using Method 0030, and should be sampled using Methods 0031 and/or 0040.

[2] Certain compounds, including acetone, acrylonitrile, and iodomethane, cannot be reliably determined using the VOST methodology (either Method 0030 or Method 0031). VOST results obtained for these compounds should be considered semi-quantitative, at best. However, the compounds have been retained on the target analyte list to provide the most complete emissions characterization possible using currently available analytical methods.

[3] These constituents have a boiling point greater than 100EC, as specified in Method 0030. Although these compounds are listed as Method 8260B target analytes, the reliability of the VOST sampling methodology for these compounds should be demonstrated or the analytes should be added to the SVOC target analyte list.

[4] Two constituents, 2-butanone and dichlorodifluoromethane, have been retained from the former Method 8240 target list because these compounds are regularly observed in stack emissions.

TABLE B.2-2

VOCs FOR WHICH FIELD METHOD EVALUATION DATA ARE AVAILABLE

Results for Method 0030 halogenated compounds laboratory study and four field tests.

Compound	First Field Test[a]		Second Field Test[b]		Third Field Test[c]		Laboratory Studies[d]		Fuerst, *et al.* Field Test[e]	
	Percent Recovery	Percent RSD	Percent Recovery	Percent RSD	Percent Recovery	Percent RSD	Percent Recovery	Percent RSD	Percent Recovery	Percent RSD
methyl chloride (chloromethane)	937	53.8	243	62.8	255.3	58.1	101.2	8.10		
ethylidene dichloride (1,1-dichloroethane)	75.7	13.7	82.2	23.3	86.0	13.2	108.8	3.97		
chlorobenzene	88.2	22.0	81.2	22.1	84.8	27.9	94.2	14.56		
vinyl chloride	110.4	27.3	41.8	44.6	37.3	39.5	90.4	12.01		
vinylidene chloride (1,1-dichloroethylene)	88.0	31.3	77.8	24.2	77.8	25.1	123.0	4.56		
chloroform	81.8	14.8	91.3	24.6	95.3	14.3	117.4	4.92	127	12
propylene dichloride (1,2-dichloropropane)	67.2	9.6	121	24.8	117.7	30.0	98.0	9.52		
methyl bromide (bromomethane)	53.7	20.2	54.8	26.2	52.8	27.8	97.4	9.78		
ethyl chloride (chloroethane)	50.3	28.7	33.7	36.9	31.4	37.6	95.8	11.2		
methylene chloride	77.7	27.1	89.9	14.3	90.8	11.7	101.6	2.84		
methyl chloroform (1,1,1-trichloroethane)	110	43.5	91.1	31.1	96.8	19.4	103.4	12.28		
carbon tetrachloride	107	47.2	81.2	23.6	85.7	13.8	108.4	14.97	108	8
ethylene dichloride (1,2-dichloroethane)	76.6	33.0	72.3	37.5	78.6	27.7	95.8	6.19		
trichloroethylene	126	15.6	119	26.2	124.0	16.8	110.0	6.88		
cis-1,3-dichloropropene	137	26.0	79.5	27.6	83.5	16.1	109.0	14.59		
trans-1,3-dichloropropene	135	38.1	52.3	35.4	47.9	35.0	96.6	18.00		
1,1,2-trichloroethane	98.0	22.1	79.7	27.2	81.4	14.4	106.4	13.71		

TABLE B.2-2

VOCs FOR WHICH FIELD METHOD EVALUATION DATA ARE AVAILABLE (Continued)

Compound	First Field Test[a]		Second Field Test[b]		Third Field Test[c]		Laboratory Studies[d]		Fuerst, *et al.* Field Test[e]	
	Percent Recovery	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**
tetrachloroethene	97.7	21.9	60.1	27.9	57.5	12.5	111.6	6.72	122	8
methyl iodide (iodomethane)	72.8	37.6	79.5	63.1	77.8	20.4	108.4	5.28		
allyl chloride (3-chloropropene)	29.9	19.5	35.6	33.3	36.4	29.6	127.2	5.43		
ethylene dibromide (1,2-dibromoethane)	34.9	31.6	79.6	37.4	81.6	31.0	97.0	14.86		
chloroprene	40.1	22.4	72.4	23.0	76.4	12.3	104.2	4.31		
vinyl bromide	60.7	34.3	29.8	29.7	28.4	30.9	110.8	9.30		
trichlorofluoromethane (freon 11)	not tested		not tested		not tested		not tested		93	10

[a] Mean of six replicate quadruple sampling train runs, with dynamic spiking. Coal fired power plant. (McGaughey 1993; McGaughey 1994a)

[b] Mean of eight replicate quadruple sampling train runs, with dynamic spiking. Organic chemical manufacturing facility. (McGaughey 1994a; McGaughey 1994c).

[c] Mean of six replicate quadruple sampling train runs, with dynamic spiking. Organic chemical manufacturing facility. (McGaughey 1994d; McGaughey 1994b; Jackson 1994; McGaughey 1994c).

[d] Mean of five replicate quadruple sampling train runs. Full scale sampling train, dynamic spike, stack simulator. (Bursey 1993; McGaughey 1994a)

[e] Mean of 11-16 replicate quadruple sampling train runs, with dynamic spiking. Hazardous waste combustor. (Fuerst 1987)

Note: References gathered and results summarized by Larry D. Johnson, in “Methods 98. Status of Stationary Source Methods for Air Toxics” available at http://www.epa.gov/ttnemc01/news.html.

TABLE B.2-2

VOCs FOR WHICH FIELD METHOD EVALUATION DATA ARE AVAILABLE (Continued)

Results for Method 0030 nonhalogenated organic compounds, laboratory study and three field tests.

Compound	**First Field Test**[a]		**Second Field Test**[b]		**Laboratory Test**[c]		**Fuerst, *et al.* Field Test**[d]	
	Percent Recovery	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**
2,2,4-trimethylpentane	63.1	18.3	75.9	27.7	69/83	13/11		
carbon disulfide	63.8	23.6	42.0	27.7	54/60	21/15		
n-hexane	79.2	22.6	92.9	23.5	88/105	13/8		
benzene	106.3	25.6	100.1	23.6	66/99	7/6	106	6
toluene	77.9	17.5	98.8	30.3	60/*	21/*		

[a] Mean of 9 replicate quadruple sampling train runs, with dynamic spiking. Coal-fired power plant. (Bursey 1997a; Jackson 1996a)
[b] Mean of 11 replicate quadruple sampling train runs, with dynamic spiking. Chemical manufacturing facility waste burner. (Bursey 1997a; Jackson 1997a)
[c] Mean of 10 replicate quadruple sampling train runs, with dynamic spiking at two concentration levels. Source simulator. (Jackson 1996a; Bursey 1997a)
[d] Mean of 16 replicate quadruple sampling train runs, with dynamic spiking. Hazardous waste combustor. (Fuerst 1987)

* Invalid results due to laboratory contamination.

TABLE B.2-3

CANDIDATE ANALYTES FOR METHOD 0040

Compounds that Met Method 301 Acceptance Criteria in a Field Method Evaluation	
1,1,1-trichloroethane	71-55-6
trichloroethene	79-01-6
1,1-dichloroethane	75-34-3
1,1-dichloroethene	75-35-4
2,2,4-trimethylpentane	540-84-1
allyl chloride	107-05-1
benzene	71-43-2
carbon tetrachloride	56-23-5
methyl chloride (chloromethane)	74-87-3
hexane	110-54-3
methylene chloride	75-09-2
toluene	108-88-3
trichlorofluoromethane	353-54-8
vinyl bromide	593-60-2
vinyl chloride	75-01-4
Compounds that Failed to Meet Method Acceptance Criteria in a Field Method Evaluation	
methyl bromide	74-83-9
1,3-butadiene	106-99-0
dichlorodifluoromethane	75-71-8
Appropriate Candidates for Method 0040 Not Tested	
1,2-dichloro-1,1,2,2-tetrafluoroethane	76-14-2
1,1,2-trichlorofluoroethane	76-13-1
chloroform	67-66-3
1,2-dichloropropane	78-87-5
tetrachloroethene	127-18-1

TABLE B.2-4

CLEAN AIR ACT ANALYTES DEMONSTRATED TO BE INAPPROPRIATE FOR VOST IN LABORATORY TESTING[1]

Volatile Organic Compound	CAS Number	Comment
acetaldehyde	75-07-0	Polar, water-soluble, reactive
acetonitrile	75-05-8	Polar, water-soluble
acrolein	107-02-8	Polar, water-soluble, reactive
acrylonitrile	107-13-1	Polar; purges poorly
allyl chloride	107-05-1	Reactive
bis(chloromethyl) ether	92-87-5	Reactive
1,3-butadiene	106-99-0	Reactive
carbonyl sulfide	463-58-1	Too highly volatile; quantitative collection questionable
chloromethyl methyl ether	107-30-2	Reactive; may decompose during sampling
1,4-dioxane	123-39-11	Polar, water-soluble; low analytical system response in laboratory testing
epichlorohydrin	106-89-8	Reactive
ethyl acrylate	140-88-5	Polymerizes easily
ethylene imine	151-56-4	Water-soluble; polymerizes
ethylene oxide	75-21-8	Reactive
formaldehyde	50-00-0	Polar; water-soluble; reactive
methanol	67-56-1	Polar; water-soluble
methyl hydrazine	60-34-4	Polar; water-soluble; reactive
methyl isocyanate	624-83-9	Polar; water-soluble; reactive
methyl methacrylate	80-61-6	Polar; water-soluble; may polymerize during sampling
methyl *tert*-butyl ether	1634-04-4	Polar; water-soluble; low analytical system response during laboratory testing
phosgene	75-44-5	Reactive
triethylamine	121-44-8	Polar; water-soluble
vinyl acetate	108-05-4	Polar; water-soluble; low analytical system response during laboratory testing

[1] Note: References gathered and results summarized by Larry D. Johnson, in "Methods 98. Status of Stationary Source Methods for Air Toxics" available at http://www.epa.gov/ttnemc01/news.html.

For all of the VOC sampling and analytical methods, laboratories generally base their analytical target list upon Method 8260B (or the most current version of the analytical purge and trap GC/MS method). Some laboratories have eliminated from their target lists compounds known to be inappropriate analytes or compounds that cannot be analyzed successfully. The permit writer should be aware which of the compounds from Table B.2-1 are not appropriate for the sampling and analytical methodology and should request demonstration of the effectiveness of the methodology for compounds where appropriateness of the methodology has not been demonstrated. Some laboratories may also have eliminated compounds from their target lists that have not historically been found in stack emissions. Documents which can be reviewed to identify compounds which have historically been found in stack emissions include the EPA OSW risk assessment guidance (EPA 1998a) and various studies that attempt to identify products of incomplete combustion (Lemieux and Ryan 1997 and 1998; EPA 1997a; MRI 1997; EER 1997).

In addition to the complete target analyte list for the method, EPA OSW recommends that non-target compounds (i.e., TICs) be characterized. Since the Method 8260B analytical methodology uses GC/MS (usually in the full scan mode), the methodology is amenable to the characterization of tentatively identified compounds, according to the criteria for identification presented in Method 8260 and summarized in Section B.11, in order to make the characterization of the source as complete as possible. For the Total Organics Emissions (TOE) analysis discussed later in Section B.7, total organic mass in the volatile range is one of the components of the total recoverable organic mass that can be calculated. All organic compounds that are identified and quantified are ultimately subtracted from the total organic emissions mass value. It is, therefore, beneficial for the laboratory to identify and quantify the maximum number of compounds when the analysis is performed. Although it is in the facility’s interest to characterize as many TICs as possible, extensive characterization of TICs involves a significant commitment of time and expertise and can reach a point of diminishing returns. Therefore, it is recommended that TICs be characterized when the peak intensity is 10 percent or more of full chromatographic scale, and that a quantitative estimate of the value be obtained using the nearest-eluting internal standard and a response factor of 1. Unless the identification of the TIC is confirmed by the analysis of an authentic standard, the quantitative value should be qualified as “estimated.”

None of the methods for VOCs described above are appropriate for polar water-soluble compounds. There are some methods available in draft versions for specific VOCs; extended applicability of these methods to VOCs other than the specific analyte has not been demonstrated, but in some cases, field method validation data are available for the compound specified in the method. These polar water-soluble analytes are shown in Table B.2-5. It is possible that these methods have a wider application, but the extended application remains to be demonstrated if these methods are used.

TABLE B.2-5

POLAR WATER-SOLUBLE ANALYTES FOR WHICH DRAFT METHODS ARE AVAILABLE

Volatile Organic Compound	Method
methyl isocyanate	Sampling and Analysis of Isocyanates (McGaughey 1995) Draft Method 207.1 Draft Method 207.2
acetonitrile	Sampling and Analysis for Acetonitrile Emissions from Stationary Sources (Steger 1997)
methanol	Test Method for the Measurement of Methanol Emissions from Stationary Sources (Pate 1994; Peterson 1995)

B.2.2 SIMPLE HYDROCARBONS

Analysis of samples using the Method 8260B GC/MS target analyte list and Method 8260B analytical conditions will not provide analytical results for the more volatile alkanes, alkenes, and alkynes such as methane, ethane, ethene, acetylene, propene, and propyne. Methane and other aliphatics can comprise a significant percentage of total stack organics, and specific determinations for methane, ethane, propane, and other short-chain aliphatics are recommended to increase the completeness of the emissions characterization and potentially alleviate concerns about the percentage of the total organic mass that might be toxic. To achieve accurate measurements for these more volatile compounds, a Method 0040 Tedlar® bag determination with GC/FID analysis for the appropriate compounds will generally be necessary.

One simple way to quantify simple hydrocarbons without expanding the sampling effort is to utilize information already available as part of the Total Organic Emissions determination (Section B.7). The TOE determination involves measurements of volatile organics by field gas chromatography (FGC), and an initial calibration is performed using methane, ethane, propane, butane, pentane, hexane, and heptane. If the analysis shows that a stack gas constituent has the same retention time as one or more of the calibration standards, then that constituent can be quantified and included in the "identified" portion of the stack emissions. A facility may also choose to calibrate the field gas chromatograph with additional compounds to identify more volatile hydrocarbons, thereby moving those compounds from the "unknown" to the "identified" portion of the stack emissions. Additional information is provided in Section B.7.

B.3 SEMIVOLATILE AND CONDENSIBLE COMPOUNDS

The SW-846 Method 0010 sampling train provides the technical foundation for the sampling methods pertaining to the following groups of semivolatile organic compounds, defined as organic compounds with boiling points > 100EC:

- Dioxins/Furans (D/Fs);
- Polynuclear Aromatic Hydrocarbons (PAHs);
- Polychlorinated biphenyls (PCBs);
- Chlorobenzenes (CBs) and chlorophenols (CPs); and
- All other semivolatile organic compounds (SVOCs) with boiling points above 100EC.

The Method 0010 sampling train consists of a heated filter, a solid sorbent (XAD-2®) collection module, and a number of impingers. The chief difference in the applicability of the Method 0010 sampling train to each of the different groups of analytes lies in the standards used to spike the sorbent resin prior to collecting the semivolatile organic compounds, and the sample recovery procedures and analytical finish. Appendix B of Method 0010 includes procedures for preparation of the Method 0010 sampling train components for Total Chromatographable Organic Material analysis, but the Appendix B procedures have been superseded by SW-846 Method 3542 (Extraction of Semivolatile Analytes Collected Using Modified Method 5 (Method 0010) Sampling Train). The components of the Method 0010 sampling train are recovered in the field with subsequent preparation (according to Method 3542) in the analytical laboratory. The field recovery procedures generate six sets of train components to be shipped to the laboratory:

- A particulate matter filter (prepared by Soxhlet extraction; dried, and concentrated for analysis);
- A front half rinse (filtered; filtrate added to Soxhlet extraction of the filter);
- A condenser rinse and rinse of all sampling train components located between the filter and the sorbent module (methylene chloride extraction with water separation; combined with filter extract, dried, and concentrated for analysis);

C A sorbent trap section (combined with both filter holder back half rinse and condenser rinse after water separation; Soxhlet extraction; dried; concentrated for analysis);

C Condensate and condensate rinse (methylene chloride extraction with water separation; dried; concentrated for analysis); and

C Silica gel (weighed to determine moisture content).

The rinse used to recover the Method 0010 sampling train in the field consists of a 1:1 mixture of methylene chloride and methanol. Thus, any of the train components that include a rinse will contain methanol. If any methanol is retained in extracts when they are concentrated for analysis, the resulting concentrate will consist of all or mostly methanol and cannot be analyzed successfully. It is therefore essential that any steps of Method 3542 that include a rinse component include a water separation step to ensure removal of all of the methanol prior to concentration and analysis of the extract.

Application of Method 3542 to the preparation of Method 0010 train components ultimately produces three 5-mL extracts for analysis: the filter/front half rinse, the XAD-2® resin/back half rinse, and the condensate/condensate rinse. A final extract volume of 5 mL ensures that the more volatile of the semivolatile components (i.e., boiling points of 100-150EC) will be recovered quantitatively in the sample concentration step. Several laboratories have demonstrated extensive losses of these types of compounds when an extract is concentrated below 5 mL. This area of concern becomes especially important if additional constituents from the Method 8260B target list are included in the semivolatile target list. At present, because of the surrogate spiking scheme used in the current version of Method 3542, the three extracts cannot be combined and analyzed. Research efforts are currently in progress to identify a surrogate spiking scheme that will allow combination of the extracts.

An additional area of concern for the operation of the Method 0010 sampling train is sufficient cleanliness of the XAD-2® resin used to collect the semivolatile organic compounds. The XAD-2® resin as supplied by the manufacturer is impregnated with a bicarbonate solution to inhibit microbial growth during storage. The salt solution, any residual extractable monomer and polymer species, and any residual organic chemicals used in the synthesis of the resin has to be removed before use of the resin in a Method 0010 sampling train. There is no guarantee that “pre-cleaned” XAD-2® purchased from a commercial vendor will be sufficiently clean to be used for its intended purpose. Furthermore, cleaned XAD-2® in storage at room temperature for more than 30 days should be re-cleaned in order to remove contaminants collected in storage. Appendix A of Method 0010 includes a procedure for the preparation of XAD-2® sorbent resin that uses extraction with a sequence of solvents (water, methyl alcohol, methylene chloride) followed by careful drying of the resin to prevent breaking the resin particles in the drying process. Method 0010 also provides quality control procedures for determination of residual methylene chloride in the cleaned, dried resin, as well as for determination of residual extractable organics. A standard procedure in many laboratories has been to use a cleanliness criterion of <10 µg/g of Total Chromatographable Organics extracted from a 20±0.1 gram (g) sample of dried resin, as specified in Method 0010. These standard procedures and quality criteria were developed to achieve environmental assessment screening studies of combustion sources (EPA 1978). However, this criterion for cleanliness is not sufficient to ensure adequate resin cleanliness for all Method 0010 applications. To ensure adequate cleanliness for all applications, the following procedures are recommended:

- Extract an aliquot of resin equal to the size resin sampling module that will be used in the Method 0010 sampling train (a 40 gram resin sample is usually used);
- Concentrate the extract to the same volume that will be used for the samples in the ultimate analysis; and
- Screen the resin blank according to the analysis that will be performed, at the Method Detection Limit for each compound of interest.

The standard analytical procedures for semivolatile organic compounds collected in the Method 0010 sampling train are found in Method 8270 (Method 8270C is the current version from SW-846 On-Line). Individual laboratories may have target analyte lists that differ slightly from Method 8270C and Table B.3-1. If a laboratory does not include all of the Table B.3-1 compounds on their standard semivolatile target analyte list, EPA OSW recommends that the laboratory identify the excluded compounds and explain the reason for the exclusion. The permit writer can then review the laboratory's proposed list considering the laboratory's rationale for exclusion of certain compounds, as well as a review to ensure that the excluded compounds have not historically been found in stack emissions based on Appendix A-1 of the *Human Health Risk Assessment Protocol for Hazardous Waste Combustion*

TABLE B.3-1

SEMIVOLATILE ORGANIC COMPOUND TARGET LIST - METHOD 8270C ANALYTES

Semivolatile Organic Compound	**CAS Number**
acenapththene	83-32-9
acenaphthylene	208-96-8
acetophenone	98-86-2
4-aminobiphenyl	92-67-1
aniline	62-53-3
anthracene	120-12-7
benzidine	92-87-5
benzoic acid[1]	65-85-0
benzo(a)anthracene	56-55-3
benzo(b)fluoranthene	205-99-2
benzo(k)fluoranthene	207-08-9
benzo(g,h,i)perylene	191-24-2
benzo(a)pyrene	50-32-8
benzyl alcohol[1]	100-51-6
bis(2-chloroethoxy)methane	111-91-1
bis(2-chloroethyl) ether	111-44-4
bis(2-ethylhexyl) phthalate[2]	117-81-7
4-bromophenyl phenyl ether	101-55-3
butylbenzyl phthalate[2]	85-68-7
4-chloroaniline	106-47-8
4-chloro-3-methylphenol	59-50-7
1-chloronaphthalene	90-13-1
2-chloronaphthalene	91-58-7
2-chlorophenol	95-57-8
4-chlorophenyl phenyl ether	7005-72-3
chrysene	218-01-9
dibenz(a,j)acridine	224-42-0
dibenzo(a,h)anthracene	53-70-3
dibenzofuran	132-64-9

TABLE B.3-1

SEMIVOLATILE ORGANIC COMPOUND TARGET LIST - METHOD 8270C ANALYTES (Continued)

Semivolatile Organic Compound	**CAS Number**
di-*n*-butyl phthalate[2]	84-74-2
1,2-dichlorobenzene[3]	95-50-1
1,3-dichlorobenzene[3]	541-73-1
1,4-dichlorobenzene[3]	106-46-7
3,3'-dichlorobenzidine	91-94-1
2,4-dichlorophenol	120-83-2
2,6-dichlorophenol	87-65-0
diethyl phthalate[2]	84-66-2
p-dimethylaminoazobenzene	60-11-7
7,12-dimethylbenz(a)anthracene	57-97-6
á, á-dimethylphenethylamine	122-09-8
2,4-dimethylphenol	105-67-9
dimethyl phthalate[2]	131-11-3
4,6-dinitro-2-methylphenol	534-52-1
2,4-dinitrophenol	51-28-5
2,4-dinitrotoluene	121-14-2
2,6-dinitrotoluene	606-20-2
di-*n*-octyl phthalate[2]	117-84-0
diphenylamine	122-39-7
ethyl methane sulfonate	62-50-0
fluoranthene	206-44-0
fluorene	86-73-7
hexachlorobenzene	118-74-1
hexachlorobutadiene[3]	87-68-3
hexachlorocyclopentadiene	77-47-4
hexachloroethane	67-72-1
indeno(1,2,3-cd)pyrene	193-39-5
isophorone	78-59-1
3-methylcholanthrene	56-49-5

TABLE B.3-1

SEMIVOLATILE ORGANIC COMPOUND TARGET LIST - METHOD 8270C ANALYTES (Continued)

Semivolatile Organic Compound	**CAS Number**
methyl methane sulfonate	66-27-3
2-methylnaphthalene	91-57-6
2-methylphenol	95-48-7
4-methylphenol	106-44-5
naphthalene	91-20-3
1-naphthylamine	134-32-7
2-naphthylamine	91-59-8
2-nitroaniline	88-74-4
3-nitroaniline	99-09-2
4-nitroaniline	100-01-6
nitrobenzene	98-95-3
2-nitrophenol	88-75-5
4-nitrophenol	100-02-7
N-nitroso-di-*n*-butylamine	924-16-3
N-nitrosodimethylamine	62-75-9
N-nitrosodiphenylamine	86-30-6
N-nitroso-di-*n*-propylamine	621-64-7
N-nitrosopiperidine	100-75-4
2,2'-oxy *bis*(1-chloropropane) *bis*(2-chloroisopropyl) ether	108-60-1
pentachlorobenzene	608-93-5
pentachloronitrobenzene	82-68-8
pentachlorophenol	87-86-5
phenacetin	62-44-2
phenanthrene	85-01-8
phenol	108-95-2
2-picoline	109-06-8
pronamide	23950-58-5
pyrene	129-00-0

TABLE B.3-1

SEMIVOLATILE ORGANIC COMPOUND TARGET LIST - METHOD 8270C ANALYTES (Continued)

Semivolatile Organic Compound	CAS Number
1,2,4,5-tetrachlorobenzene	95-94-3
2,3,4,6-tetrachlorophenol	58-90-2
1,2,4-trichlorobenzene	120-82-1
2,4,5-trichlorophenol	95-95-4
2,4,6-trichlorophenol	88-06-2
Additional Constituents from the Method 8260B Target List with Boiling Points >100EC	
bromoform[3]	75-25-2
chlorobenzene[3]	108-90-7
ethylbenzene[3]	100-41-4
styrene[3]	100-42-5
1,1,2,2-tetrachloroethane[3]	79-34-5
toluene[3]	108-88-3
1,2,3-trichloropropane[3]	96-18-4
xylenes (total)[3]	1330-02-7

Notes:

[1] Common oxidation products of XAD-2® resin either due to the presence of ozone in ambient air or in the oxidizing stationary source matrix. When these compounds are reported, they should be qualified so the evaluator of the data can consider the possibility that these compounds are artifacts of the sampling process.

[2] The phthalate esters are common laboratory contaminants. The presence and concentrations of these compounds in the laboratory and field blanks should be monitored carefully.

[3] These compounds have boiling points between 100EC and 150EC and can easily be lost if an extract is concentrated below 5 mL prior to analysis.

Facilities (EPA 1998a) and various studies that attempt to identify products of incomplete combustion (Lemieux and Ryan 1997 and 1998; EPA 1997a; MRI 1997; EER 1997).

A further consideration in selection of a target list for the analytical method is the data that are available from several field method evaluation studies using quadruple Method 0010 sampling trains, dynamic spiking, and EPA Method 301 (40 CFR Part 63 Appendix A) statistical data evaluation procedures. Data for the halogenated semivolatile organic compounds tested are included in Table B.3-2, and for non-halogenated semivolatile organic compounds in Table B.3-3. The collected data demonstrate that successful performance in the methodology is compound- and source-dependent and that, in general, non-polar, hydrophobic compounds tend to perform more successfully in the methodology than polar, water-soluble compounds. Data and information included in Attachment 2 describe the compounds listed in the Clean Air Act Amendments of 1990, with status relative to sampling and analytical methods. Comments and suggestions are also included, with references. This information was gathered by Dr. Larry D. Johnson (EPA, retired) and is available on-line in the document "Methods 98. Status of Stationary Source Methods for Air Toxics" (http://www.epa/gov/ttnemc01/news.html).

In addition to the complete target list for the method, EPA OSW recommends that non-target compounds (i.e., TICs) be characterized. Since the Method 8270C analytical methodology uses GC/MS (usually in the full scan mode), the methodology is amenable to the characterization of tentatively identified compounds, according to the criteria for identification presented in Method 8270 and summarized in Section B.11, in order to make the characterization of the source as complete as possible. In the Total Organics Emissions (TOE) analysis, total organic mass in the semivolatile range is one of the components of the total recoverable organic mass that can be calculated. All organic compounds that are identified and quantified are ultimately subtracted from the total recoverable organic mass value. It is therefore beneficial for the laboratory to identify and quantify the maximum number of compounds when the analysis is performed. Although it is in the facility's interest to characterize as many TICs as possible, extensive characterization of TICs involves a significant commitment of time and expertise and can reach a point of diminishing returns. Therefore, EPA OSW recommends that TICs be characterized when the peak intensity is 10 percent or more of full chromatographic scale, and that a quantitative estimate of the value be obtained using the nearest-eluting internal standard and a response factor of 1. Unless the identification of the TIC

TABLE B.3-2

FIELD METHOD EVALUATION DATA FOR SELECTED HALOGENATED SEMIVOLATILE ORGANIC COMPOUNDS

Results for Method 0010 halogenated semivolatile organic compounds, laboratory study and five field tests.

Compound	First Field Test[a]		Second Field Test[b]		Third Field Test[c]		Laboratory Test[d]		Margeson, *et al.* Two Field Tests[e]	
	Percent Recovery	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**
bis(chloromethyl) ether	0.0	0.0	0.0	0.0	36.4	44.9	80.7	23.2		
epichlorohydrin	6.0	128.1	13.4	44.2	58.5	39.7	187.0	11.7		
cis-1,3-dichloropropene	49.1	37.5	50.3	48.3	73.8	25.1	51.9	12.9		
trans-1,3-dichloropropene	52.0	35.2	79.8	63.4	79.4	21.9	29.3	13.1		
1,1,2-trichloroethane	56.4	37.7	60.3	38.2	79.8	17.6	84.4	13.5		
1,2-dibromoethane	58.9	36.9	62.5	40.4	85.3	19.4	83.9	12.7		
tetrachloroethene	53.2	37.2	49.4	52.5	73.8	30.7	78.7	17.6		
chlorobenzene	62.3	43.2	65.1	40.7	76.4	18.2	86.2	11.9	86/86	22/14
bromoform	59.8	37.6	69.3	35.7	87.0	17.3	123.0	14.2		
1,1,2,2-tetrachloroethane	64.0	35.3	73.9	34.5	81.7	18.5	79.7	10.5	81.5	32.9
dichloroethyl ether	60.9	34.7	77.0	34.3	80.3	17.4	82.5	10.5		
1,4-dichlorobenzene	56.2	35.2	73.5	35.7	84.2	15.9	78.7	12.5		
benzyl chloride	67.4	33.4	73.9	34.9	82.1	20.9	77.9	11.7		
hexachloroethane	74.0	36.9	70.9	35.6	83.6	15.5	84.6	13.3		
1,2-dibromo-3-chloropropane	44.8	36.0	73.8	35.7	84.3	16.8	69.8	11.4		
1,2,4-trichlorobenzene	59.5	35.7	76.1	34.5	86.8	14.2	67.7	13.3		
hexachlorobutadiene	65.4	43.1	77.1	34.3	84.7	16.6	68.1	14.0		
benzotrichloride	60.1	36.5	72.4	38.0	75.2	20.5	85.7	16.8		

TABLE B.3-2

FIELD METHOD EVALUATION DATA FOR SELECTED HALOGENATED SEMIVOLATILE ORGANIC COMPOUNDS (Continued)

Compound	**First Field Test[a]**		**Second Field Test[b]**		**Third Field Test[c]**		**Laboratory Test[d]**		**Margeson, *et al.* Two Field Tests[e]**	
	Percent Recovery	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**
2-chloroacetophenone	56.0	40.7	79.5	32.7	66.1	44.6	89.1	11.7		
hexachlorocyclopentadiene	42.3	61.8	59.6	37.7	68.5	35.1	975.5	24.8		
2,4,6-trichlorophenol	49.8	47.0	75.4	35.2	77.1	15.8	72.8	26.2		
2,4,5-trichlorophenol	62.7	35.3	76.6	34.5	80.7	16.1	76.1	23.8		
hexachlorobenzene	44.6	33.9	56.5	31.0	82.6	12.7	73.3	10.0		
pentachlorophenol	42.4	41.5	60.3	25.6	64.3	49.2	57.5	60.3	124	46.3
pentachloronitrobenzene	43.4	37.9	58.5	28.9	87.5	15.8	79.2	10.1		
chlorobenzilate	40.7	50.6	61.8	33.1	78.0	17.0	131.6	32.0		
3,3'-dichlorobenzidine	4.4	164.9	0.6	264.6	10.0	78.8	1352.4	43.4		

[a] Mean of 12 replicate quadruple sampling train runs. Coal fired power plant. (McGaughey 1993; McGaughey 1994a)

[b] Mean of 4 replicate quadruple sampling train runs. Organic chemical manufacturing facility. (McGaughey 1994b; Jackson 1996b; McGaughey 1996a)

[c] Mean of 10 replicate quadruple sampling train runs. Organic agricultural chemical manufacturing facility. (Jackson 1995c; Bursey 1997a)

[d] Mean of 7 replicate quadruple sampling train runs. Full scale sampling train, dynamic spike, stack simulator.   (McGaughey 1994a)

[e] Mean of 13-39 replicate quadruple sampling train runs, with dynamic spiking. Two hazardous waste incinerators. (Margeson 1987)

TABLE B.3-3

FIELD METHOD EVALUATION DATA FOR SELECTED NON-HALOGENATED SEMIVOLATILE ORGANIC COMPOUNDS

Results for Method 0010 nonhalogenated semivolatile organic compounds, laboratory study and four field tests.

Compound	First Field Test[a]		Second Field Test[b]		Laboratory Test[c]		Margeson, *et al.* Two Field Tests[d]	
	Percent Recovery	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**
di-*n*-butyl phthalate	46	54	107	14	118	10		
bis(2-ethylhexyl) phthalate	48	23	65	93	110	32		
m-/*p*-cresol	69	14	65	49	105	5		
dimethyl phthalate	82	17	123	7	105	9		
phenol	89	9	56	22	96	7	96	14
o-cresol	90	15	71	34	100	5		
2,4-dinitrophenol	111	31	24	87	5	155		
4-nitrophenol	114	31	59	18	38	33		
4,6-dinitro-*o*-cresol	122	14	53	34	44	44		
quinone	2	438	not tested		28	97		
hexamethylphosphoramide	14	118	not tested		49	74		
trifluralin	27	41	not tested		149	11		
dimethylaminoazobenzene	31	51	17	67	106	16		
3,3'-dimethoxybenzidine	37	38	6	129	20	50		
o-anisidine	39	39	4	149	67	17		
o-toluidine	56	30	24	70	80	22		
benzidine	65	119	8	95	8	81		
N,N,-dimethylaniline	67	24	54	31	97	12		
aniline	70	24	35	45	67	11		
4,4'-methylene *bis*(2-chloroaniline)	89	36	25	49	75	27		
3,3'-dimethylbenzidine	92	44	6	129	28	51		

TABLE B.3-3

FIELD METHOD EVALUATION DATA FOR SELECTED NON-HALOGENATED SEMIVOLATILE ORGANIC COMPOUNDS (Continued)

Compound	First Field Test[a]		Second Field Test[b]		Laboratory Test[c]		Margeson, *et al.* Two Field Tests[d]	
	Percent Recovery	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**
N,N-diethylaniline	95	19	54	31	104	16		
carbaryl	99	19	125	51	94	22		
ethyl carbamate	103	14	27	33	69	21		
caprolactam	114	12	22	107	91	18		
N-nitrosomorpholine	116	12	81	26	85	23		
N-nitrosodimethylamine	117	13	81	27	96	9		
propoxur	123	12	75	61	97	20		
2-acetylaminofluorene	147	23	49	45	106	17		
styrene oxide	0.5	1481	not tested		49	66		
phthalic anhydride	5	144	not tested		2	136		
methoxychlor	73	19	75	51	73	30		
toluene	76	11	97	11	340	45	75/85	26/15
m-/p-xylene	79	12	79	12	104	9		
quinoline	80	19	82	30	99	8		
styrene	84	10	39	81	104	8		
o-xylene	85	11	97	9	103	8	99	8
1,4-dioxane	87	11	79	21	92	8	86	17
cumene	88	11	95	9	102	9		
ethylbenzene	89	12	93	9	94	10		
parathion	89	28	76	28	96	11		
isophorone	93	12	96	13	106	13		

TABLE B.3-3

FIELD METHOD EVALUATION DATA FOR SELECTED NON-HALOGENATED SEMIVOLATILE ORGANIC COMPOUNDS (Continued)

	First Field Test[a]		**Second Field Test[b]**		**Laboratory Test[c]**		**Margeson, *et al.* Two Field Tests[d]**	
Compound	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**	**Percent Recovery**	**Percent RSD**
acetophenone	96	12	98	13	132	12		
naphthalene	96	11	94	10	107	8	106	16
dibenzofuran	100	12	103	12	110	11		
dichlorvos	101	18	57	27	68	30		
DDE	102	15	93	24	120	10		
4-nitrobiphenyl	102	14	104	10	104	12		
heptachlor	103	12	35	107	95	9		
biphenyl	103	12	105	12	106	9		
lindane	104	12	104	8	107	9		
nitrobenzene	109	12	100	10	97	9	117	17
2,4-dinitrotoluene	109	12	102	21	110	24		
methyl isobutyl ketone	112	11	101	11	103	9		
chlordane	142	16	85	25	93	14		
pyridine	not tested		not tested		not tested		82/71	24/18

[a] Mean of 10-20 replicate quadruple sampling train runs, with dynamic spiking. Coal-fired power plant. (Jackson 1996b; Bursey 1997b)

[b] Mean of 8-19 replicate quadruple sampling train runs, with dynamic spiking. Chemical manufacturing facility waste burner. (Jackson 1997b; Bursey 1997c)

[c] Mean of 6-14 replicate quadruple sampling train runs, with dynamic spiking. Source simulator. (Jackson 1995b; Bursey 1993)

[d] Mean of 13-39 replicate quadruple sampling train runs, with dynamic spiking. Two hazardous waste incinerators. (Margeson 1987)

is confirmed by the analysis of an authentic standard, the quantitative value should be qualified as "estimated."

B.4 OTHER ORGANIC COMPOUNDS

There is considerable variability in the analyses offered by commercial laboratories. EPA OSW recommends that specialized analyses to address specific groups of semivolatile organic compounds be utilized to the extent possible. Examples of specialized analyses for semivolatile compounds are discussed below.

B.4.1 CHLOROBENZENES/CHLOROPHENOLS (CBS/CPS)

Some commercial laboratories offer an expanded GC/MS target list for CBs/CPs, with a specialized target list as shown in Table B.4-1. There is some overlap with the semivolatile organic analytes on the SW-846 Method 8270C target list, but the specialized CB/CP list is more extensive and use of the extended target list is recommended. Since the CB/CP analysis uses the same extracts that have been prepared for analysis using Method 8270C procedures, there is no technical reason why the additional compounds cannot be added to the calibration compounds for Method 8270C and determined in a single analysis. If a dual analysis is performed for Method 8270C analytes and CB/CPs, there should be no adverse impact upon Method Detection Limits for either determination. If a CB/CP compound is detected in both the Method 8270C SVOC analysis and in the CB/CP analysis, EPA OSW recommends that the higher of the two results (if there is a difference) be used for the risk assessment and in the summation of the total identified organics. If a compound is not detected, EPA OSW recommends that the lower of the two detection limits (if there is a difference) be used.

B.4.2 POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

Consistent with current EPA OSW guidance (EPA 1998a), PAHs are recommended for evaluation as COPCs in site-specific risk assessments. The following PAHs are commonly detected: benzo(a)pyrene (BaP); benzo(a)anthracene; benzo(b)fluoranthene; benzo(k)fluoranthene; chrysene; dibenz(a,h)anthracene; and indeno(1,2,3-cd)pyrene. EPA considers all of these compounds to be carcinogenic; all except chrysene are known to be animal carcinogens. However, an oral cancer slope factor is available for only one PAH, BaP. Although the analyte list for Method 8270C includes most PAHs, the detection limits for PAHs have

TABLE B.4-1

CHLOROBENZENES AND CHLOROPHENOLS

Chlorobenzenes	CAS Number	Chlorophenols	CAS Number
1,2-dichlorobenzene[1]	95-50-1	2-chlorophenol[1]	95-57-8
1,3-dichlorobenzene[1]	541-73-1	3-chlorophenol[3]	108-43-0
1,4-dichlorobenzene[1]	106-46-7	4-chlorophenol[3]	106-48-9
1,3,5-trichlorobenzene	108-70-3	2,4-dichlorophenol[1]	120-83-2
1,2,4-trichlorobenzene[1]	120-82-1	2,5-dichlorophenol	583-78-8
1,2,3-trichlorobenzene	87-61-6	2,3-dichlorophenol	576-24-9
1,2,3,5-tetrachlorobenzene[2]	634-90-2	2,6-dichlorophenol[1]	87-65-0
1,2,4,5-tetrachlorobenzene[1,2]	95-94-3	3,5-dichlorophenol	591-35-5
1,2,3,4-tetrachlorobenzene	634-66-2	3,4-dichlorophenol	95-77-2
pentachlorobenzene[1]	608-93-5	2,3,5-trichlorophenol	933-78-8
hexachlorobenzene[1]	118-74-1	2,4,6-trichlorophenol[1]	88-06-2
		2,4,5-trichlorophenol[1]	95-95-4
		2,3,4-trichlorophenol	15950-66-0
		2,3,6-trichlorophenol	933-75-5
		2,3,5,6-tetrachlorophenol[4]	935-95-5
		2,3,4,5-tetrachlorophenol[4,5]	490-151-3
		pentachlorophenol[1]	87-86-5

Notes:

[1] This compound is also included on the list of Method 8270C analytes.

[2] Co-elute; reported as totals.

[3] Co-elute; reported as totals.

[4] Co-elute; reported as totals.

[5] The analyte list for CB/CPs does not include 2,3,4,6-tetrachlorophenol (58-90-2), which is included on the list of Method 8270C analytes.

been found to be critical for the indirect risk pathway. Using selected ion monitoring mass spectrometric techniques in the Method 8270C analysis will improve the detection limits for the PAHs, but this improvement may not be sufficient for the risk assessment. It is therefore recommended that, for the lowest possible method detection limits, PAHs be determined by a separate analysis using HRGC coupled with HRMS or possibly low resolution mass spectrometry (LRMS) in the selected ion monitoring mode after the application of chromatographic cleanup procedures designed to remove interfering organic compounds. If a PAH is detected in both the SVOC (Method 8270C) analysis and in a specialized PAH analysis, EPA OSW recommends that the higher of the two results be used for the risk assessment and in the summation of total identified organic compounds. If a PAH is not detected in either of the two analyses, EPA OSW recommends that the lower of the two detection limits be used.

CARB Method 429 (Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Stationary Sources) [http://www.arb.ca.gov/testmeth/vol3/vol3.htm] applies to the determination of 19 PAHs listed in Table B.4-2. In this method, particulate and gas phase PAH are extracted isokinetically from the stack and collected by a Method 0010 sampling train. The analytical methodology used is isotope dilution mass spectrometry combined with HRGC. Isotope dilution entails the addition of internal standards to all samples in known quantities, matrix-specific extraction of the sample with appropriate organic solvents, preliminary fractionation and cleanup of extracts, and analysis of the processed extract for PAH using HRGC coupled with either HRMS or LRMS operated in the selected ion monitoring mode.

EPA OSW recommends that the decision regarding specific analytical procedures for the PAHs be made considering the detection limits which are determined to be necessary for PAHs based upon a preliminary risk evaluation. PAHs analyzed by LRMS have detection limits in the range of 1-5 µg/fraction; PAHs analyzed by HRMS typically have detection limits in the range of 10-50 ng/fraction. The actual detection limits that can be achieved are limited by interferences remaining in the extract and the background level of PAHs observed in the XAD-2® resin used to collect the PAH.

It may be possible to combine CARB Method 429 analytical procedures with SW-846 Method 0023A D/F analytical procedures or with SW-846 Method 0010/3542 SVOC analysis using careful planning. An

TABLE B.4-2

TARGET ANALYTES FOR CARB METHOD 429

Polycyclic Aromatic Hydrocarbons	CAS Number
acenaphthene	83-32-9
acenaphthylene	208-96-8
anthracene	120-12-7
benzo(a)anthracene	56-55-3
benzo(a)pyrene	50-32-8
benzo(b)fluoranthene	205-99-2
benzo(e)pyrene	192-97-2
benzo(ghi)perylene	191-24-2
benzo(k)fluoranthene	207-08-9
chrysene	218-01-9
dibenz(a,h)anthracene	53-70-3
fluoranthene	206-44-0
fluorene	86-73-7
indeno(1,2,3-cd)pyrene	193-39-5
2-methylnaphthalene	91-57-6
naphthalene	91-20-3
perylene	198-55-0
phenanthrene	85-01-8
pyrene	129-00-0

extract that has been subjected to the specialized cleanup procedures for PAHs cannot be used for any other semivolatile determination. However, without the final cleanup step, sample preparation and extraction can be designed to achieve multiple types of determinations for semivolatile organic compounds. The user should be aware that one effect of a scheme that involves splitting the sample for different analyses may be an unacceptable increase in the detection limits that the methodology is capable of achieving. There are presently several laboratories that are performing combined methodologies. There is, however, no numbered EPA method that has been evaluated and is accepted for its ability to perform combined analyses on a single sample. Laboratories that perform combined analytical procedures regard their specific procedure as proprietary and have not published any data to support their specific analysis to demonstrate compound recoveries and effects upon method detection limits. Potential implications of combined methodologies are discussed further in Section B.8.

B.5 POLYCHLORINATED BIPHENYLS

Stack determinations for polychlorinated biphenyls (PCBs) are recommended during risk burns, based on evidence that PCBs can be emitted from combustion sources regardless of PCB contamination in the feed. An increasing body of information supports the likelihood that PCBs may be formed as by-products of the combustion process, similar to D/Fs.

The need for sampling and analysis of polychlorinated biphenyls (PCBs) was first discussed in detail in the *Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities* (EPA 1998a). That guidance cites limited laboratory and field studies showing that PCBs can be formed during the combustion of hazardous waste. Stack tests performed in U. S. EPA Region 10 on a boiler and an incinerator burning waste with 0.07 and 1.4 percent chlorine, respectively, confirmed the presence of PCBs in the stack gases (Kalama Chemical, Inc. 1996; Idaho National Engineering Laboratory 1997). The concentration of total PCBs detected in the incinerator stack gas was 211 ng per dry standard cubic meter (dscm) @ 7% oxygen at low temperature conditions (1,750°F) and 205 ng/dscm @ 7% oxygen at high temperature conditions (2,075°F). For the incinerator test, PCBs with more than four chlorine atoms in the molecule comprised 51 percent of the total PCBs in the low temperature test and 59 percent of the total PCBs in the high temperature test. The EPA OSW risk assessment guidance (EPA 1998a) also references laboratory studies suggesting the possibility of formation of PCBs as products of incomplete combustion from hazardous waste with a high chlorine content. When chlorinated paraffins (such as pesticides) were heated under conditions similar to incinerator conditions, the combustion of highly chlorinated (60 percent or higher) wastes was demonstrated to produce PCBs (Bergmann 1984). The EPA OSW risk assessment guidance (EPA1998a) provides the following general recommendations with regard to the testing of PCBs:

- PCBs should be tested at combustion units that burn PCB-contaminated wastes or waste oils;
- PCBs should be tested at combustion units that burn variable waste streams such as municipal and commercial wastes for which it is reasonable to suspect PCB contamination; and
- PCBs should be tested at facilities that burn highly chlorinated waste streams.

Concerning testing for PCBs at facilities other than the facilities described above, the guidance states: “Due to the toxicity and uncertainties associated with combustion chemistries, the permitting authority may choose to confirm the absence of these compounds from stack emissions via stack gas testing for units burning hazardous wastes” (EPA 1998a).

Since the time that the EPA OSW risk assessment guidance (EPA 1998a) was released, an increasing body of information has been developed which supports the likelihood that PCBs may be formed as by-products of the combustion process, similar to D/Fs. Lemieux hypothesized that, if PCBs and D/Fs are formed by similar mechanisms, then emissions of PCBs should correlate with emissions of D/Fs (Lemieux and others 1999). This hypothesis was tested by reviewing data where both PCBs and D/Fs were measured. In most cases, PCBs were found in the stack even when there were no PCBs in the feed. Overall, PCB emissions exceeded D/F emissions by approximately a factor of 20, and this trend appeared to hold over five orders of magnitude in D/F emissions. In addition, Alcock has established that waste combustion units contribute significantly to total emission inventories of PCBs, and that PCBs can be important from a risk standpoint (Alcock and others 1999). In the United Kingdom, where a TEQ is used to assess the potential toxicity of complex mixtures of D/Fs and PCBs, the PCBs contributed up to 60 percent of the TEQ for a cement kiln facility. For other sources, the PCB contribution was more minimal (Alcock and others 1999).

Based on evidence that PCBs can be emitted from combustion sources regardless of PCB contamination in the feed, EPA OSW now recommends stack determinations for polychlorinated biphenyls (PCBs) during risk burns even if the facility does not burn PCB-contaminated, highly variable, or highly chlorinated waste streams. With proper planning, the PCB determination can be made using portions of the D/F sampling train extracts. Combined measurement methodologies are discussed further in Section B.8.

The current toxicity approach for PCBs (EPA 1996c; Van den Berg and others 1998) calls for data on:

- The total PCB concentration; and
- Congener-specific analyses for the 12 toxic dioxin-like coplanar and mono-ortho-substituted PCBs listed in Table B.5-1.

TABLE B.5-1

POLYCHLORINATED BIPHENYLS

Dioxin-Like Coplanar PCBs	IUPAC Number	CAS Number
3,3',4,4'-tetrachlorobiphenyl	77	32598-13-3
3,4,4',5-tetrachlorobiphenyl	81	70362-50-4
2,3,3',4,4'-pentachlorobiphenyl	105	32598-14-4
2,3,4,4',5-pentachlorobiphenyl	114	74472-37-0
2,3',4,4',5-pentachlorobiphenyl	118	31508-00-6
2',3,4,4',5-pentachlorobiphenyl	123	65510-44-3
3,3',4,4',5-pentachlorobiphenyl	126	57465-28-8
2,3,3',4,4',5-hexachlorobiphenyl	156	38380-08-4
2,3,3',4,4',5-hexachlorobiphenyl	157	69782-90-7
2,3',4,4',5,5'-hexachlorobiphenyl	167	52663-72-6
3,3',4,4',5,5'-hexachlorobiphenyl	169	32774-16-6
2,3,3',4,4',5,5'-heptachlorobiphenyl	189	39635-31-9
Total Homolog Groups Summed to Determine Total PCBs		
monochlorobiphenyls	hexachlorobiphenyls	
dichlorobiphenyls	heptachlorobiphenyls	
trichlorobiphenyls	octachlorobiphenyls	
tetrachlorobiphenyls	nonachlorobiphenyls	
pentachlorobiphenyls	decachlorobiphenyl	

TEFs are applied to the congener-specific concentrations to evaluate dioxin-like toxicity. Risks from the dioxin-like congeners (evaluated using the slope factor for dioxin) are then added to risks from the rest of the mixture (evaluated using the slope factor for PCBs, applied to total PCBs reduced by the amount of dioxin-like congeners).

Earlier EPA OSW guidance (EPA 1994a, 1994b, 1994c and 1994d) recommended that all PCB congeners (209 different chemicals) be treated in a risk assessment as a mixture having a single carcinogenic potency. Additional research on PCBs has been reported since the original compilation of PCB data by EPA (ATSDR 1995; EPA 1996c; Van den Berg and others 1998). The most important result of this additional research is the demonstration that some of the moderately chlorinated PCB congeners can have dioxin-like effects (EPA 1996c; ATSDR 1995; Van den Berg and others 1998). The following PCB congeners have been identified as dioxin-like or coplanar PCBs (EPA 1996c; Van den berg and others 1998) because when the rings rotate into the same plane, the shape of the PCB molecule is very similar to the shape of a polychlorinated dibenzofuran molecule:

- 3,3',4,4'-tetrachlorobiphenyl (Chemical Abstracts Services (CAS) Number 32598-13-3)
- 3,4,4',5-tetrachlorobiphenyl (CAS 70362-50-4)
- 2,3,3'4,4'-pentachlorobiphenyl (CAS 32598-14-4)
- 2,3,4,4',5-pentachlorobiphenyl (CAS 74472-37-0)
- 2,3',4,4',5-pentachlorobiphenyl (CAS 31508-00-6)
- 2',3,4,4',5-pentachlorobiphenyl (CAS 65510-44-3)
- 3,3',4,4',5-pentachlorobiphenyl (CAS 57465-28-8)
- 2,3,3',4,4',5-hexachlorobiphenyl (CAS 38380-08-4)
- 2,3,3',4,4',5'-hexachlorobiphenyl (CAS 69782-90-7)
- 2,3',4,4',5,5'-hexachlorobiphenyl (CAS 52663-72-6)
- 3,3',4,4',5,5'-hexachlorobiphenyl (CAS 32774-16-6)
- 2,3,3',4,4',5,5'-heptachlorobiphenyl (CAS 39635-31-9).

The World Health Organization has derived interim toxicity equivalency factors for these coplanar PCBs (Van den Berg and others 1998). Additional congeners are suspected of producing similar biochemical responses, but there are not sufficient data to derive toxicity equivalency factors for these additional congeners. EPA OSW has recommended that permitting authorities estimate risks from coplanar PCBs by applying a toxicity equivalency factor (TEF) to each coplanar PCB and then applying a slope factor for dioxin (EPA 1998a). Risks from the rest of the mixture are calculated by applying a slope factor for total PCBs.

PCBs were originally prepared and used commercially as mixtures of compounds called Aroclors. Several analytical methods using gas chromatography focus on the identification and quantitative analysis of PCBs as Aroclors. This type of analytical methodology is inappropriate for site-specific risk assessments at combustion facilities because the Aroclor mixtures of PCBs are altered both in the combustion process and in weathering, and because the PCBs which may be formed in a combustion process would not be expected to resemble a commercial mixture. PCBs as analyzed in stationary source emissions are therefore not recognizable as Aroclors, and these types of analytical methods therefore cannot generally be used to identify individual PCB congeners. A sampling and analytical method specific for the identification and quantitative analysis of both the coplanar PCBs and total PCBs in stationary sources at each chlorination level is being developed and is not currently available even in draft form. Currently available analytical methodology includes:

C SW-846 Method 8082: Polychlorinated Biphenyls (PCBs) by Gas Chromatography

Method 8082 is used to determine the concentrations of PCBs as Aroclors or as specific individual PCB congeners (not specifically the coplanar PCBs) in extracts from solid and aqueous matrices. No sampling procedures for stationary sources are included, and no sample spiking/preparation procedures for a solid sorbent matrix are included. This method is not applicable to the determination of PCBs in a stationary source matrix.

C Office of Water Method 1668A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by High Resolution Gas Chromatography/High Resolution Mass Spectrometry

Method 1668A applies to determination of the toxic PCBs in water, soil, sediment, sludge, tissue, and other sample matrices by HRGC/HRMS. The coplanar PCBs and other specific congeners, as well as homolog totals, may be determined by this method. The Method Detection Limit for a specific compound in water has been determined experimentally at the parts per quadrillion (ppq) level. There is no sampling procedure for stationary sources included in the method, nor are sample preparation procedures included for stationary source matrices. However, the analytical methodology should be applicable for the analysis of the coplanar PCBs and other specific congeners, as well as the determination of total PCBs at each chlorination level, and can be combined with a semivolatile sampling procedure (such as Method 0023A or CARB 428) with appropriate sample recovery and preparation steps.

C CARB Method 428: Determination of Polychlorinated Dibenzo-*p*-Dioxin (PCDD), Polychlorinated Dibenzofuran (PCDF), and Polychlorinated Biphenyl Emissions from Stationary Sources (http://www.arb.ca.gov/testmeth/vol3/vol3.htm).

CARB Method 428 applies to the determination of D/Fs and PCBs in emissions from stationary sources at nanogram to picogram levels, with the sensitivity ultimately achievable for a given sample dependent upon the types and concentrations of potentially interfering compounds present, the original sample size, and the instrument sensitivity. The analytical methodology uses HRGC/LRMS or HRGC/HRMS. CARB Method 428 is intended to determine PCBs as homolog groups (by level of chlorination) in samples containing PCBs as single congeners or as complex mixtures. CARB Method 428 without modification calls for analysis of PCBs using HRGC/LRMS, with detection limits ranging from 0.1 to 1.0 µg/sample per homolog group when both D/F and PCBs are determined from the same sample. Since PCBs can be risk drivers, EPA OSW recommends that CARB 428 be used with HRMS to provide PCB homolog group concentrations at lower detection limits. CARB Method 428, as written, does not specifically provide information on the 12 coplanar PCBs. However, if CARB Method 428 procedures are combined with appropriate analytical procedures, such as those described by EPA Office of Water Method 1668A for spiking standards, calibration standards, and subsequent analysis by HRMS, then specific characterization of the 12 coplanar PCBs as well as each homolog group should be achieved at the highest possible sensitivity.

In summary, a combination of methodologies may be needed for determination of both coplanar and total PCBs. A semivolatile sampling procedure, such as Method 0023A or CARB 428, can be combined with appropriate sample recovery and preparation steps, similar to those described in CARB 428, and followed by HRGC/HRMS analytical determinations such as those described in Method 1668A for coplanar PCBs and homolog totals. Whenever a combined or modified sampling and analytical method is used, EPA OSW recommends that the user demonstrate performance for the analytes of interest at the stationary source of interest. Combined methodologies are discussed further in Section B.8.

B.6 POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS

Consistent with current EPA OSW guidance (EPA 1998a), EPA OSW recommends that polychlorinated dibenzodioxins and polychlorinated dibenzofurans (D/Fs) be addressed in site-specific risk assessments for combustion facilities. There are 210 individual polychlorinated dibenzodioxin and dibenzofuran compounds or congeners; all of these compounds do not have equivalent toxic properties. The most toxic dioxin is 2,3,7,8-tetrachlorodibenzodioxin (TCDD) (EPA 1994e). The D/F congeners with chlorine atoms substituted in the 2,3,7 and 8 positions, a total of 17 compounds, are assigned a value, referred to as a toxicity equivalency factor (TEF), which relates the toxicity to that of 2,3,7,8-TCDD, which has a TEF value of 1. Since 2,3,7,8-TCDD is the most toxic, all other D/F congeners have decimal TEF values. Current analytical methodology is designed to focus on obtaining accurate values for the 17 specific D/Fs listed in Table B.6-1, as well as total quantities for other remaining congeners at each level of chlorination.

TABLE B.6-1

2,3,7,8-SUBSTITUTED D/Fs

Dioxin Congener	Furan Congener
2,3,7,8-tetrachlorodibenzo-*p*-dioxin	2,3,7,8-tetrachlorodibenzofuran
1,2,3,7,8-pentachlorodibenzo-*p*-dioxin	1,2,3,7,8-pentachlorodibenzofuran
1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin	2,3,4,7,8-pentachlorodibenzofuran
1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin	1,2,3,4,7,8-hexachlorodibenzofuran
1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin	1,2,3,6,7,8-hexachlorodibenzofuran
1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin	1,2,3,7,8,9-hexachlorodibenzofuran
octachlorodibenzo-*p*-dioxin	2,3,4,6,7,8-hexachlorodibenzofuran
	1,2,3,4,6,7,8-heptachlorodibenzofuran
	1,2,3,4,7,8,9-heptachlorodibenzofuran
	octachlorodibenzofuran

As indicated in Table B.1-4, SW-846 Method 0023A is recommended for stack sampling and sample preparation to determine D/Fs, with analytical procedures performed according to SW-846 Method 8290. Method 8290 is an isotope dilution HRGC/HRMS analytical method. The sampling methodology for Method 0023A is basically Method 0010, modified by the use of specific isotopically-labeled D/F standards to spike the sorbent prior to use in the field and specific sampling train recovery procedures to be used in the field. Since this sampling train will collect all SVOCs, including D/Fs, PAHs, PCBs, CB/CPs, it is possible to modify the sample preparation and analytical methodology to encompass one or more of these additional compound classes. However, EPA OSW recommends that any modification of the methodology be described to the regulatory authority in detail, and that the user demonstrate acceptable detection limits and performance for the modified methodology. Combined methodologies are discussed further in Section B.8.

Method 0023A supersedes Method 23 (40 CFR Part 60 Appendix A) for Resource Conservation and Recovery Act (RCRA) testing (EPA 1997b). Procedures for addition of isotopically-labeled standards to both the XAD-2® sorbent trap and filter, as well as separate extraction and analysis of the sorbent and filter, have been added in order to quantify recoveries from each fraction. The isotopically-labeled surrogate standards are spiked onto the XAD-2® sorbent prior to sampling, and onto the filter prior to extraction. Use of Method 0023A entails additional analysis, which can increase cost as well as detection limits. However, there is an important tradeoff from a quality assurance perspective. Specifically, Method 0023A provides surrogate compound recovery data for each train fraction, whereas Method 23 does not. For this reason, EPA OSW continues to recommend use of Method 0023A.

Target detection limits for D/Fs should be considered very carefully. Section 6.2.3 of Method 0023A provides guidance on determining a minimum sampling time based upon desired D/F detection limits. EPA OSW recommends that the desired D/F detection limits be determined prior to testing by performing a preliminary risk assessment. If lower method detection limits are desired, it may be possible to sample for a longer time: D/F testing for periods as long as 6-8 hours has been performed.

Field sample recovery and laboratory sample preparation steps determine whether Method 0023A can be modified to provide simultaneous determination of PAHs, PCBs, SVOCs, or CB/CPs. Method 0023A specifies sequential acetone, methylene chloride, and toluene rinses of the front half and back half portions of the sampling train to recover the train, with all of the solvents combined in one container for the front half rinse and another for the back half rinse. If SVOCs and CB/CPs are being determined simultaneously with the D/Fs, it is appropriate to separate the toluene rinse from the acetone and methylene chloride because SVOCs could be lost in subsequent laboratory sample preparation steps. If the sampling train is to be analyzed exclusively for D/Fs, the impinger liquid may be discarded after weight or volume is recorded because D/Fs will not be found dissolved in the aqueous impingers. However, if other SVOCs are being determined, SVOCs that are sufficiently volatile and water-soluble may be found in the impingers, so the condensate and the impinger solutions should be retained and analyzed.

In the laboratory, surrogate standards are added to the filter and internal standards are added to both the filter/front half and XAD-2$^{®}$ resin/back half fractions. The two fractions are then extracted separately using Soxhlet extraction with toluene, then each fraction is concentrated. One half of each fraction is archived, and the other half is solvent-exchanged to hexane and then subjected to cleanup procedures using three different chromatographic columns according to the procedures described in Method 8290, after addition of isotopically-labeled standards to monitor recovery through cleanup. Additional isotopically-labeled standards are added to each fraction prior to analysis by Method 8290 HRGC/HRMS techniques (target compounds for Method 8290 are shown in Table B.6-2). SW-846 Method 8280 is available with a HRGC/LRMS analytical methodology, but detection limits achieved with the LRMS analytical method are an order of magnitude higher than the detection limits that can be achieved with HRMS. Use of Method 8280 is therefore not appropriate for the generation of risk burn data without modification of the methodology. For data reporting, the results from each sampling train fraction will need to be added together to arrive at a total mass for each sampling train. If all of the fractions are non-detects, then EPA OSW recommends that the sum of the non-detects should be reported with a “less than” sign. If D/Fs are detected in some of the train fractions but not in others, then EPA OSW recommends that the data be reported as a range (i.e., “greater than” the total detected amount, but “less than” the total detected amount plus the non-detects). Also, Section 7.4 of Method 0023A allows a “non-detect” to be treated as zero if it is less than 10 percent of the total detected amount, subject to approval by the regulatory agency.

TABLE B.6-2

COMPOUNDS THAT CAN BE DETERMINED BY METHOD 8290

Dioxins	CAS Number	Furans	CAS Number
2,3,7,8-tetrachlorodibenzo-*p*-dioxin	1746-01-6	2,3,7,8-tetrachlorodibenzofuran	51207-31-9
1,2,3,7,8-pentachlorodibenzo-*p*-dioxin	40321-76-4	1,2,3,7,8-pentachlorodibenzofuran	57117-41-6
1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin	57635-85-7	2,3,4,7,8-pentachlorodibenzofuran	57117-31-4
1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin	39227-28-6	1,2,3,6,7,8-hexachlorodibenzofuran	57117-44-9
1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin	19408-74-3	1,2,3,7,8,9-hexachlorodibenzofuran	72918-21-9
1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin	35822-39-4	1,2,3,4,7,8-hexachlorodibenzofuran	70648-26-9
octachlorodibenzo-*p*-dioxin	3268-87-9	2,3,4,6,7,8-hexachlorodibenzofuran	60851-34-5
		1,2,3,4,6,7,8-heptachlorodibenzofuran	67562-39-4
		1,2,3,4,7,8,9-heptachlorodibenzofuran	55673-89-7
		octachlorodibenzofuran	39001-02-0
Totals for Each Congener Group			
tetrachlorodibenzo-*p*-dioxins		tetrachlorodibenzofurans	
pentachlorodibenzo-*p*-dioxins		pentachlorodibenzofurans	
hexachlorodibenzo-*p*-dioxins		hexachlorodibenzofurans	
heptachlorodibenzo-*p*-dioxins		heptachlorodibenzofurans	

EPA is currently evaluating the potential for formation of fluorine- and bromine-substituted D/Fs, as well as sulfur-analogs of D/Fs, but analysis of stack samples for these types of compounds is not anticipated at this time (EPA 1996d and 1996e). Few calibration standards are commercially available to perform the analysis, and analytical methods are not yet developed. EPA has conducted preliminary studies of chlorinated, brominated, and mixed bromochloro-D/Fs in stack emissions (Lemieux and Ryan 1997 and 1998), but further research is necessary to provide better quantitative analysis for these compounds and to develop and validate the appropriate sampling and analytical methodologies. The *Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities* (EPA 1998a) recommends that these compounds be addressed in the uncertainty section of the risk assessment.

Even though the primary focus in this document and in the EPA OSW risk assessment guidance is on the tetra- through octa- D/F congeners, EPA has developed analytical standards for certain mono- through tri-congeners. EPA OSW encourages stack gas analysis for these mono- through tri-congeners whenever possible. The analysis can be performed at very little increased cost, and the results may support development of a database to determine which (if any) of the mono- through tri-chloro congeners can act as surrogates for the tetra- through octa-congeners. Identification of an easily measurable surrogate may support future development of a continuous emissions monitoring system to indicate D/F emissions (see http://www.epa.gov/appcdwww/crb/empact/index.htm).

B.7 TOTAL ORGANIC EMISSIONS

The *Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities. Volume One* (EPA 1998a) states:

> "Although U. S. EPA OSW will not require a risk assessment for every possible metal or PIC from a combustion unit, this does not imply that U. S. EPA OSW will allow only targeted sampling for COPCs during trial burn tests. Based on regional permitting experience and discussions with regional analytical laboratories, U. S. EPA OSW maintains that complete target analyte list analyses conducted when using U. S. EPA standard sampling methods (e.g., 0010 or 0030) do not subject facilities to significant additional costs or burdens during the trial burn process. Facilities conducting stack emission sampling should strive to collect as much information as possible which characterizes the stack gases generated from the combustion of hazardous waste. Therefore, every trial burn or "risk burn" should include, at a minimum, the following tests: Method 0010, Method 0030 or 0031 (as appropriate), total organic compounds (using the Guidance for Total Organics, including Method 0040), Method 23A, and the multiple metals train. Other test methods may be approved by the permitting authority for use in the trial burn to address detection limit or other site-specific issues."

To determine the potential risk from a hazardous waste combustor, EPA OSW recommends that emissions be identified and quantified to the maximum extent practicable. However, the numbered methods listed above are not sufficient to characterize all organic emissions from waste combustion. Studies (Harris 1982; EPA 1984) have shown that standard analyses will often account for less than 20 percent of the total organic material in an emission sample. To evaluate the uncertainty associated with a risk assessment, EPA OSW has recommended that a measure of the completeness of the emissions characterization be developed based on a Total Organic Emissions (TOE) analysis quantifying the total recoverable organic mass emitted from the source (EPA 1998a). The quantity of unidentified organic compounds can then be estimated based on the difference between the TOE mass and the total quantity of identified organic compounds.

The fundamental research for the TOE analysis was performed by EPA's Office of Research and Development between 1976 and 1985 as part of the environmental assessment of stationary sources (EPA 1976). Gas sample analysis (compounds with boiling point less than 100EC) was performed using a gas chromatograph in the field, with calibration performed using a series of hydrocarbon standards as well as individual organic compounds of interest due to toxicity or potential response in the analysis methods. The result of that research was a guidance manual for performing base level characterization of emission sources (EPA 1978). From 1990 to 1997, EPA Office of Research and Development validated RCRA methods including SW-846 Method 0010, Method 3542, and Method 8270 on a variety of hazardous waste combustion sources (Johnson 1998). To date, the methods recommended in EPA's TOE guidance (EPA 1996a) are the best suited for general characterization of the recoverable organic mass from stationary sources. Mass balance between identified compounds and the TOE analysis has shown anywhere from a 20 percent to 80 percent agreement. Combustion sources that emit higher concentrations of non-volatile material (as determined gravimetrically) tend also to be the sources that are not characterized well by target compound methods. Sources that have more volatile organic emissions where the compounds can be analyzed by a combination of GC and GC/MS tend to have better agreement and closure with the TOE methods. These results lead EPA to conclude that a procedure that provides information on gravimetric (GRAV) material is important to assess the uncertainty associated with the measurement methods that are used to identify specific target compounds in hazardous waste combustion samples. Until and unless more compounds can be identified, TOE analysis continues to be the best scientific measure currently available to cost-effectively direct resources and regulatory action to the highest potential for risk of organic material from affected facilities.

TOE analysis, as determined by the published methodology (EPA 1996a), means the total amount of organic material which is recoverable by means of analysis of gaseous components, solvent extraction or other preparatory steps, and gravimetric analysis. The TOE analysis is not suitable for collection/analysis of polar water-soluble compounds or highly reactive compounds. Results are reported as a sum of "µg total organics per m^3"; these results can be compared directly to the summed mass of all of the identified constituents. In order to determine the unidentified organic mass, the masses of the specific quantified toxic organic compounds, including D/Fs, VOCs, SVOCs, PAHs, PCBs, and TICs, are subtracted from the results of the TOE determination. The mass of organic material remaining after correction for identified compounds is referred to as the "unspeciated (or unidentified) organic mass" (EPA 1998a).

Two separate sampling procedures are needed to generate the samples for TOE analysis:

C A VOC fraction is collected using SW-846 Method 0040 sampling procedures with a Tedlar® bag. Condensate collected during the Method 0040 sampling is returned to the laboratory for analysis. The VOCs in the Tedlar® bag are analyzed by field gas chromatography (FGC). The VOCs in the condensate are determined by purge and trap GC. The VOC fraction determines organics in the boiling point range <100EC.

C Total chromatographable organic (TCO) and gravimetric (GRAV) fractions are collected using a SW-846 Method 0010 sampling train, operated during the same sampling period as the Method 0040 train. The Method 0010 sampling train operates in the same mode for TOE as for SVOC collection, but the present TOE guidance recommends the operation of a *separate* Method 0010 train. With careful attention to procedures to avoid bias as discussed in Section B.8.9, it may be possible to use a single train for the SVOC and TOE determinations in some cases. The TCO fraction determines organics in the boiling point range between 100EC and 300EC, and the GRAV fraction determines organics with boiling points >300EC.

Research has recently been performed to evaluate and clarify the analytical procedures for the TOE determination. Revised technical details for TOE analysis are included in this guidance, and will be incorporated in a revised TOE guidance expected to be released later in 2001. Analysis of the three TOE fractions, including the updated technical details, is described below:

C FGC Fraction (Organic Compounds with Boiling Points < 100EC)

The FGC fraction is collected by Method 0040, using a Tedlar® bag for the gaseous component, and the collected condensate fraction is transferred to a zero-headspace vial. Analysis of the gaseous component is performed in the field using a gas chromatograph with a flame ionization detector. The field GC is calibrated with a gaseous hydrocarbon mixture containing methane, ethane, propane, *n*-butane, *n*-pentane, *n*-hexane, and *n*-heptane (C_1 - C_7). The chromatographic column used in the field GC should be capable of resolving the C_1 - C_7 hydrocarbons at baseline level. A minimum of three multi-component standards at different concentration levels spanning the expected sample concentration range is analyzed in triplicate to calibrate the gas chromatograph; more concentrations may be used, if desired. The additional concentrations can be prepared by dilution of the stock standard. Gaseous standards in cylinders are usually sold in ppm concentrations. However, the gas chromatograph should be calibrated in specific units of µg/m^3 to provide results compatible with the other parts of the TOE analysis. To convert the units for each component of the multi-component standard from the cylinder concentration (ppm) to µg/m^3, the following equation (based on the Ideal Gas Law at Standard Temperature and Pressure) is used:

$$C_{\mu g/m^3} \;\text{'}\; C_{ppm} \frac{GMW}{24.04} \; x \; 1000$$

where:

$C_{\mu g/m3}$ = concentration of each hydrocarbon expressed in µg/m^3;

C_{ppm} = concentration of each hydrocarbon expressed in ppm;

GMW = gram molecular weight of each hydrocarbon.

24.04 = liters/gram-mole ideal gas @ 293EK; 760 mm Hg

The following steps are applied to each component of the multi-component standard:

Step 1. Determine the concentration of each component of the standard in ppm.

Step 2. Using the equation above, convert the concentration of each component to µg/m^3.

Step 3. Sum the concentrations of each of the components in µg/m^3 to obtain a total concentration, which can then be related to the sum of the chromatographic peak areas at each concentration level.

To determine total mass of the hydrocarbons for the calibration curve, the concentrations of each of the hydrocarbons (in µg/m^3) are summed, and total mass (Ó$C_{\mu g/m3}$ for each of the components of the standard) is plotted vs. area counts. The calibration procedure is conducted using a mean response factor (relative standard deviation of 20 percent or better) or a linear regression ($r^2 = 0.995$ or better, b<<y). The sample is analyzed using duplicate injections, and integrated from a retention time of zero to the end of the C_7 peak. A total mass in µg/m^3 is calculated for the entire integrated area from zero through the end of C_7 to yield the value for the gaseous volatile portion of the TOE analysis.

The aqueous portion of the TOE sample generated from the condensate of the Method 0040 sampling train is analyzed in the laboratory using purge-and-trap gas chromatography with flame ionization detection, with the gas chromatograph calibrated from C_4 through C_7 in micrograms. The sample is integrated from zero through the end of C_7, and the answer is expressed in terms of total number of µg/volume of condensate (µg/mL). The total volume of condensate has been measured, so the answer can be expressed as a total number of µg per sampling train. The stack gas volume sampled in the field (expressed as m^3) is known from the Method 0010 sample volume, and the value is expressed as µg/volume sampled (expressed as m^3) to make the result compatible with the values determined for the other portions of TOE.

Determination of Qualitative/Quantitative Values for Specific FGC Components

Compounds such as methane, ethane, and propane may constitute major components of the emissions sample. In performing the risk assessment calculation, it may be highly desirable to subtract the mass of these compounds from the TOE value as part of the determination for unspeciated organic compounds, if these specific compounds are indeed major components of the emissions. Since the field gas chromatograph is calibrated with a standard that contains the specific C_1 through C_7 *n*-alkanes, and it is therefore possible to determine retention times and compound-specific response factors for these compounds. If data from the FGC calibration are collected as peak areas for individual compounds in the original FGC calibration, a retention time and a response factor for each compound may be calculated from the original FGC calibration data. Alternatively, an additional multipoint calibration series can be analyzed to determine retention times and response factors for the individual compounds. In the analysis of the emission sample, the *n*-alkanes from C_1 through C_7 can then be identified and a specific quantitative analysis performed for these compounds. When the ultimate risk assessment calculation is performed, the concentrations of the identified compounds can then be subtracted from the unspeciated mass to reduce the uncertainty associated with the TOE value. However, no subtraction of specifically identified and quantified compounds should be performed in determining the TOE value itself; the TOE value should be reported as the summation of the individual components: FGC + TCO + GRAV. The use of additional gas standards to aid in the speciation of FGC compounds is encouraged, particularly standards containing compounds that may not be amenable to identification and quantitation by the target-analyte-specific volatile organic GC/MS approaches. Gas mixtures containing hydrocarbons such as C_2 through C_4 alkanes, alkenes, and alkynes may also be useful in characterizing the composition of the FGC TOE fraction.

C TCO Fraction (Boiling Point between 100EC and 300EC)

TCO and GRAV fractions are both collected using the SW-846 Method 0010 sampling train, with samples prepared using Method 3542. There are several changes to Method 3542 which are recommended to ensure complete removal of water and inorganic interferents:

S All three sample fractions should be reverse-extracted in a separatory funnel with dichloromethane and water under base and acid conditions. Surrogate or internal standard compounds are not added to any of the fractions. The XAD-2® resin is initially Soxhlet extracted according to Method 3542 and then extracted with dichloromethane and water under base and acid conditions. Acid/base extractions follow the procedures in Method 3542. The extraction removes any soluble inorganic salts that might provide a high bias to the GRAV results.

S After extraction, components are combined into a single pooled extract. The Method 3542 extract is dried by filtration through sodium sulfate as specified in the method. The drying/filtration step is performed using pre-washed cellulose filter medium (Whatman #1 filter paper or equivalent) rather than the glass wool specified in the extraction procedure. As in Method 3542, the extract may be taken to a final volume of 5 mL for TCO and GRAV analysis.

S At no time should any of the extracts be reduced to volumes less than 3 mL, or loss of semivolatile compounds may occur. As a final step, the extract is filtered through a 0.45 micron (μm) Teflon® syringe filter, then diluted to 5.0 mL.

After the three methylene chloride extracts resulting from Method 3542 are combined and concentrated, the TCO and GRAV analyses are performed. TCO analysis is performed by GC/FID, with a total mass between boiling points 100EC and 300EC calculated by integrating the entire area under the response curve from C_7 through the C_{17} range. The analysis window is established by injecting *n*-heptane (C_7) and *n*-heptadecane (C_{17}) during calibration to establish the retention time reference peaks between which the TCO determination will occur. The calibration curve is generated with hydrocarbon standards which fall within the TCO range, specifically decane (C_{10}), dodecane (C_{12}), and tetradecane (C_{14}). A multipoint calibration of at least three points (in triplicate) is generated in units of μg/mL. The response factor for TCO is calculated based on the total area of the three calibration standards. For analysis of the stack sample, integration of detector response beginning immediately after the C_7 retention maxima and terminating immediately before the C_{17} maxima constitutes the TCO response. The response factor for the entire TCO range, as determined during calibration, is then used to calculate compound mass in this boiling point range. The TCO concentration is initially expressed as μg/mL based on the chromatograph area and the TCO calibration curve. The final TCO value, in units of μg/m^3, is calculated by multiplying the μg/mL value by the volume of the original Method 0010 extract and dividing by the stack gas volume sampled in the field (in m^3). The use of both TCO and GRAV does not duplicate the assessment of the quantity of extractable organic material in a sample. Recent research results demonstrate that the C_{17} cutoff point for TCO provides a reasonable and consistent measure of semivolatile versus nonvolatile organic material in Method 0010 samples (Ryan and others 1999).

C GRAV Fraction (Boiling Point > 300EC)

The GRAV procedure is carried out by analysis of an aliquot of the same methylene chloride extract that was used for the TCO determination. The aliquot is placed in a weighing pan, allowed to dry, and weighed. The mass of the residue (μg) is recorded. The total μg per sampling train divided by the gaseous volume sampled (m^3) is the GRAV value. EPA OSW is aware of technical issues that affect results of the GRAV analysis. The issues of inorganic salts, as well as contamination of the samples by microfragments of XAD-2® and other fine particulate matter, have been known since the development of these procedures. EPA OSW continues to recommend preparation of Method 0010 samples using Method 3542 with the modifications described previously. Method 3542 procedures for removal of water/methanol by pH-adjusted back-extraction with water will solve the water-soluble inorganic salts problems incurred by the presence of water, methanol, and methylene chloride in the sample extract. Fine solid particles may cause interferences with the condensible fraction analysis and, since filtration of the samples is a critical part of the preparation step, EPA OSW in this guidance encourages laboratories to filter XAD-2® extracts with an inert pre-washed cellulose filter medium that is capable of removing fine solid particles that could interfere with analysis of condensibles.

Because high field blank results for the GRAV fraction have been reported, trouble-shooting measures have been identified to minimize potential sources of contamination (EPA 1997c). In order to obtain the most accurate results possible for the GRAV fraction, the XAD-2® resins used in the Method 0010 sampling train have to be clean. High field blank results have been attributed to the use of old and contaminated XAD-2® resin in the Method 0010 sampling train. Only recently-cleaned (within 14 days of the sample analysis) XAD-2® resin should be used in the Method 0010 sampling train. A summary of "lessons learned" is provided below:

S Assure that all glassware and field and laboratory equipment have been cleaned thoroughly with high quality reagents.

– Use high quality reagents for performing procedures (extractions, rinses, etc.) "Ultrapure" reagents are recommended.

– Cover the weighing pan to which composite extracts are transferred for drying by building a tent with aluminum foil, shiny side out.

– Run control pans: pan blank (dust blank) and solvent blank. Blank weighing pans without solvent or sample should be carried through the evaporation and drying process as a quality control check for each set of samples. Solvent blank samples consisting of concentrated reagent solvent should be analyzed in duplicate for each batch of samples. Sample weights should be corrected for blank weighing pan mass gain using the dust blank.

– Check balance calibration prior to each weighing.

– Use a balance precise to at least 10 µg.

– Handle XAD-2® resin with extra care: make sure that resin particles do not float out of extraction thimble.

– Confirm that the XAD-2® used in the laboratory and in the field meets appropriate cleanliness standards and has been cleaned within two weeks of analysis.

– For samples where there can be significant sources of sulfur in the fuels or wastes, reconstitute the GRAV sample and analyze for rhombic sulfur using GC/MS. Also analyze the TCO fraction by GC/M S for rhombic sulfur. Significant quantities of rhombic sulfur, if present, can be dissolved in methylene chloride.

The TOE measurement is an estimate. For fractions where GC/FID is used for the analysis, there are discrepancies in detector response for various hydrocarbons, including halogenated compounds, and oxygenated compounds. However, the TOE measurements are strongly believed to be the best currently available procedure for generation of a TOE value to indicate uncertainty due to the organic compounds that have not been quantified. The final calculated TOE value is the sum of the values for each component:

$$TOE = TO_{FGC} + TO_{CON} + TO_{TCO} + TO_{GRAV}$$

where:

TOE = stack concentration of Total Organic Emissions, including identified and unidentified compounds ($\mu g/m^3$)

TO_{FGC} = stack concentration of Total Organic Emissions, including identified and unidentified compounds ($\mu g/m^3$), as determined by FGC

TO_{CON} = stack concentration of Total Organic Emissions, including identified and unidentified compounds ($\mu g/m^3$), as determined by analysis of the Method 0040 condensate

TO_{TCO} = stack concentration of Total Organic Emissions, including identified and unidentified compounds ($\mu g/m^3$), as determined by TCO analysis

TO_{GRAV} = stack concentration of Total Organic Emissions, including identified and unidentified compounds ($\mu g/m^3$), as determined by gravimetric analysis

EPA OSW recommends that values for the individual components of the TOE determination also be reported, since this information may be useful during later interpretation of the results. For example, unidentified mass in the GRAV range cannot be due to vinyl chloride, just as unidentified material in the FGC analysis cannot be dioxin or PAH (Johnson 1996a). EPA OSW has recommended that the TOE data be used in conjunction with the data for positively identified compounds to compute a TOE factor, defined as the ratio of the TOE mass to the mass of identified organic compounds:

$$F_{TOE} = \frac{TOE}{\sum_i C_i}$$

where:

F_{TOE} = TOE factor (unitless)

TOE = total organic emissions (µg/m^3)

C_i = stack concentration of the i^{th} identified organic compound (µg/m^3)

(EPA 1998a). A critical component in the calculation of the TOE factor is the identification of the organic compounds for the denominator of the calculation. Although the permitting authority may not ask a facility to analyze the organic compounds with all possible analytical methods, gaps in the compound identification can have a dramatic effect upon the TOE factor. EPA OSW recommends that permitting authorities include TICs in the denominator when computing the TOE factor to ensure that appropriate credit is given to defensible efforts to identify the maximum number of organic compounds (EPA 1998a). The TOE factor is used in the uncertainty section of the risk assessment report to evaluate the risks from the unknown fraction of organic compounds. Permitting authorities can evaluate the TOE factor and assess to what extent actual risks may be greater than estimated risks (EPA 1998a).

Estimates of compounds that are potentially associated with the three TOE fractions are summarized below (MRI 1997):

- The FGC fraction would be expected to contain lighter hydrocarbons and halogenated alkanes and alkenes such as methane, and halogenated ethanes, ethenes, and propanes.

- The TCO fraction would be expected to contain a wide range of semivolatile compounds such as D/Fs, phthalates, phenols, halogenated aromatic compounds, and nitrogenated and sulfonated compounds.

- The GRAV portion has been very difficult to characterize, but would be expected to contain high molecular weight organic compounds such as hydrocarbons of C_{17} or greater, D/Fs, PAHs, and high molecular weight organic acids and salts.

One attempt to characterize the GRAV fraction of reaction products from D/Fs sorbed on a calcium-based sorbent used thin-layer chromatography followed by multiple analytical techniques (Gullett 1997). The analytical results showed that the GRAV portion consisted of higher molecular weight chlorinated compounds with both aromatic and aliphatic components, most likely not detectable by conventional GC/MS analysis. Application of non-routine analytical methods such as High Performance Liquid Chromatography (HPLC)/Mass Spectrometry would probably be necessary to perform significant amounts of characterization of the non-volatile compounds to be found in the GRAV fraction.

B.7.1 PREPARATION OF XAD-2®

XAD-2® is a macroreticulate porous polymer synthesized from styrene (vinylbenzene) and divinylbenzene. The emulsion block co-polymerization used to crosslink the resin gives it a pore structure and chemical stability that are ideally suited for the sampling and recovery of semivolatile organic compounds from the Method 0010 sampling train. The synthesis process for preparing the polymer also exposes the raw resin to high concentrations of naphthalene, styrene (vinylbenzene), divinylbenzene, and low molecular weight byproducts of these reagents and the polymerization reaction. The typical amount of resin used in the sampling module of the Method 0010 sampling train is 40 grams and, especially for the TOE determination, it is essential that this resin be clean and free of fines and contaminants that could contribute a positive bias to the TCO and GRAV determinations. Some forms of “pre-cleaned” resin are commercially available, but all XAD-2® used for TCO and GRAV analysis should be analyzed before use using the TCO and GRAV preparation/analysis procedures in order to ensure that the background of extractable semivolatile organic compounds meets the appropriate quality standards. Preparation of the XAD-2® resin within two weeks of the sampling episode where it is to be used provides sufficient time for the cleaning and drying processes and avoids extended storage, which may result in contamination and elevated levels of semivolatile organic compounds in the blanks. The cleaning method described below has proven to be a cost-effective and high quality procedure for obtaining XAD-2® resin.

The procedures for cleaning XAD-2® are derived from EPA’s Level 1 Procedures Manual (EPA 1978). The original methodology has been improved to provide a reproducible method for preparation of sorbent material clean enough for low level organic compound capture and analysis. The complete cleaning cycle takes approximately five working days to complete. Typical background values of blank total organic concentrations from XAD-2® prepared according to these procedures are on the order of 1 µg/g sorbent medium. The recommended cleaning procedures include the following steps:

- Obtain resin, either directly from the manufacturer or supplier, or recycled from previous use. Resin that has been cleaned by a secondary vendor should be treated like recycled resin. Recycled and re-cleaned resin usually contain less organic contamination and are preferred over raw material straight from the manufacturer.

- Soak the resin and wash several times with deionized water if the resin is new from the manufacturer. Resin “fines” float to the surface of the water and are removed before the next cleaning step.

- Load washed or recycled resin directly into the extractor for solvent cleaning. The entire cleaning procedure is done “wet” with final drying taking place only at the end of the process.

- Use an extractor capable of holding 900 grams of resin to extract the resin sequentially with methanol, methylene chloride, and methylene chloride again. Solvents used in this step should be chromatographic grade. Solvent is drained after each extraction sequence, and the extractor is pre-rinsed with the solvent to be used in the next step.

- After the final extraction, drain the methylene chloride and remove the extractor body to a hood where the resin is dried. Drying is accomplished using a gentle stream of nitrogen generated by a heat exchanger attached to the gas output of a liquid nitrogen tank to avoid introducing contaminants through the nitrogen.

- Transfer dried resin to a clean, dry glass jar with a screw-cap lid. For quality control of a blank, at least one portion of the dried sorbent equal to the contents of a typical Method 0010 sampling module (usually 40 grams) is extracted, prepared, and analyzed according to the method that will be used for the field samples.

- If the analysis of the clean XAD-2® meets method acceptance criteria, label the jar with a laboratory identification number and store at room temperature in a clean, solvent-free cabinet for use in sampling activity. Clean resin is stable and can be stored for 2-3 weeks. Longer storage times are possible if the material is refrigerated in a solvent-free refrigerator, but a blank sample should be checked before material stored for longer than three weeks is used for field sampling.

EPA OSW recommends that a sufficient quantity of clean resin be prepared to collect the number of samples indicated in the QAPP, to provide one or two spares in case of breakage, to provide a field blank, and to allow resin from the same batch to be available in the laboratory for use as method spikes/method spike duplicates.

Analytical interferences are generally contaminants that appear in the resin after storage and may cause the cleaned resin to fail the quality control specifications for the analytical method used in sample analysis or oxidation products from exposing the resin to an oxidizing stationary source matrix. Contaminants originate from both external contamination and internal “bleeding” of manufacturing chemicals or other entrained chemicals (possibly from a previous use) from very small or inaccessible pores in the resin. Subsequent re-cleaning and reuse reduces the internal contributions to organic compound contamination during storage. Contaminant levels in the XAD-2® resin may also increase if the XAD-2® has been exposed to high concentrations of oxidizing agents such as ozone or oxides of nitrogen.

B.7.1.1 Quality Control Procedures for Cleaned XAD-2®

The cleaned XAD-2® resin can be checked for contamination by extracting a quantity of resin equivalent to the amount used during sampling, typically 40 grams. The resin is prepared for analysis using the same volumes of solvent and preparation procedures that will be used for the field samples following the procedures in SW-846 Method 3542 for Method 0010 samples. Extracts are analyzed for TCO and GRAV and should meet the quality control criteria shown in Table B.7-1 in order to be used for sampling. If the extracted resin fails to meet acceptance criteria, the resin should be re-cleaned by Soxhlet extraction with methanol and methylene chloride. A sample of resin failing to meet acceptance criteria after re-cleaning should be discarded and no further attempts made to clean that batch.

TABLE B.7-1

GUIDELINES FOR CLEANLINESS OF XAD-2® RESIN

Analysis	Maximum Blank Concentration/g Resin
TCO	1 µg/g resin
GRAV	10 µg/g resin

B.8 COMBINED MEASUREMENT TECHNIQUES

The SW-846 Method 0010 sampling train simultaneously collects all semivolatile organic compounds, including SVOCs, D/Fs, CB/CPs, PAHs, and PCBs, with adaptations for specific groups of analytes. In some cases (e.g., to increase sampling efficiency, to cut costs), it may be necessary or desirable to analyze a single Method 0010 sample for multiple pollutant classes encompassing all of the groups of compounds listed above. For these situations, EPA OSW recommends that all aspects of the sampling and analysis be considered carefully to ensure that the resulting data will be acceptable for risk assessment. Modifications to the sample preparation methodology may invalidate the data for one or more of the compound classes. If extracts are divided to be used for different purposes, EPA OSW recommends that the effect upon the method detection limits be carefully evaluated to ensure that appropriate detection limits can be achieved.

EPA OSW recommends that procedures for combined measurements be described in detail in the QAPP for the risk burn and approved by the regulatory agency prior to sampling. The documentation provided should include detailed information on sampling, recovery, spiking, analysis, quality assurance and quality control procedures, and anticipated effect on detection limits for all of the compound groups analyzed. In addition, the facility should demonstrate that the modified methodology performs acceptably. Providing an appropriate level of description may be difficult, since laboratories that have developed these combined methods consider the exact procedures and standard spiking schemes to be proprietary information and have not published the procedures and supporting data in the open literature. There is also no recognized numbered EPA method that combines measurement procedures for all possible groups of semivolatile analytes, so no data are available to demonstrate performance of this type of methodology. Thus, combined analysis schemes can be described only in general outlines, and detailed procedures are not generally available.

The potential liabilities that are associated with combination of analytical methodology for various groups of semivolatile analytes have been discussed (Johnson 1995); a brief summary of key information is presented below for the convenience of the reader.

B.8.1 EFFECT ON METHOD DETECTION LIMITS

One effect of combining analytical procedures for multiple groups of analytes may be an elevation of the detection limit. If it is necessary to split a sample or an extract to allow two different extraction or cleanup procedures, each part of the sample or extract may have its detection limit increased proportionally to the size of the sample or extract used. If, on the other hand, a second analysis is performed on one extract, there will be no effect on the detection limits. EPA OSW recommends that assistance be obtained from a well-qualified and experienced analytical chemist who understands the methods and calculations involved, as well as the detection limits needed for the risk assessment.

B.8.2 EFFECT ON SAMPLE PREPARATION PROCEDURES

Sample preparation procedures for semivolatile organic compounds ultimately involve concentration of an extract prior to analysis. If solvents are combined in the preparation process (i.e., methylene chloride and toluene), the more volatile solvent and the more volatile analytes will be lost when the extract is concentrated.

Cleanup procedures are an integral part of most semivolatile organic compound sample preparation procedures. Because many of the analyses for semivolatile components are performed using high resolution mass spectrometry, cleanup procedures typically involve the use of column chromatography and/or gel permeation chromatography to remove the potentially interfering compounds with minimal effect on target analytes. When sample preparation procedures are used for multiple classes of analytes, it is important to verify that compounds of interest are not removed in sample cleanup. A judicious selection of appropriate isotopically labeled standards added to the extract prior to cleanup can be used to demonstrate recoveries of the appropriate analytes. The methods for D/Fs, PAHs, and PCBs each designate specific extract cleanup procedures intended to remove two of the groups of analytes as potential analytical interferences; the resulting extract is thus unsuitable for any other determinations. Splitting the sample after recovery and extraction may be necessary to allow unique cleanup procedures to be used for specific analytical targets, and splitting samples may have an effect on detection limits. EPA OSW recommends that assistance be obtained from a well-qualified and experienced analytical chemist who understands the methods and calculations involved, as well as the detection limits needed for the risk assessment.

B.8.3 EFFECT ON THE SELECTION OF STANDARDS

Each of the isotope dilution methods discussed (D/Fs, PAHs, PCBs) involves the use of internal standards, pre-sampling surrogate standards, and recovery standards. SW-846 Method 8270, the generic semivolatile organic compound analytical method, involves the use of pre-extraction surrogate standards and internal standards. The isotope dilution methods typically involve the use of high resolution mass spectrometry in the selected ion monitoring mode and correspondingly lower levels of standards spiked at all stages of the preparation and analytical procedures. Method 8270 is generally applied to low resolution mass spectrometry in the full scan mode, and involves correspondingly higher levels of all standards. The two different standard spiking schemes could be a source of incompatibility between methods.

A judicious selection of isotopically-labeled standards can be used to demonstrate acceptable measurement performance of the combined methodologies when they are spiked at various stages of the sampling and analytical procedures:

- Standards (pre-sampling surrogates) can be added to the sorbent in the sampling module prior to sampling, to estimate potential losses during sampling.

- Standards (pre-extraction surrogates/internal standards) can be added to the different Method 0010 train components (i.e., filter, sorbent, impinger contents) to provide an estimate of compound loss through extraction, concentration, and cleanup.

- Standards (internal standards/recovery standards) can be added immediately before analysis to perform quantitative calculations and to provide a final check on the effects of the sample matrix.

The standards described above constitute the minimum for the semivolatile organic compound sampling, preparation, and analytical methods. EPA OSW recommends that additional standards be added as necessary to address specific concerns with combined methodologies, and that assistance be obtained from a well-qualified and experienced analytical chemist who understands the methods and calculations involved, as well as the detection limits needed for the risk assessment.

B.8.4 EXAMPLE OF A COMBINED MULTIPLE POLLUTANT SAMPLING/ ANALYTICAL SCHEME

It is possible to make all semivolatile determinations (D/Fs, SVOCs, CB/CPs, PAHs, and PCBs) from a single SW-846 Method 0010 sampling train that has been spiked with the SW-846 Method 0023A standards. However, toluene train rinses from the D/F recovery have to be stored separately from other train rinses, the condensate and impinger contents and rinses have to be retained and analyzed, and two separate Soxhlet extractions using different solvents are necessary.

The general combined process used by one laboratory is described below:

- Perform a first Soxhlet extraction of Method 0010 train components with methylene chloride.
- Remove the methylene chloride from the extraction flask. Split the methylene chloride extract in half, one half for the D/F analysis and the other half for everything else.
- Add the toluene rinse to the remaining contents of the Soxhlet extractor, and perform a second extraction with toluene.
- Remove the toluene extract from the extraction flask. Combine half of the toluene extract with half of the methylene chloride extract and subject the combined extract to D/F cleanup and analysis; archive the other half of the toluene extract.
- Divide the remaining methylene chloride extract into three portions: perform PAH cleanup and analysis on one portion, PCB cleanup and analysis on a second portion, and analyze the third portion directly for SVOCs and/or CB/CPs.

The detection limit for D/F analysis is not compromised by combining the methodologies because Method 0023A already specifies archiving half of the extract. Depending upon the exact scheme followed for the additional analyses, the SVOC detection limits may be doubled or tripled because of a 1:1 or 1:2 split of the methylene chloride extract. The detection limits for the PCBs and PAHs may or may not be affected, depending upon the cleanup procedures and the final volume to which the extracts are concentrated before analysis. EPA OSW recommends that assistance should be obtained from a well-qualified and experienced analytical chemist who understands the methods and calculations involved, as well as the detection limits needed for the risk assessment.

The scheme described above is used in one laboratory; other laboratories have developed their own schemes. The methodology is presented only in general outline because the laboratory considers the exact procedure and the standard spiking scheme to be proprietary information, as well as any supporting data developed by the laboratory. There are numerous alternatives to the scheme described above. CARB Method 428 describes the analysis of Method 0010 samples for D/Fs and PCBs. CARB 429 describes the analysis of PAHs. The combination of CARB Methods 428 and 429 and comparison of this combined methodology with the individual sampling trains and individual analysis has been discussed (Steiner 1994). Results for triplicate tests of combined vs. individual sampling trains and analyses show correspondence for the two groups of analytes ranging from 14-32 relative percent difference. Standard recoveries were closely comparable between the individual trains and the combined train on a compound-by-compound basis. The effect of the combined scheme on detection limits was not discussed.

B.8.5 USE OF TWO METHOD 0010 SAMPLING TRAINS

If two Method 0010 sampling trains can be used, use of one train for Method 0023A and CARB Method 428 (D/Fs and PCBs) is reasonable since both analyte groups are amenable to toluene extraction. The other Method 0010 sampling train could then be used for all other semivolatile organic analytes. IF PCBs and D/Fs are determined in combination from a single sampling train, EPA OSW recommends that at least four isotopically-labeled PCB surrogate compounds be spiked onto the XAD-2® resin together with the designated D/F surrogate compounds before sampling. The amount of the surrogate compounds and internal standards added to the XAD-2® and the sample extracts should be adjusted to compensate for the additional analysis (Ryan 1998). The two Method 0023A sampling train fractions should be processed separately as outlined in that method. Each fraction would be extracted with toluene, and the resulting extracts would be split: one portion for D/F cleanup and analysis, and another portion for PCB cleanup and analysis. Since Method 0023A procedures call for archiving one half of the toluene extract, the D/F detection limits would not be compromised. The impact on the PCB detection limits would depend upon the size of the portion of the extract used and the final volume to which the extract is concentrated before analysis.

The components of the second Method 0010 sampling train would be extracted as per Method 3542 with methylene chloride. One analytical scheme might be to divide the extracts from Method 3542 and subject one portion to PAH cleanup and analysis and analyze another portion directly for SVOCs and/or CB/CPs. In this scheme, the impact upon the detection limits would depend upon the sizes of the portions used for each part of the scheme and the final volume of the extract before analysis. Alternatively, general SVOC, CB/CP, and PAH analyses could all be done using the same extract, subject to the following limitations:

- Additional standards to encompass the additional CB/CP compounds (if desired) should be added to the Method 8270 SVOC calibration mixture.
- An appropriate spiking scheme for isotopically-labeled PAHs should be developed to allow concentration of the extract with subsequent analysis of PAHs using selected ion monitoring mass spectrometry.
- The standard spiking scheme for Method 3542 should be modified to allow combination/concentration of the three extracts generated in the methodology, and the standards should be carefully selected to ensure that the standards for one analytical scheme do not interfere with the standards needed for another analytical scheme.
- The impact of every step of the process on the method detection limits should be carefully evaluated.

Research is currently in progress to modify the standard spiking scheme for Method 3542 in order to allow combination/concentration of the three extracts.

B.8.6 PAH ANALYSIS

It may be possible to determine PAHs with the D/F extract because both groups of compounds can be extracted with toluene (Johnson 1995). However, D/F cleanup procedures are specifically designed to remove PAHs from the extract used to analyze D/Fs, because PAHs are interferences in this analysis: the presence of high levels of PAHs in the extract analyzed for D/Fs will compromise the D/F analysis and may prevent quantitative analysis of some of the D/F isomers. In any extract to be analyzed for PAHs, care should be taken not to take the extract to dryness in a concentration step because the more volatile PAHs (i.e., naphthalene, methylnaphthalene, acenaphthene, acenaphthylene, fluorene) could incur significant losses with complete evaporation of the extract. If a single toluene extract is divided into thirds for separate D/F cleanup and analysis, PCB cleanup and analysis, and PAH cleanup and analysis, detection limits for each of the analytes would be raised, depending upon the final volume of the extract used for analysis.

B.8.7 CLEANUP PROCEDURES

Extract cleanup procedures are optional for Method 8270; methods for D/Fs, PAHs, and PCBs each specify cleanup procedures designed to remove potential interferents from the extract ultimately analyzed. An extract that has been subjected to any one of these specialized cleanup procedures should not be analyzed for other SVOCs. It should be possible, however, to design cleanup steps that allow extraction and preparation of a combined extract. EPA OSW recommends that assistance be obtained from a well-qualified and experienced analytical chemist who understands the methods and calculations involved, as well as the detection limits needed for the risk assessment.

B.8.8 MULTIPLE ANALYSES OF SINGLE EXTRACTS

For any determinations that involve multiple injections of a single extract (for example, SVOCs and CB/CPs if analyzed separately), there is no compromise in detection limits. It is also possible to perform one analysis of a given extract for one compound group and then to concentrate the extract to perform another analysis without affecting detection limits.

B.8.9 TOE DETERMINATION AND COMBINED MEASUREMENT TECHNIQUES

Historically, a separate Method 0010 sampling train has been needed for the TOE determination to avoid potential biases associated with the use of surrogate and internal standards used by other measurement methods, the primary concern being that compounds in these standards would add a positive bias to the TOE measurement. This concern is only partially valid, because the surrogates and internal standards themselves are accurately measured in the same manner as target analytes, or are of known mass (some internal standards are added at the time of analysis), and therefore can be subtracted from the TOE mass just as would be done for an identified analyte. A greater concern is whether the diluent solvent that the surrogate or internal standard is contained in or prepared in is compatible with the TCO measurement. Analytical standards are commonly prepared as solutions with solvents such as dichloromethane, methanol, hexane, nonane, isooctane, and toluene. Of these, only dichloromethane and methanol would not be measured by TCO.

A major benefit of being able to combine the Method 0010 portion of the TOE measurement with a target-analyte-specific SVOC method is that measurement quality assurance/quality control information would then be available for the TOE data. The target-analyte-specific SVOC methods make use of pre-sampling and pre-extraction surrogates to define and assess measurement performance through recovery efficiencies. This option has not been employed for the TOE methodology for the reasons discussed above. However, it is indeed possible to incorporate these highly valuable data quality indicators into the TOE measurement. Another benefit of combining the Method 0010 portion of the TOE measurement with a target-analyte-specific SVOC method is that compounds identified and quantified by the target-analyte-specific SVOC method would then be subtracted directly from the same sample used for the TOE determination, thereby reducing the uncertainty of subtracting mass of one sample from a sample that has little or no quality assurance/quality control information.

It is possible to use a single sampling train for both the TOE determination and for target analyte SVOC determinations, provided that all procedural compatibility issues for the combined methods can be achieved. This is only possible in limited situations. The most compatible measurement with potential for combination is the Method 0010/8270 train. The surrogate and internal standard solutions typically use dichloromethane and/or methanol as the solvent. Care should be taken to ensure that any standards used during sampling and common analysis do not contain compounds that can bias the TCO and/or GRAV measurement. For example, D/F, PCB and PAH standard solutions commonly use nonane as the solvent, precluding them from use with simultaneous TOE measurement. While the benefit of generating TOE data of known quality is obvious, the use of combined measurement techniques involving the TCO and GRAV fractions of the TOE determination should be implemented with caution. EPA OSW recommends that assistance be obtained from a well-qualified and experienced analytical chemist. Should the Method 0010 portion of the TOE measurement and a target-analyte-specific SVOC method be combined, the above issues should be discussed in detail in the test plan to ensure data of acceptable quality.

B.9 ALDEHYDES AND KETONES

Stack determinations for aldehydes and ketones (A/Ks) involve a separate sampling and analytical methodology, although some of these compounds are included on the volatile target list (acetone, 2-butanone) and the SVOC (Method 8270) target list (acetophenone, isophorone). A/Ks are generally polar water-soluble compounds; many of the compounds in the class exhibit a high level of reactivity as well. The quantitative nature of the VOST determination for these type of compounds is questionable because VOST tubes are purged through water and significant amounts of the volatile A/Ks will not be purged from the water used in the VOST analytical determination. If A/Ks are sampled using the Method 0040 train, these types of compounds would be found mostly in the condensate of the train. If any A/Ks are collected in the Tedlar® bag, the stability of A/Ks in this medium is questionable and the likelihood of wall effects is very high. VOST and Method 0040 can, at best, provide qualitative information for A/Ks. SVOC analysis will provide accurate and quantitative information for the semivolatile A/Ks with a significant amount of hydrocarbon character. For the most polar A/Ks, the quantitative recovery from XAD-2® becomes progressively more questionable as the compounds become more polar.

To provide a reliable measurement for A/Ks, specific sampling and analytical procedures are necessary. SW-846 Method 0011 (Sampling for Selected Aldehyde and Ketone Emissions from Stationary Sources) is used to withdraw gaseous and particulate pollutants isokinetically from an emission source and collect these emissions in aqueous acidic 2,4-dinitrophenylhydrazine (DNPH). A/Ks present in the emissions react with the DNPH to form a dinitrophenylhydrazone derivative to stabilize the reactive A/Ks. The field samples are returned to the laboratory where the derivatized A/Ks are extracted, solvent-exchanged, concentrated, and then analyzed using HPLC according to SW-846 Method 8315 (Determination of Carbonyl Compounds by High Performance Liquid Chromatography (HPLC)). The analytical methodology is applicable to far more analytes than the sampling methodology because of the kinetics of formation of the derivatives under stack sampling conditions. For some A/Ks, the derivative as it is formed under stack sampling conditions is not stable and decomposition occurs. If the A/K is sufficiently volatile, the compound may be lost from the sampling train and the methodology will be biased low. Because the derivatization reaction is based on the formation of an equilibrium state between reactants and products, for some compounds quantitative recoveries may not be achieved until the concentration exceeds 200 parts-per-billion volume. Field method evaluation data are available to support the applicability of Method 0011/Method 8315 to the following A/Ks (Steger 1996):

- Formaldehyde (CAS Number 50-00-0);
- Acetaldehyde (CAS 75-07-0);
- Acetophenone (CAS 980-86-2);
- Isophorone (CAS 78-59-1);
- Propionaldehyde (CAS 123-38-6).

Method 0011/Method 8315 has been applied specifically to the above analytes. The methodology is possibly applicable to other A/Ks from stationary sources, but performance should be demonstrated for other compounds. The method has been shown not to be applicable to quinone (CAS 106-51-4), acrolein (CAS 107-02-8), methyl ethyl ketone (CAS 78-93-3), and methyl isobutyl ketone (CAS 108-10-1).

Method 0011 is particularly sensitive to oxidizing agents such as NO_2. If strong oxidizing agents are present in the flue gas emissions, then special care should be taken to guarantee an excess of derivatizing agent, or another technique should be used. Formaldehyde is often the highest concentration carbonyl compound from a combustion source, and measurement of formaldehyde in relatively high NO_2 gas streams have been demonstrated successfully using EPA Method 320 (40 CFR Part 63 Appendix A).

EPA OSW recommends that the need for Method 0011 A/K sampling be considered carefully. In some cases, a facility may wish to submit a justification for use of A/K data from a similar facility or for A/K data collected previously at the same facility, unless the facility burns large quantities of A/K wastes. Also, as stated previously, at least some qualitative data may be provided by the VOST and Method 0040, although the data for the compounds listed above would not be of the same quality (quantitative analysis would be biased low) as the data generated by Methods 0011/8315. For the semivolatile A/Ks listed above, Method 0010/3542/8270 should generate accurate quantitative data.

B.10 FACILITY-SPECIFIC COMPOUNDS

Previous sections have identified methods with target analyte lists applicable to numbers of compounds and generally applicable to most facilities. However, it may also be appropriate for individual facilities to sample and analyze for additional compounds based upon the constituents contained in their waste feed. Potential candidates for additional facility-specific determination include any highly toxic, persistent, or bioaccumulative constituents burned in large quantities. Section 5.2.2 of *Risk Burn Guidance for Hazardous Waste Combustion Facilities* lists examples of historical waste feed information that EPA OSW recommends be compiled to determine which constituents may be burned in large quantities, as well as to identify highly toxic, persistent, or bioaccumulative constituents. If a constituent ranks prominently on one or both of these rankings, then EPA OSW recommends that the constituent also be considered a candidate for sampling and analysis during the risk burn. Facility-specific constituents to be considered for sampling and analysis during the risk burn include compounds such as pesticides, herbicides, nitroaromatics, cyanides, and isocyanates, as well as other groups/families of compounds and/or individual compounds. Sampling and analysis for these constituents is recommended as an addition to, not as a substitute for, the target analytes described previously in this appendix.

Table B.10-1 lists organochlorine pesticides that can be determined by SW-846 Method 8081A (Organochlorine Pesticides by Gas Chromatography) using GC/ECD, together with the waste codes that might contain these types of compounds. However, including these compounds in Table B.10-1 as analytes for Method 8081A DOES NOT ADDRESS the issues associated with removing these compounds from the source emissions and preparing them for analysis. Pesticides are generally semivolatile organic compounds that would be collected by the Method 0010 sampling train and prepared for analysis using Method 3542. Pesticides are also highly reactive compounds that may decompose in the hot and reactive stationary source emissions matrix, react with other compounds present in the stationary source matrix, or fail to be recovered quantitatively from the XAD-2® sorbent resin of the Method 0010 sampling train. Table B.10-1 indicates which analytes on the target list for Method 8081A have been evaluated using quadruple Method 0010 sampling trains with dynamic spiking, Method 3542 sample preparation procedures, and Method 8270 analytical procedures. Not all of the compounds tested performed successfully. EPA OSW recommends

TABLE B.10-1

ORGANOCHLORINE PESTICIDES - METHOD 8081A ANALYTES

Compound	CAS Number	Waste Codes
Aldrin	309-00-2	P004
á-BHC	319-84-6	D013, U129
â-BHC	319-85-7	D013, U129
ã-BHC (Lindane)[1]	58-89-9	D013, U129
ä-BHC	319-86-8	D013, U129
Chlorobenzilate[2]	510-15-6	U038
á-Chlordane[1]	5103-71-9	D020, K097, U036
ã-Chlordane[1]	5103-74-2	D020, K097, U036
Chlordane - mixed isomers[1]	57-74-9	D020, K097, U036
1,2-Dibromo-3-chloropropane[2]	96-12-8	U066
4,4'-DDD	72-54-8	U060, U061
4,4'-DDE[1]	72-55-9	U060, U061
4,4'-DDT	50-29-3	U060, U061
Diallate	2303-16-4	U062
Dieldrin	60-57-1	P037
Endosulfan I	959-98-8	P050
Endosulfan II	33213-65-9	P050
Endosulfan sulfate	1031-07-8	P050
Endrin	72-20-8	D012, P051
Endrin aldehyde	7421-93-4	D012, P051
Endrin ketone	53494-70-5	D012, P051
Heptachlor[1]	76-44-8	D031, K097, P059
Heptachlor epoxide	1024-57-3	D031, K097, P059
Hexachlorobenzene[2]	118-74-1	D032
Hexachlorocyclopentadiene[2]	77-47-4	U130
Isodrin	465-73-6	P060
Methoxychlor[1]	72-43-5	D014, U247
Toxaphene	8001-35-2	D015, K041, K098, P123

Notes:

[1] Acceptable recovery/reproducibility in field validation studies with Method 0010/3542/8270.
[2] Marginal to poor recovery/reproducibility in field validation studies with Method 0010/3542/8270.

that, for any of the facility-specific compounds to be tested, acceptable performance of the sampling and analytical methodology be demonstrated for the data to be accepted as valid.

Other waste streams and specific compounds that may be considered for sampling on a site-specific basis include D017 waste (2,4,5-TP [Silvex]), D016 and U240 wastes (2,4-D), K025 waste (1,3-dinitrobenzene), and cyanide wastes (F007-F012, F019, K011, K013, K027, K060, K088, and U246). SW-846 Method 8151A (Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization) provides analytical procedures for the chlorinated herbicides shown in Table B.10-2, with the same constraints on the analytical methodology due to the sampling and sample preparation methodology and the same need to demonstrate sampling and analytical method performance. SW-846 Method 8270C can provide data on some nitroaromatics, but the Method 8270 list is not exhaustive for nitroaromatics and performance of the Method 0010/Method 3542/Method 8270 sampling and analytical methodology should be demonstrated. CARB Method 426 (Determination of Cyanide Emissions from Stationary Sources) is potentially applicable to the determination of cyanide emissions from stationary sources. The method is listed as “NYA (Not Yet Available)” on the CARB web site, but directions for obtaining hard copies of the method are provided on the web site. A critical feature of CARB Method 426 is collection in an alkaline impinger. If the pH of the impinger is not monitored and controlled during sampling, the hydrogen cyanide will not be collected quantitatively.

Paint and foam rubber (polyurethane foam) incineration may warrant sampling for a facility-specific compound class called isocyanates. Draft Method 207-1 (Draft Sampling Method for Isocyanates) and Method 207-2 (Analysis for Isocyanates by High Performance Liquid Chromatography (HPLC)) have been validated for 2,4-toluene diisocyanate (CAS Number 584-84-9), 1,6-hexamethylene diisocyanate (CAS 822-06-0), methylene diphenyl diisocyanate (CAS 101-68-8) and methyl isocyanate (CAS 624-83-9) at several stationary sources (Attachment 2). Attachment 2 lists the analytes of the Clean Air Act Amendments of 1990, together with applicable or potentially applicable sampling and analytical methods, and the status of these methods relative to field evaluation.

TABLE B.10-2

CHLORINATED HERBICIDES - METHOD 8151A ANALYTES

Compound	**CAS Number**
2,4-D	94-75-7
2,4-DB	94-82-6
2,4,5-TP (Silvex)	93-72-1
2,4,5-T	93-76-5
Dalapon	75-99-0
Dicamba	1918-00-9
Dichloroprop	120–36-5
Dinoseb	88-85-7
MCPA	94-74-6
MCPP	93-65-2
4-Nitrophenol[1]	100-02-1
Pentachlorophenol[2]	87-86-5

Notes:

[1] Performance in field evaluation using Method 0010/3542/8270 ranged from acceptable to poor.
[2] Consistently poor recovery in field evaluation using Method 0010/3542/8270.

B.11 TENTATIVELY IDENTIFIED COMPOUNDS

For all methods using mass spectrometry for detection in the full scan mode (i.e., SW-846 Method 8260, Method 8270, Method 0040), EPA OSW recommends that analysis for the specific target analytes listed in the method be accompanied by an evaluation of the Tentatively Identified Compounds (TICs).

The *Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities. Volume One* (EPA 1998a) states:

> “Although U. S. EPA OSW will not require a risk assessment for every possible metal or PIC from a combustion unit, this does not imply that U. S. EPA OSW will allow only targeted sampling for COPCs during trial burn tests. Based on regional permitting experience and discussions with regional analytical laboratories, U. S. EPA OSW maintains that complete target analyte list analyses conducted when using U. S. EPA standard sampling methods (e.g., 0010 or 0030) do not subject facilities to significant additional costs or burdens during the trial burn process. Facilities conducting stack emission sampling should strive to collect as much information as possible which characterizes the stack gases generated from the combustion of hazardous waste. Therefore, every trial burn or “risk burn” should include, at a minimum, the following tests: Method 0010, Method 0030 or 0031 (as appropriate), total organic compounds (using the Guidance for Total Organics, including Method 0040), Method 23A, and the multiple metals train. Other test methods may be approved by the permitting authority for use in the trial burn to address detection limit or other site-specific issues.”

In addition to the target analytes listed in the methods, there are generally a number of non-target components observed in the chromatogram. Attempts to identify and quantify these unknown chromatographic peaks can improve the percentage of identified organic compounds and reduce overall uncertainty. However, because the instrument is not calibrated for these unknown compounds, the identification and quantitative analysis is tentative until the identification is confirmed by the analysis of a standard. The EPA OSW risk assessment guidance (EPA 1998a) recommends that TICs be considered “identified” compounds for purposes of site-specific risk assessments to ensure that appropriate credit is given to defensible efforts to identify the maximum number of organic compounds.

To identify non-target TICs, the mass spectrum can be searched against a computerized library of reference mass spectra. A forward library search selects the largest mass spectral peaks from the unknown mass spectrum and looks for reference spectra in the library that contain the peaks of the unknown. A reverse library search looks for the peaks in the reference spectrum that occur in the unknown mass spectrum. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library matches should the analyst assign a tentative identification. Any components that are identified are referred to as TICs, since no reference standard was analyzed at the same time as the unknown. Without calibration of the instrument with the actual compound, TICs are quantified using the nearest-eluting internal standard with a relative instrument response factor of 1.00. The resulting concentration is considered "estimated," because the response factor is not compound-specific. An unknown level of error in the quantitation is introduced using the response factor of 1.00; this level of error will vary from compound to compound. Methods 8260/8270 present guidelines for identification of TICs, and these guidelines are summarized below for the convenience of the reader:

- Relative intensities of major ions in the reference mass spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample mass spectrum.
- The relative intensities of the major ions should agree within ±20 percent. Example: for an ion with an abundance of 50 percent in the standard spectrum, the corresponding sample ion abundance should lie between 30 and 70 percent.
- Molecular ions present in the reference mass spectrum should be present in the sample mass spectrum.
- Ions present in the sample mass spectrum but not in the reference mass spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
- Ions present in the reference mass spectrum but not in the sample mass spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting peaks. Data system library programs can sometimes create these discrepancies.

If, in the judgment of the experienced mass spectral interpreter, no valid tentative identification can be made, the compound should be reported as "unknown." The mass spectral interpreter should give additional classification of the unknown compound, if possible (i.e., unknown aromatic compound, unknown hydrocarbon, unknown chlorinated compound). If a probable molecular weight can be distinguished, this molecular weight should also be reported. The experienced interpreter should apply this experience and judgment to the mass spectral interpretations supplied by the computerized library search. For example, if a hydrocarbon occurring 40 minutes into the chromatographic analysis is identified by the computer as "octane," analytical judgment dictates that this identification is scientifically illogical and the compound should be reported as "unknown hydrocarbon." By no means should the computer identifications be accepted uncritically.

It may be possible to prepare and analyze additional standards containing TICs to confirm the identifications, although this process is time-consuming and costly. A multi-concentration calibration curve containing the additional compounds can be used to establish relative response factors for the specific compounds. The semivolatile extracts can then be re-analyzed to improve quantitative accuracy. For VOCs, the sample generally cannot be re-analyzed, but the relative response factors can be used to re-quantify prior analyses to improve quantitative accuracy. In some cases, an authentic standard for confirmation of compound identification may not be available. Many of the mass spectral libraries were assembled using mass spectra contributed by laboratories around the world, including compounds synthesized in individual laboratories or obtained by isolation from a variety of sources. Thus, it may not always be possible to confirm a compound identification.

In the Total Organics Emissions (TOE) analysis, organic mass in both the volatile and semivolatile ranges is one of the components of the total recoverable organic mass that is calculated. All organic compounds that are identified and quantified are ultimately subtracted from the total organic emissions mass value. It is, therefore, beneficial for the laboratory to identify and quantify the maximum number of compounds when the analysis is performed, including TICs. Although it is in the facility's interest to characterize as many TICs as possible, extensive characterization of TICs involves a significant commitment of time and expertise and can reach a point of diminishing returns. Therefore, EPA OSW recommends that TICs be characterized when the peak intensity is 10 percent or more of full chromatographic scale, and a that quantitative estimate of the value be obtained using the nearest-eluting internal standard and a response factor of 1. Unless the identification of the TIC is confirmed by the analysis of an authentic standard, the quantitative value should be qualified as "estimated."

B.12 TOTAL HYDROCARBON AND CARBON MONOXIDE CONTINUOUS EMISSIONS MONITORS (CEMs)

EPA OSW has recommended (EPA 1998a) that the Total Organics Emission (TOE) measurement be performed during the risk burn to obtain the best measure of total recoverable organic mass (as indicated in Section B.1.1, a THC monitor is not appropriate for determining total organic mass). However, the TOE determination involves manual measurements, and therefore cannot be used on an ongoing, continuous basis to quantify the level of organic emissions. Continuous emissions monitors (CEMs) provide a continuing indication of source performance. CEMs for THC and carbon monoxide can both indicate whether good combustion practice is being maintained, and whether or not organics emissions have changed from the baseline determined during the risk burn.

EPA OSW recommends that THC and carbon monoxide monitoring be performed during the risk burn in conjunction with the manual organic emissions determinations. Even if THC monitoring is not required by current regulations at a facility, it can be accomplished by having a temporary monitor brought in during the testing, if necessary. The monitoring serves several purposes. One purpose is to ensure that targeted operating conditions are being maintained during the risk burn. Chapters 4 and 5 of *Risk Burn Guidance for Hazardous Waste Combustion Facilities* recommend operating scenarios to be preferentially targeted for D/F and non-D/F organic testing, including:

- Transient conditions;
- Operation with containerized or batch waste feeds; and
- High carbon monoxide (greater than 100 ppm) situations.

These scenarios are recommended to be targeted for the risk burn because of the increased potential for localized oxygen deficiencies and carbon monoxide/THC spikes. Numerous test programs have established that D/Fs can be high when oxygen is insufficient or when carbon monoxide/THC concentrations are high. CEMs for THC and carbon monoxide provide an indication that the targeted scenarios are being maintained during the test. As appropriate, permit limits for appropriate combustion parameters, including THC and carbon monoxide, may be established based on the risk burn to protect human health and the environment by continually indicating that D/F and other organic emissions are being maintained below the levels measured during the risk burn on an ongoing basis. Thus, THC and carbon monoxide monitoring may also serve the purpose of providing ongoing compliance assurance. Finally, THC and carbon monoxide monitoring can indicate whether ongoing organic emissions may have changed from the baseline measured during the risk burn. Performance specifications for THC and carbon monoxide monitoring are provided in 40 CFR Part 266, Appendix IX, Section 2.0.

B.13 METALS

Metals that may be measured during the risk burn and subsequently evaluated in site-specific risk assessments include antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium, as well as aluminum, copper, cobalt, manganese, nickel, selenium, vanadium, and zinc (EPA 1998a and 2000). There are two methods available for the determination of metals emissions: SW-846 Method 0060 (Determination of Metals in Stack Emissions) and EPA Method 29 (Determination of Metals Emissions from Stationary Sources, 40 CFR Part 60 Appendix A). Both methods state that they are applicable to the determination of metals emissions from stationary sources. In both of these methods, a stack sample is withdrawn isokinetically from the source. Particulate emissions are collected in the probe and on a heated filter and gaseous emissions are collected in a series of chilled impingers: two impingers are empty, two impingers contain an aqueous solution of dilute nitric acid combined with dilute hydrogen peroxide, two other impingers contain acidic potassium permanganate solution, and the last impinger contains a desiccant. Method 0060 is paired with the SW-846 6000 and 7000 series of methods for preparation and analysis. Preparation and analysis procedures are included in Method 29. The target lists for the two methods are the same and are shown in Table B.13-1. CARB Method 436 (Determination of Multiple Metals Emissions from Stationary Sources) is also available as a sampling and analytical method for metals in stationary source emissions that uses basically the same collection of impingers for collection of metals in stationary source emissions. It should be noted that aluminum (Al) and vanadium (V) are not included on the target list of analytes for Method 0060 and Method 29, but the sampling methodology should be amenable. CARB Method 436, using the same sampling and analytical methodology, includes aluminum (Al) and vanadium (V) on the method target list.

Iron can be a spectral interference during the analysis of arsenic, chromium, and cadmium by inductively coupled plasma (ICP) spectroscopy. Aluminum can be a spectral interference during the analysis of arsenic and lead using ICP. These interferences can generally be reduced by diluting the sample, but dilution increases the method detection limit. There are three metals (mercury, chromium, and nickel) for which speciation is an issue. These metals are discussed individually.

TABLE B.13-1

TARGET LIST FOR METALS MEASUREMENT METHODS

Analyte	CAS Number
antimony (Sb)	7440-36-0
arsenic (As)	7440-38-2
barium (Ba)	7440-39-3
beryllium (Be)	7440-41-7
cadmium (Cd)	7440-43-9
total chromium (Cr)	7440-47-3
cobalt (Co)	7440-48-4
copper (Cu)	7440-50-8
lead (Pb)	7439-92-1
manganese (Mn)	7439-96-5
mercury (Hg)	7439-97-6
nickel (Ni)	7440-02-0
phosphorus (P)	7723-14-0
selenium (Se)	7782-49-2
thallium (Tl)	7440-28-0
zinc (Zn)	7440-66-6

B.13.1 MERCURY

Stack emissions containing mercury include both vapor and particulate forms of mercury. Vapor mercury emissions are thought to include both elemental (Hg^0) and oxidized (Hg^{+2}) chemical species, while particulate mercury emissions are thought to be composed primarily of oxidized compounds due to the relatively high vapor pressure of elemental mercury (EPA 1997d). While coal combustion is responsible for more than half of all emissions of mercury in the United States due to anthropogenic sources, the fraction of coal combustion emissions in oxidized form is thought to be less than from waste incineration and combustion (EPA 1997d).

There is no generally accepted numbered EPA method for accurate and reproducible speciation of mercury from exit vapors and emission plumes. Development and evaluation of sampling and analytical methods to provide reliable speciation of mercury is currently an active area of research. The exit stream is thought to range from almost all divalent mercury to nearly all elemental mercury, with true speciation of mercury from the various source types still uncertain and thought to vary, not only among source types but also for individual plants as feed stocks and operating conditions change (EPA 1997d). Data on mercury speciation in emissions exiting the stack are very limited, and the behavior of mercury close to the point of release has not been extensively studied. This lack of information results in a significant degree of uncertainty in modeling of mercury emissions. Additional areas of uncertainty include precision of measurement techniques, estimates of pollution control efficiency, and limited availability of data specific to source class and activity level.

The *Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities* (EPA 1998a) provides recommended mercury speciation assumptions for site-specific risk assessments of 20 percent divalent particulate mercury, 60 percent divalent mercury vapor, and 20 percent elemental mercury vapor consistent with the latest scientific literature on the subject (EPA 1997d). A facility may prefer to perform speciation sampling for mercury during the risk burn to replace the recommended assumptions with site-specific data. For example, some data suggest that the percentage of elemental mercury may be higher for certain units equipped with wet scrubber systems.

A review of design and operating parameters affecting mercury emissions has been performed (EPA 1999). For incinerators, mercury speciation in the flue gas depends upon factors such as waste composition (in particular, chlorine and sulfur levels), flue gas temperature profile, and type of air pollution control. If chlorine is not present or sulfur levels are high, elemental mercury can comprise a significant fraction of the total mercury. Elemental mercury is not soluble in water and is usually not well controlled by wet scrubbers. Control of elemental mercury may involve use of carbon injection or carbon beds.

In the presence of chlorine, formation of divalent mercury is thermodynamically favored in combustion systems. Mercuric chloride is soluble in water and is readily captured by wet scrubbers. Slow gas cooling (instead of rapid quenching) has been shown to maximize the levels of soluble mercuric chloride and increase wet scrubber performance.

Among the measurement methods which have been evaluated for their ability to provide information on speciated mercury emissions from stationary sources are:

- EPA Method 29 (or EPA SW-846 Method 0060);
- EPA Draft Method 101B (Research Triangle Institute);
- Ontario Hydro method (Ontario Hydro); and
- Alkaline Mercury Speciation (AMS) method (Research Triangle Institute).

The sampling train configuration of the impingers for all of these methods is based on the Method 29/0060 train, but different impinger solutions are utilized as shown in Table B.13-2. All of the methods rely on acidified potassium permanganate solution ($H_2SO_4/KMnO_4$) in the final impinger of the sampling train for the ultimate collection of elemental mercury. The methods differ with respect to the chemistry of the impingers located upstream of the potassium permanganate impingers. The upstream impingers collect divalent mercury. The use of various upstream impinger solutions has been proposed in an attempt to minimize potential interferences (most notably SO_2 and Cl_2) known to cause oxidation of elemental mercury in the Method 29 nitric acid/hydrogen peroxide (HNO_3/H_2O_2) impingers (thus resulting in over-reporting divalent mercury and under-reporting elemental mercury). Much of the research and method development to

TABLE B.13-2

COMPARISON OF IMPINGER CONTENTS FOR MERCURY SAMPLING TRAINS

Impinger	Method 29	Method 101B	Ontario Hydro	AMS
1	Empty (optional)	Empty (optional)	KCl (1N)	NaOH (1N)
2	5% HNO_3 10% H_2O_2	H_2O	KCl (1N)	NaOH (1N)
3	5% HNO_3 10% H_2O_2	H_2O	KCl (1N)	H_2O
4	Empty	5% HNO_3 10% H_2O_2	5% HNO_3 10% H_2O_2	Empty
5	10% H_2SO_4 4%$KMnO_4$	Empty	10% H_2SO_4 4%$KMnO_4$	10% H_2SO_4 4%$KMnO_4$
6	10% H_2SO_4 4%$KMnO_4$	10% H_2SO_4 4%$KMnO_4$	10% H_2SO_4 4% $KMnO_4$	10% H_2SO_4 4%$KMnO_4$
7	Silica Gel	10% H_2SO_4 4%$KMnO_4$	10% H_2SO_4 4% $KMnO_4$	Silica Gel
8	--	Silica Gel	Silica Gel	–

date has focused on coal-fired utility sources, where higher SO_2 emissions are a concern. All of the more recent methods (Method 101B, Ontario Hydro, and AMS) are less prone to SO_2 interference than Method 29. Less research is available for hazardous waste combustor applications, where higher Cl_2 concentrations from combustion of highly chlorinated waste streams may exist. Each of the methods is discussed below in more detail.

Method 29: The Method 29 (and Method 0060) sampling trains were developed and validated only for total mercury (including both elemental and ionized forms). Method 29 was not developed with the intent of speciating mercury emissions. However, due to the manner in which the mercury is captured and subsequently analyzed in the Method 29 train, it has been suggested (Krivanek 1993) that the results can be used to estimate speciation for three forms of mercury:

- *Condensed solid particulate mercury (primarily HgO)* – Captured on the filter and in the front half sample nozzle and probe wash (up to the filter).
- *Soluble divalent mercury vapors ($HgCl_2$, etc.)* – Captured in the aqueous nitric acid and hydrogen peroxide (5% HNO_3/10% H_2O_2) impingers located downstream of the filter.
- *Elemental mercury (Hg^0)* – Captured in the final two impingers of sulfuric acid/potassium permanganate (10% H_2SO_4/4% $KMnO_4$).

Pilot-scale work has shown that Method 29 does not properly speciate mercury under conditions of high SO_2, with the method overstating the divalent mercury up to 50%. The high bias for the ionic form of mercury has also been confirmed in field tests for utility sources (EPA 1997d). In other studies, high concentrations of SO_2 (approximately 1000 ppm) caused 23 percent of the elemental mercury to be oxidized to divalent mercury (Giglio 1998). For hazardous waste combustion sources, trace levels (in excess of 1 ppm) of Cl_2 may result in oxidation of elemental mercury in the nitric acid impingers, thus overstating the divalent mercury and under-reporting the elemental mercury (Giglio 1998).

Draft Method 101B: EPA Draft Method 101B was developed in an attempt to reduce SO_2 interference. Because of the high solubility of SO_2 in the Method 29 nitric acid/hydrogen peroxide impingers, the first acidified peroxide impinger was replaced with two deionized water impingers. The water impingers capture divalent mercury, while the acidified peroxide solution absorbs SO_2. Draft Method 101B has been formally evaluated for utility sources using the validation protocol established in EPA Method 301. Since there is no reference method for comparison, only the precision and bias associated with the sampling procedures were evaluated based on dynamic spiking of the flue gas stream. Method 101B passed the Method 301 criteria, but showed more variability than the Ontario Hydro method (EPA 1997d). Method 101B has also been evaluated for Cl_2 interference, to determine applicability to hazardous waste combustion sources. At Cl_2 levels of approximately 18 ppm Cl_2, up to 93% of elemental mercury was oxidized to divalent mercury in the water impingers. This result was not surprising, considering that the solubility of Cl_2 in water may have resulted in conditions conducive to a liquid-phase reaction between Cl_2 and elemental mercury. For hazardous waste combustion sources, trace levels (in excess of 1 ppm) of Cl_2 may result in oxidation of elemental mercury in the water impingers, thus overstating the divalent mercury and under-reporting the elemental mercury (Giglio 1998).

Ontario Hydro: The Ontario Hydro method (Curtis 1995) was also developed to address SO_2 interference. The Ontario Hydro method has been formally evaluated for utility sources using the validation protocol established in EPA Method 301. Since there is no reference method for comparison, only the precision and bias associated with the sampling procedures were evaluated based on dynamic spiking of the flue gas stream. The Ontario Hydro method passed the Method 301 acceptance criteria, and showed less variability than EPA Draft Method 101B. Ontario Hydro has been recommended by the U.S. Department of Energy as the best method for speciating mercury in coal-fired systems (EPA 1997d). For hazardous waste combustion sources, Cl_2 may result in oxidation of elemental mercury in the KCl impingers, thus overstating the ionic mercury and under-reporting the elemental mercury. The Cl_2 interference appears to be more pronounced at increased Cl_2 concentrations (Giglio 1998).

AMS Method: The AMS method was developed in an attempt to reduce Cl_2 interference. The method was developed considering the principle of Method 26 (40 CFR Part 60 Appendix A), which employs sodium hydroxide (NaOH) impingers for collection of Cl_2, resulting in the formation of the chloride (Cl^-) and hypochlorite (OCl^-) ions. A later modification (Method 26A) incorporates sodium thiosulfate ($Na_2S_2O_8$) to convert Cl_2 entirely to Cl^-. The AMS method uses a NaOH medium in place of the Draft Method 101B water impingers to collect water-soluble ionic mercury while preventing oxidation by Cl_2. Bench and pilot-scale tests have showed that the AMS method effectively speciates elemental and divalent mercury emissions in the presence of SO_2 levels exceeding 1500 ppm. However, mixed results have been observed when Cl_2 is introduced as an interferent (Giglio 1998).

Speciated mercury measurements continue to be an active research area within EPA. Potential modifications to the Ontario Hydro method are currently being investigated, including the addition of sodium thiosulfate to the KCl impingers to reduce Cl_2 interference (Ryan 2000).

At present, EPA Method 29 (or Method 0060) is the only field-tested methodology which can provide valid data on the entire list of total metals as well as limited data on speciated mercury, recognizing that, at worst, Method 29 may over-report the divalent form of mercury in the presence of SO_2 or Cl_2. Over-reporting of divalent mercury should generally be conservative for multi-pathway risk assessments, in that risks will generally be over-estimated. Higher percentages of divalent mercury tend to increase risk, because the risk methodology assumes that 68 percent of divalent mercury vapor deposits near the source, whereas only 1 percent of elemental mercury vapor is presumed to deposit near the source.

B.13.2 CHROMIUM

The oxidation state of chromium (Cr) is a crucial issue in evaluating the toxicity of this metal and the risks associated with exposure. Hexavalent chromium (Cr^{+6}) is the most toxic valence state of chromium and has been demonstrated to be a human carcinogen (EPA 1996f). Trivalent chromium (Cr^{+3}), a commonly found, less oxidized form of chromium, has not been shown to be carcinogenic in either humans or laboratory animals (EPA 2000). EPA has indicated that chromium emitted from a combustion source is not likely to be in the hexavalent form (EPA 1990a and 1990b). However, there are not sufficient data to reliably estimate the partitioning of chromium emissions between the two valence states. Therefore, unless site-specific process or sampling information is provided, a worst-case assumption—that 100 percent of the facility chromium emissions are in the hexavalent form—has been recommended for risk assessments (EPA 1998a).

Because medium-specific chromium speciation information is difficult to obtain, EPA OSW has recommended that risk assessments generally be prepared following the conservative initial assumption that all exposure is to hexavalent chromium (EPA 1998a). However, EPA OSW recognizes that chromium may exist partially or in some cases entirely as trivalent chromium in various media. For example, in biological materials, chromium is probably always trivalent. Therefore, in the event risks or hazards associated with chromium exceed target levels based on the initial conservative assumption that exposure is entirely to hexavalent chromium, EPA OSW has recommended that risks and hazards be re-calculated assuming potential receptors are exposed through indirect exposure pathways (e.g., ingestion of fish, beef, pork, chicken, dairy products, and produce) to trivalent chromium (EPA 1998a). These additional risk estimates can then be presented in the report with the hexavalent chromium estimates, and discussed in the uncertainty section of the risk assessment report (EPA 1998a).

Based on the conservative nature of the assumptions for chromium recommended in the EPA OSW risk assessment guidance, a facility may prefer to perform speciation sampling during the risk burn and utilize site-specific data in the risk assessment. It should be noted that Method 0060 and Method 29 measure total chromium only, since the acidic conditions associated with the sampling train would reduce Cr^{+6} to Cr^{+3}, and all chromium is measured in the reduced form. Specialized sampling trains that stabilize the Cr^{+6} species in base are available for sampling the hexavalent form: SW-846 Method 0061 (Determination of Hexavalent Chromium Emissions from Stationary Sources) and CARB Method 425 (Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources). Method 0061 provides procedures for the determination of hexavalent chromium emissions from hazardous waste incinerators, municipal waste incinerators, municipal waste combustors, and sewage sludge incinerators using a sampling train constructed of Teflon® (evaluated only at temperatures less than 300EC). Emission samples are collected with a recirculating train where the impinger reagent is continuously recirculated to the nozzle of the sampling train. The pH of the recirculating fluid should be monitored during sampling to maintain basic conditions; recovery procedures include a post-sampling purge and filtration. Analysis involves the use of an ion chromatograph equipped with a post-column reactor and a visible wavelength detector. The CARB 425 method collects sample for hexavalent chromium in impinger solutions of 0.1M sodium hydroxide, with direct sample injection and post-column derivatization with a colorimetric reagent and photometric detection.

B.13.3 NICKEL

EPA OSW (EPA 1998a) has recommended that permitting authorities evaluate nickel as an inhalation carcinogen in site-specific risk assessments because some forms of nickel—including nickel carbonyl, nickel subsulfide, and nickel refinery dust—are considered to be carcinogens (EPA 2000). Previously under the boiler/industrial furnace (BIF) regulations, nickel was not treated as a carcinogen because the BIF regulations assumed that nickel can only be emitted as nickel oxide, which, by itself, is not considered to be a carcinogen (EPA 1991). However, because nickel oxide is a major component of nickel refinery dust, and because the component of nickel refinery dust causing it to be carcinogenic has not been established, EPA OSW now recommends that nickel emissions be evaluated as a potential carcinogen (EPA 1998a). Also, nickel oxides can be reduced to nickel sulfates (which are carcinogenic) in the presence of sulfuric acid

(Weast 1986). Hazardous waste combustion units that burn wet wastes containing significant amounts of nickel and sulfur may need to be especially concerned with nickel emissions.

The standard metals sampling methods (SW-846 EPA Method 0060, 40 CFR Part 60 Appendix A Method 29, and CARB Method 436) all include nickel on their target lists. However, these methods detect nickel only and do not speciate nickel (i.e., differentiate the carcinogenic forms from non-carcinogenic forms). There are currently no methods available to detect, for example, nickel carbonyl or nickel sulfate as a distinct species. EPA OSW therefore recommends (EPA 1998a) that nickel be evaluated as an inhalation carcinogen using the inhalation unit risk factor for nickel refinery dust. However, if the permitting authority has information at points of potential inhalation exposure that demonstrate the absence of nickel refinery dust components or the presence of non-carcinogenic nickel species such as soluble salts, EPA OSW has recommended that this information be used as the basis for supplemental non-carcinogenic calculations (EPA 1998a).

B.14 PARTICLE-SIZE DISTRIBUTION

Information on particle-size distribution and particle density of emissions are utilized in the air dispersion and deposition modeling that supports risk assessments (EPA 1998a). Inputs to the air models include: 1) particle density; 2) mass distribution by particle-size category; and 3) surface area distribution by particle-size category. A minimum of three particle-size categories (> 10 microns, 2-10 microns, and < 2 microns) are recommended (EPA 1998a). A representative particle-size distribution can be difficult to predict, and EPA OSW has therefore indicated that site-specific measurements are preferred whenever possible (EPA 1998a). However, a site-specific particle-size distribution measurement may not be possible for all situations. Other alternatives, such as use of literature estimates or vendor information, are described in Chapter 7 of *Risk Burn Guidance for Hazardous Waste Combustion Facilities*.

To perform particle-size distribution measurements, CARB Method 501 (Determination of Size Distribution of Particulate Matter Emissions from Stationary Sources) is recommended. In operation of CARB 501, particulate matter is withdrawn isokinetically from the source and segregated by size in a cascade impactor at the sampling point exhaust conditions of temperature, pressure, etc. Cascade impactors use inertial separation to size-segregate particle samples from a particle-laden gas stream. The mass of each size fraction is determined gravimetrically. CARB Method 501 recommends stage configurations representing a range of 0.25 to 10 microns, with five to eight cuts and a total sample size of 50 milligrams (mg). For hazardous waste combustion facilities with very low particulate emissions, a very long sampling period may be needed to achieve resolution for the smaller sizes. In some cases, the weight gain on the filter may be negligible or zero.. Hazardous waste combustion facilities with wet stacks may experience a problem with particle agglomeration.

High temperature environments (temperatures above 1300EF) are difficult to test because of the need for sampling equipment that can withstand high temperatures. High moisture environments are also difficult to test. In a high moisture environment, the moisture promotes the formation of droplets that can overload the system or wash the sample off the collection surfaces. Modifications to the CARB 501 cascade impactor methodology for sizing of particles have been developed to address sampling of both high-temperature and high-moisture gas streams. The modifications are described by McCain and Fowler (McCain and Fowler

1994). For both types of gas streams, large drops and/or particles are collected in adaptations of a right-angle pre-collector. In wet stream sampling, the remaining droplets are passed to the impactor through a heated inlet tube, where they are evaporated to dryness. In the high temperature case, the sampled gases are passed through an air-cooled tube until they are cool enough for collection in a standard impactor.

The high moisture particle-size measurement apparatus is the same as the apparatus used for CARB Method 501, with additions. In the modified method, a Pilat Mark V cascade impactor is used, with a liquid droplet pre-collector, a heated interconnecting tube, a heating jacket for the impactor body, thermocouples, and temperature controllers. The liquid droplet pre-collector is an EPA right-angle pre-collector modified to include greater internal volume, permitting collection of relatively large amounts of water. Prior to sampling, heaters are all brought to optimum operating temperatures. The high temperature modification of CARB Method 501 likewise uses a Pilat Mark V cascade impactor, with a Hayes high temperature “super alloy” that allows operation up to 2000EF, a sheathed air-cooled probe, a heating jacket for the impactor body, thermocouples with braided ceramic insulation, temperature controllers, and a blower to provide cooling air for the probe. Before fabricating the new sampling equipment, the investigators produced a review of the fundamentals of basic particle sizing techniques, including optical and inertial methods (McCain and Fowler 1994). In sampling at a wet stack, stack temperatures averaged about 160EF and the moisture content ranged from 30 to 35 percent. Most of the fine dry particulate matter collected was smaller than one micrometer in diameter and the evaporative residues from the pre-collector were all quite small (a few micrograms). The method appeared to perform well (McCain and Fowler 1994).

In the application of CARB Method 501 for the determination of particle-size distribution, a determination of ñ$_p$, the particle density, is necessary. CARB Method 501 specifies the use of a helium pycnometer to perform the determination of particle density. There is no recognized numbered EPA, American Society for Testing and Materials, or CARB method available for performing this determination, but a number of commercial laboratories have procedures for performing the measurement. In the use of a helium pycnometer, after properly preparing the collected particle sample with heat or vacuum, helium gas fills all spaces and all but the smallest micropores open to the atmosphere. Knowing the volume of the container and the volume of the gas at standard temperature and pressure, the volume of the sample is easily determined, the weight of the sample is available, and the density is then calculated.

Additional information regarding source test cascade impactors may be found at the cascade impactor web site (http://www.cascadeimpactor.com/). This site describes the Source Test Cascade Impactors developed at the University of Washington (Seattle, Washington) Department of Civil Engineering by Professor M. J. Pilat and his graduate students specifically for measuring the particle-size distribution in stacks and ducts at air pollution sources. The web site describes at least one cascade impactor that includes multi-jet stages and a number 1 inlet sampling nozzle stage that can be arranged in at least four different jet stage configurations depending upon the desired aerodynamic cut diameters. The site also includes an Operations Manual for Pilat (University of Washington) Mark 3 and Mark 5 Source Test Cascade Impactors which presents sampling procedures for stationary source testing, and reference literature.

Numerous tests have been performed to determine particle-size distributions from a variety of stationary sources using cyclones, but there is no formal written method or a numbered EPA method describing a specific procedure. Cyclones are better suited than impactors for sampling large particles because particle bounce and re-entrainment are less severe. Also, cyclones have the practical advantage that the inlet is at right angles to the axis of the cyclone proper. Hence, the nozzle can be pointed directly into the gas stream and the problem of transporting large particles around bends is absent. Although the flow in cyclones is complicated and no theory exists to predict their behavior adequately, several experimental investigations have been performed demonstrating their utility for separating and sizing small particles (Rusanov 1969; Hochstrasser 1976). The curves of collection efficiency vs. particle diameter for small cyclones can be as steep as those of impactors, and significant re-entrainment has not been observed (Smith 1979; John 1980). One study reports using Standard EPA Method 5 with a cyclone and Method 0060 sampling and analytical procedures to determine total particulate and metal concentrations. Particle-size distributions were determined by electrical mobility and inertial impaction for sampled aerosols and light scattering for in situ in-stack analyses (Linak 1999). Another study describes a system consisting of two cyclones and a filter in series to be used as the primary system for measuring the total particulate concentration and the inhalable particulate concentration in two size fractions. The cyclones were specially designed to encompass the size regions of interest (Smith 1982). Another study used the three cyclones from the High-Volume Source Assessment Sampling System train to collect particulate in four size fractions (Mann 1978), while another paper describes the development and evaluation of a five-stage cyclone sampler, using a series of cyclones with progressively decreasing cut points which performed similarly to impactors (Wilson 1979). There are thus numerous reported applications of cyclones in particle sizing, although there is no specific written method that will produce the particle-size distribution test results needed for use in the ISCST3 model. EPA OSW recommends that the potential user of the cyclone methodology write a procedure for review by the regulating agency and demonstrate that the procedure works effectively for his application.

Without consideration of the method used to collect the particulate matter, there are several methods available to determine particle-size distribution. The cascade impactor and the cyclone estimate the aerodynamic diameter of the particle, whereas the physical measurement methods estimate physical diameter. The particle-size distributions produced by the two methods are not equivalent; one measure cannot be translated into the other without additional information on factors such as particle density and particle shape. However, the ISCST3 model used to perform the risk assessment calculations is not overly sensitive to the difference between aerodynamic diameter and physical diameter. Some examples of analytical instrumentation that can perform particle sizing are:

- The Scanning Mobility Particle Sizer is used for measuring high-resolution size distributions of ultrafine particles in the range from 3 to 1000 nanometers in diameter. The Scanning Mobility Particle Sizer employs an Electrostatic Classifier to determine particle size and a Condensation Particle Counter to determine particle concentrations. The Scanning Mobility Particle Sizer uses an electrical mobility detection technique. During operation, the aerosol sample first passes through a single-stage inertial impactor to remove large particles outside the measurement range. The aerosol next passes through a bipolar ion neutralizer to impart a high level of positive and negative ions. The charged particles then enter a Differential Mobility Analyzer that separates particles according to their electrical mobility. After exiting the Differential Mobility Analyzer, the classified particles enter a Condensation Particle Counter which provides a measure of particle concentration.

- A Coulter Counter is used for rapid, accurate particle counting and sizing. The Coulter Counter provides number, volume, and surface area distributions in one measurement, with an overall range of 0.4 µm - 1200 µm. The Coulter Counter can provide accurate particle counting and size distribution determination on dilute samples, so a dilution system would be necessary to sample a stationary source. The Coulter Method of sizing and counting particles is based on measurable changes in electrical resistance produced by non-conductive particles suspended in an electrolyte. An aperture between electrodes is the sensing zone through which suspended particles pass. In the sensing zone each particle displaces its own volume of electrolyte. Volume displaced is measured as a voltage pulse, with the height of each pulse being proportional to the volume of the particle. Several thousand particles per second are individually counted and sized with great accuracy.

C The Aerodynamic Particle Sizer spectrometer provides aerodynamic size and relative light scattering intensity. The Aerodynamic Particle Sizer spectrometer detects particles in the range from 0.37 to 20 µm, with high-resolution sizing from 0.5 to 20 µm aerodynamic diameter. Time-of-flight particle sizing technology involves measuring the acceleration of aerosol particles in response to the accelerating flow field of a nozzle. The aerodynamic size of a particle determines its rate of acceleration, with larger particles accelerating more slowly due to increased inertia. As particles exit the nozzle, their flight time between two laser beams is recorded and, using a calibration curve, converted to aerodynamic diameter.

C The Scanning Electron Microscope (SEM) focuses a beam of electrons and scans across the sample. The signal from the detected scattered and emitted electrons is used to form a magnified image with better resolution and depth of view than an optical microscope could give. Filter samples are photographed at magnification, and diameter measurements of the individual particles are made. The data can then be processed to produce particle-size distributions. The SEM analysis approach should not be used for particles collected on a glass fiber or quartz filter. A polycarbonate filter has been used successfully in a number of applications. It is important that the filter has sufficient, but not excess, mass. Particle agglomeration can be a problem with SEM. The SEM provides physical particle-size information rather than aerodynamic diameter.

With the exception of the application of SEM and research papers describing applications of the other techniques, the instrumentation described above has not been generally applied to the determination of particle-size distribution in stationary sources. EPA OSW recommends that a facility planning to use this type of instrumentation to perform particle-size distribution determinations supply detailed procedures in the QAPP for the risk burn, so the procedures can be reviewed prior to use, and demonstrate that the procedure works effectively to perform the determination indicated.

B.15 HYDROGEN CHLORIDE AND CHLORINE

EPA OSW has recommended that hydrogen chloride and chlorine be evaluated for potential risks in site-specific risk assessments (EPA 1998a). As part of the risk burn, facilities may need to characterize their stack emissions for HCl and Cl_2.

The following methods are applicable to the determination of hydrogen chloride and chlorine:

- SW-846 Method 0050 (Isokinetic HCl/Cl_2 Emission Sampling Train)
  EPA Method 26A (Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources Isokinetic Method, 40 CFR Part 60 Appendix A)

  Method 0050/26A collects the emission sample isokinetically and is therefore particularly suited for sampling at sources such as those controlled by wet scrubbers that emit acid particulate matter (i.e., HCl dissolved in water droplets). 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. Acidic and alkaline absorbing solutions collect gaseous HCl and Cl_2, respectively. The method has potential for collection of all halogens and halogen acids but has not yet been fully evaluated for that application. For analytical determination of HCl/Cl_2, SW-846 Method 9057 (Determination of Chloride from HCl/Cl_2 Emission Sampling Train (Methods 0050 and 0051) by Anion Chromatography) is used. For analytical determination of additional halides, SW-846 Method 9056 (Determination of Inorganic Anions by Ion Chromatography) is used.

- SW-846 Method 0051 (Midget Impinger HCl/Cl_2 Emission Sampling Train)
  EPA Method 26 (Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources Non-Isokinetic Method, 40 CFR Part 60 Appendix A)

  Method 0051/26 is designed to collect HCl/Cl_2 in their gaseous forms from hazardous waste incinerators and municipal waste combustors. Use of Method 0051 is limited to the sampling of relatively dry, particulate-free gas streams. Sample collection is similar to Method 0050. The method has potential for collection of all halogens and halogen acids but has not yet been fully evaluated for that application. For analytical determination of HCl/Cl_2, SW-846 Method 9057 (Determination of Chloride from HCl/Cl_2 Emission Sampling Train (Methods 0050 and 0051) by Anion Chromatography) is used. For analytical determination of additional halides, SW-846 Method 9056 (Determination of Inorganic Anions by Ion Chromatography) is used.

C EPA Method 320 (Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy, 40 CFR Part 63 Appendix A)

Method 320 applies to the analysis of vapor phase organic or inorganic compounds which absorb energy in the mid-infrared spectral region. The method is used to determine compound-specific concentrations in a multi-component vapor phase sample. Spectra of gaseous emission samples are collected using double beam infrared absorption spectroscopy, and a computer program is used to analyze spectra and determine compound concentrations. Range and sensitivity of the technique are compound-dependent and the ability of FTIR to attain the detection limits needed for risk assessment should be carefully evaluated for each application.

Johnson has summarized research evaluating the use of Methods 0050/0051 for hydrogen chloride and chlorine determinations (Johnson 1996c). Methods 0050/0051 are very sensitive to train operating temperature. If the train is maintained at temperatures below those specified in the method, HCl may condense in the probe/filter assembly and not be reported. Several studies found that operating the sampling train at higher temperatures (170EC [338EF]) increased the precision of the HCl measurement and reduced the loss of HCl in the cyclone. Additional data are also available to show that operating the train at 200EC (400EF) eliminates the negative bias reported when sampling sources containing less than 20 ppmv HCl. However, operating the sampling train at higher temperatures significantly increases the positive bias in the HCl measurement when ammonium chloride is present in the source sample, because breakthrough of ammonium chloride may be enhanced. There are compromises that will be made in the operation of the method on a source-specific basis in order to obtain optimum results using the manual train.

An area of concern repeatedly noted by cement kiln representatives is that HCl determinations based on Methods 0050/0051 or 26/26A could be biased high because volatile particulate chloride salts, such as ammonium chloride, could penetrate the filter and be converted to HCl within the sampling train (Gossman 1997). Industry has proposed correcting the HCl results based upon ion chromatographic analysis of the impinger solutions for cations (Na^+, Ca^{+2}, K^+, and NH_4^+). EPA has considered this issue and, on the basis of the study results summarized by Johnson (Johnson 1996c) and revised standards (EPA 1996f), does not believe that the presence of salts will significantly bias the results. Johnson emphasizes that the correction of HCl results for the presence of other salts is not appropriate, because the ion chromatographic analysis that detects the cations cannot determine in what form the ionic material entered the impingers (Johnson 1996c). The filter specified for use in the sampling train will not pass significant quantities of solid halide salts such as sodium chloride (NaCl), calcium chloride ($CaCl_2$), or potassium chloride (KCl). The presence of sodium, calcium or potassium ions in the impingers could reflect contamination during handling, a torn filter, or operation with a wet filter. These problems can be addressed by use of a cyclone and adequate heating in the sampling train, coupled with careful handling of the sampling train components to minimize contamination.

There is some evidence that it may be possible for ammonium chloride to penetrate the filter in the vapor phase. Under all conditions tested in the laboratory (EPA 1993), the presence of ammonium chloride in the sampled gas introduced a positive bias into the HCl measurement. The positive bias increased when the temperatures of the probe and filter were increased and as the amount of moisture in the sampled stream decreased, and appeared to be independent of the type of filter used in the sampling train. When both HCl and ammonium chloride were present in the sampled gas, a synergistic effect increased the positive bias in the HCl measurement. If ammonium chloride is believed to be the cause of significant bias, then application of an FTIR or infrared (IR) gas-filter correlation (GFC) method for HCl measurement may be considered.

Test Method 321 (Measurement of Gaseous Hydrogen Chloride Emissions at Portland Cement Kilns by Fourier Transform Infrared (FTIR) Spectroscopy, 40 CFR Part 63 Appendix A) and Proposed Test Method 322 (Measurement of Hydrogen Chloride Emissions from Portland Cement Kilns by GFCIR, 40 CFR Part 63 Appendix A) are specifically applicable to the determination of HCl concentrations in emissions from Portland cement kilns. Method 321 relies on Method 320 procedures but is specifically designed for the application of FTIR spectrometry in extractive measurements of gaseous HCl concentrations in Portland cement kiln emissions. Method 322 is an instrumental method for the measurement of HCl using an extractive sampling system and an infrared (IR) gas-filter correlation (GFC) analyzer, and is intended to provide the cement industry with a direct interface instrumental method. Method 322 is considered self-validating provided that the methods for sample collection, preservation, and storage are followed. In the application of Method 322, kiln gas is continuously extracted from the stack or duct using either a source level, hot/wet extractive system or an in-situ dilution probe or heated out-of-stack dilution system. The sample is then directed by a heated sample line maintained above 350EF to a GFC analyzer having a range appropriate to the type of sampling system. The gas filter correlation analyzer incorporates a gas cell filled with HCl. This gas cell is periodically moved into the path of an infrared measurement beam of the instrument to filter out essentially all of the HCl absorption wavelengths. Spectral filtering provides a reference from which the HCl concentration of the sample can be determined. Interferences are minimized in the analyzer by choosing a spectral band over which compounds such as CO_2 and H_2O either do not absorb significantly or do not match the spectral pattern of the HCl infrared absorption.

B.16 PROCESS SAMPLES

EPA OSW recommends that risk burn protocols address analytical procedures for complete characterization of materials to be burned during the risk burn, including wastes, fuels, raw materials, and spike materials. These data define a baseline for the facility with respect to long-term impacts and potential effects on human health and the environment. If there are significant changes to the baseline of the facility, additional risk-based data collection and/or risk analyses may be appropriate.

EPA OSW recommends that the following types of data typically be generated for process samples in the characterization of the stationary source:

- Proximate analysis, or a comparable evaluation, to determine physical properties including moisture, percent solids, heating value, ash, and viscosity or physical form, as well as chemical properties including total organic carbon, total chlorine, total organic halogens, and elemental composition;

- Quantitative analysis of total metals feed rates for the following metals: aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, selenium, silver, thallium, vanadium, and zinc;

- Survey analysis or a comparable evaluation to provide an overall description of the chemistry of the sample in terms of the major types and quantities of organic compounds that are present, as well as identification and quantitation of trace levels of persistent, bioaccumulative and toxic constituents based on GC/MS analysis for VOCs, SVOCS, PCBs and PAHs. As warranted (based on the wastes handled by a particular facility), analysis for pesticides, herbicides, and other facility-specific toxic compounds using standard analytical methods may also be appropriate.

Standard methods for performing inorganic and organic analysis are available in SW-846 (EPA 1996b). For organic analysis, the sample preparation procedures usually involve dilution of the sample with an appropriate solvent (i.e., methanol for VOCs, methylene chloride for SVOCs) until the diluted sample can be subjected to the appropriate analytical procedure using a capillary gas chromatographic column coupled with mass spectrometry (Method 8260 for VOCs, Method 8270 for SVOCs). Standard VOC or SVOC analytical procedures may not be adequate for determining trace components in the presence of very large quantities of major components. If complete characterization of constituents of a process sample is necessary, a sample preparation and analysis scheme will need to be carefully designed by an experienced analytical chemist and approved by the regulating agency.

Another difficulty in application of standard methods lies in the preparation of the waste feed samples for analysis. The chemical and physical nature of process samples is so variable from facility to facility that development of a generic method appropriate for all process samples is not straightforward. The nature of process samples may range from nearly pure organic solvent to oils to tars (both viscous and solidified), and the major analytical problems may arise from handling the samples in the laboratory to produce a diluted/extracted/digested medium which can be subjected to the standard laboratory analytical procedures.

Once the sample has been prepared for analysis, analytical problems can arise from the presence of interferences in the sample. A process sample that contains significant amounts of an organic solvent will need to be diluted until an analysis of the major component can be performed using the calibration range for the analytical instrument. The result of the necessary dilution will be to dilute trace constituents of the process sample below the level at which they can be detected in the analysis. EPA OSW recommends that assistance should be obtained from a well-qualified and experienced analytical chemist who understands the methods involved, as well as the objectives for the risk assessment.

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ATTACHMENT 1

METHOD 0040 CLARIFICATIONS

(3 pages)

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL EXPOSURE RESEARCH LABORATORY
Research Triangle Park, NC 27711

Office of
Research and Development

MEMORANDUM:

DATE: April 3, 1998

SUBJECT: Method 0040 Questions

FROM: Larry D. Johnson
Source Apportionment and Characterization Branch (MD-47)

TO: Catherine Massimino, U.S. EPA Region 10

This memo is to transmit clarifications to the passages of Method 0040 about which you asked questions. I'm also sending it to Beth Antley so she can include the explanations in her new Trial Burn Guidance. Other interested parties are also receiving copies. The appropriate section of M0040 is reproduced below in Arial type. Your question, as understood by me, follows in italics. The answer follows in regular GC Times type. If I misinterpreted or omitted any of the questions, or if the explanations aren't clear, please let me know. Thank you very much for bringing these confusing instructions to our attention.

7.4.3.4 Draw at least eight times the sample volume of flue gas, or purge for at least 10 minutes, whichever is greater.

Isn't eight times the sample volume an unreasonably large amount of purge volume, it takes a long time to carry this out in the field.

You certainly have a good point. The confusion here is that "sample volume" refers to the volume contained in the part of the train being purged (the probe and lines, typically less than a liter) rather than the bag volume of 30-40 liters. Purging 40 liters times 8 at 0.5 liters per minute would take 640 minutes. The 10 minute purge mentioned in the method would give an 8 fold volume exchange for a 0.6 liter train volume (at 0.5 liters per minute). If the train volume is estimated to be larger than 0.6 liters, then the purge time needs to be increased accordingly.

7.6.5.2 Rinse the condenser, the condensate trap and the sample line three times with 10 mL of HPLC grade water and add the rinsings to the measuring cylinder containing the condensate. Record the final volume of the condensate and rinse mixture on the field sampling data form. High moisture sources (such as those with wet control devices) may require a 150-mL or 200-mL measuring cylinder while low moisture sources (such as some rotary kilns and pyrolytic incinerators) may require only a 100-mL size.

Does the method mean 3 rinses of 10 mL each, or three rinses totaling 10 mL?

Three rinses of 10 mL each was the intended instruction. The contractor who wrote and field tested the method, feels that it is difficult to achieve an adequate rinse with much less than 10 mL.

7.6.5.3 Pour the contents of the measuring cylinder into a 20- or 40-mL amber glass VOA vial with a Teflon® septum screw cap. Fill the vial until the liquid level rises above the top of the vial and cap tightly. The vial should contain zero void volume (i.e., no air bubbles). Discard any excess condensate into a separate container for storage and transport for proper disposal.

If three rinses of 10 mL each are carried out, there will always be a minimum of 30 mL of condensate. Why is a 20 mL vial an option? Do you throw out the extra liquid?

The section above does instruct the sampler to discard any excess condensate, so the 20 mL vial would be an option, but not necessarily the best one. If more than 10 mL of actual condensate is collected, even the 40 mL vial would not hold the combined volume. If the analytical method is to use purge-and-trap technology (it usually does), then it is best to discard as little of the liquid as possible. The detection limit may be minimized by purging the target compound from as much of the original volume as possible.

This question also brings up another important point which is inadequately addressed in the method. In Section 7.6.5.2 above, the sampler is instructed to record the final volume of condensate and rinse mixture on the field sampling data form (shown in Figure 6). This volume is called "Total condensate volume" on the form in Fig.6, and becomes V_{lc} as defined (Total volume of liquid collected in the condensate knockout trap) in Section 7.8.2. V_{lc} is used in equation 15 in Section 7.8.9.2 to calculate the amount of target compound collected in the condensate. This whole sequence is all well and good, as long as there is excess condensate, or exactly enough to fill a vial. However, in the case where the condensate and rinses do not completely fill the vial and the vial must be "topped off" with rinse water as described in Section 7.6.5.3, then the vial volume should be used as V_{lc} rather than using the volume measured with the measuring cylinder (and recorded as "Total condensate volume" on the form in Fig. 6).

Example:

Given that the condensate plus rinses makes up 30 mL. If a 20 mL vial is used to ship the sample, then V_{lc} should be 30 mL, since the sample concentration determined in the lab was contained in 30 mL of liquid. If a 40 mL vial was used, then the sample was diluted with 10 mL of water, so V_{lc} must be 40. The lab determined concentration was contained in 40 mL rather than the original 30. In this example, the use of the wrong volume would introduce a negative bias of 25% into the condensate result. The magnitude in actual cases would depend on the dilution ratio. Since 30 mL is pretty much the minimum total volume, as discussed above, the example is likely to be a worst case. Of course, most of the target compound will usually be collected in the bag rather than the condensate, so even a 25% bias in the condensate value might have little effect on the overall results. This just demonstrates, once again, that no matter how many highly competent people write and review a method (and there were quite a few in this case), it takes years of use to discover all the ambiguities and oversights.

cc Beth Antley, Region 4
Bob Fuerst, ORD
Barry Lesnik, OSW
Jeff Ryan, ORD
Gene Riley, OAQPS
Joan Bursey, Eastern Research Group

ATTACHMENT 2

INFORMATION AVAILABLE FROM METHODS 98. STATUS OF STATIONARY SOURCE METHODS FOR AIR TOXICS

(22 pages)

ATTACHMENT 2

INFORMATION AVAILABLE FROM METHODS 98. STATUS OF STATIONARY SOURCE METHODS FOR AIR TOXICS

Comments and Suggestions

The following information is included to give the user of this document perspective on the information contained therein and to aid in decisions regarding its use.

1. The status table contains a summary of the methods type and status for stack sampling and analysis of each of the 189 air toxics listed in the 1990 Clean Air Act Amendments. The table and its attachments have no direct regulatory standing, and therefore do not constitute approval of the use of the methods to satisfy regulatory requirements. Such approval must always be obtained from the regulatory agency or group involved in the individual project. Hopefully this compilation will aid both the regulator and the regulated community in making planning decisions for air toxics source testing.

2. Methods 98 is a May 1998 update and expansion of the 12/14/89 version of the status table, which was originally produced primarily from memory or opinion with the use of only a very few reference texts. An intermediate partial update was produced in 1994, but was not circulated widely. A large amount of field evaluation data has been produced by EPA and its contractors since 1989, and an attempt has been made to utilize all of it in Methods 98. The 1998 status table, therefore, is based much more on field and laboratory test information than were its predecessors. No attempt has been made to perform a comprehensive literature survey and to include field test information from sources outside EPA. It is the author's opinion, however, that very little data from outside sources exist that would meet the criteria needed for useful inclusion in this table. The scope of Methods 98 has been expanded in order to give the user easy access to the papers and reports which contain the information behind the Status Table entries, and compilation tables are included which contain much of the field and laboratory data. Footnotes for each column on the compilation tables lead the reader to a corresponding item on the Reference List. The reference list contains at least one source, usually a report and a paper, for all of the recently generated data and for some of the older studies. The information in the attached tables and the referenced papers is more compact, and is usually much easier to use than that in the reports. The reports provide much more detail. Some, but not all, of the Status Table entries include suggested references. Other references may be identified by scanning the Reference List for appropriate topics.

3. Methods such as 0010 (MM5), 0030 (VOST sampling), 5041/8260 (VOST analysis), and 8270 (GC/MS) are from the SW-846 Methods Manual used by OSW and the Regions for RCRA related work. Method 5, Method 15,and Method 106 are examples of Federal Register Methods historically related to OAQPS air programs. Some of the methods have been promulgated by both groups under different method numbers. Methods and other useful material can be obtained from sources given later in this document. The SW-846 methods listed are the most recent versions, for example 8270C and 5041A. In the future, later versions of the same method should function just as well, or better. In most cases, data obtained with earlier versions of the same method will also be sound, but new tests should always utilize the most recent rendering of the procedure. Methods such as XHCN and XACN are

Office of Research and Development produced methods which have been cleared for publication, but which have not yet been promulgated by one of the program offices. Copies of the "X" methods are included in the corresponding research reports listed in the references.

4 The sampling methods listed are generally intended for relatively low concentrations of materials in stack gases. Alternate methods may be necessary for process streams or flue gases with no control devices. Not all methods that might be effective are included on the table. The Tedlar® bag version of M18 would probably be effective for the same compounds that 0040 sampled well, provided that the source did not emit sorptive particulate matter or condensable water vapor, and that sorption losses in the lines were minimal. The performance of the sorbent tube version of Method 18 would be less easy to predict, and would have little relation to 0040 performance.

5. Priority has been given in this table to methods such as 0010 (a.k.a Modified Method Five, a.k.a. SemiVOST) or Method 29/ Method 0060 (a.k.a. the Multiple Metals Train) which have the most potential for determination of many compounds or metals simultaneously. Alternate single pollutant methods are often given in the comments column. Exclusion of a method from the Status Table does not necessarily imply that it will not perform adequately.

6. Many of the compounds on this list are also on RCRA Appendix 8 but listed under a different name. In cases where common, alternate identities have been identified, these are given in the comments column. No attempt has been made to list all alternate chemical names. In some cases, two inconsistent chemical names or an inconsistent pairing of a name with a CAS number has been given on the CAAA list. Cases such as these have been noted in the Status Table, and the CAS number has been assumed to be the primary reference (*i.e.* the correct CAS number for the compound intended to be regulated). The author has no idea, whatever, what the legal ramifications are of such mistakes in the CAAA.

7. In general the compounds that have identical listings in the sampling column and in the analysis column can be determined simultaneously. Some of the analyses may require more than one GC or HPLC run to accomplish this end.

9. Unless otherwise stated, metals methods produce total Cr, total Pb, etc. Metals oxidation state or compound speciation is always difficult, often impossible, and requires special S&A.

10. Even though much less field data is available for Method 0031 than for Method 0030, the former should always perform at least as well as the latter, and often times better. The limited comparison data generally, but not always, supports this position. The author believes that 0031 can always be successfully substituted for M0030, and usually should be chosen for new projects.

11. The field and laboratory recovery tables have not been included for all compounds or all methods on the Status Table, but there should be at least one reference in the Reference List to support each "f" or "l" listing in the table. The "m" and "s" listings are more conjectural, and may or may not have direct support in the references.

12. Only CAAA toxics are included on the Status Table, but data for a few additional compounds may be found on the results tables.

13. Poor performance of one of the basic methods such as M0010 is often a result of reactivity of the target compound. The relatively non-reactive compounds will consistently show good recoveries, the highly reactive compounds will consistently exhibit very poor recoveries, but the marginally reactive compounds may show variability as a function of the reactivity of the stack gas matrix being sampled. Chloroprene, for example, yielded field test results of f2 and f4 along with l1 laboratory recoveries. Caprolactam actually showed f1, f4, and l1 results. When sampling compounds with a history of mixed performance, it is probably a good idea to spike the sorbent resin (for sorbent methods) with an isotopically labeled recovery standard before sampling. Carbon or chlorine labels are the least likely to exchange to another compound. Method 23 uses a form of this technique, as does M0040.

14. Laboratory recoveries are not usually shown on the Summary Table unless field results were poor, or the laboratory results are at odds with the field results. The code does not indicate how many field results of a given category were obtained, see the compilation tables or the reference documents for that type of information.

15. A number of the CAAA compounds were eliminated from further testing with Methods 0030 and 0010 when they failed initial laboratory studies. This was usually an analytical problem rather than a sampling deficiency. In the major studies which produced the data in the compilation tables, no effort was made to utilize alternate analysis methods. In some cases, potential alternates have been suggested in the Status Table. Method 0010 will collect any organic compound with a boiling point above 100°C. If the compound is not altered by chemical reaction during sampling, field recovery, transport or storage, then identification of a successful quantification scheme becomes a matter of finding effective extraction and determinative analytical methods. The researcher investigating a problem of this nature, should find References 32, 33, 42, 56, 57, and 58 especially helpful.

Status and Recovery Table Code Definitions

R	%Recovery of spiked standard.
C	Method 301 bias correction factor
_	An underlined method is not recommended for the listed air toxic.
?	Effectiveness of the method for the listed air toxic is questionable or showed mixed results.
f1	Data are available from at least one Method 301 field test where 143%$R $76.9% (equivalent to 0.70#C#1.30) and the relative standard deviation (RSD) of R was #50%.
f2	Data are available from at least one Method 301 field test where 150%$R $50% (equivalent to 0.67#C#2.00) and the RSD of R was #50%.
f3	Data are available from at least one field test not fully qualifying as Method 301 where 150%$R $50% (equivalent to 0.67#C#2.00) and the RSD of R was #50%. Some of the recovery data may be better than the minimum shown, and the test may only have failed to meet minimum replicate criteria for full Method 301 statistical analysis.
f4	Data are available from at least one Method 301 field test where R#50% or R$150% or the RSD of R was $50%.
f5	Data are available from at least one field test not fully qualifying as Method 301 where R#50% or R$150% or the RSD of R was $50%.
l1	Laboratory test data are available where full scale sampling equipment, dynamic spiking , and a stack simulator were utilized. The RSD of R was #50%, and 143%$R $76.9% (equivalent to 0.70#C#1.30). This is essentially a successful Method 301 test in the laboratory.
l2	Laboratory test data are available where full scale sampling equipment, dynamic spiking , and a stack simulator were utilized. The RSD of R was #50%, and 150%$R $50% (equivalent to 0.67#C#2.00).
l3	Laboratory test data are available where full scale sampling equipment, dynamic spiking , and a stack simulator were utilized. R#50% or R$150% or the RSD of R was $50% or unknown.
l4	Other laboratory test data are available, where 143%$R $76.9% (equivalent to 0.70#C#1.30) and the RSD of R#50% or unknown. The data from tests in this category may be insufficient to yield a credible RSD.
l5	Other laboratory test data are available, where 150%$R $50% (equivalent to 0.67#C#2.00) and the RSD of R#50% or unknown. The data from tests in this category may be insufficient to yield a credible RSD.

l6	Other laboratory test data are available, where R#50% or R$150% or the RSD of R was $50% or unknown. The data from tests in this category may be insufficient to yield a credible RSD.
l7	Laboratory tests showed no response in VOST analytical system (5041A & 8260B). See References 5, 7, 11, and 16.
l8	Laboratory tests showed weak response in VOST analytical system (5041A & 8260B). See References 5, 7, 11, and 16. Special attention or modification necessary for reliable operation.
s	Should work. For sampling methods, no confirmatory field or laboratory data have been identified, but the structure of the compound or its similarity to validated compounds makes the prognosis optimistic.
m	Might work. This designation usually implies that the technique given should work if the compound survives the sampling and analysis process, but that we have strong reservations about its ability to do so. This status is usually linked with reactivity/instability. Many compounds are stable enough to analyze, but will not tolerate prolonged exposure to water, NO_2, or other materials during sampling.
n	No known adequate method. This always means we know of no reliable method for this pollutant. We usually have identified a number of unreliable methods for the pollutant. **If negative data are available, the sampling method will be underlined**.
sp	Suspected problems. The suspected problem is given in the comments, and is often related to reactivity.
kp	Known problems. This is similar to the suspected problem except that our fears have been confirmed by data. **If data indicate questionable or inconsistent performance, the sampling method will be followed by a question mark.**

CAS No.	Chemical Name	Sampling Method	S. Code	Analysis Method	Comments
75-07-0	Acetaldehyde	0011	f1	8315A	Simultaneous aldehydes possible. Refs. 23, 40
60-35-5	Acetamide	0010	m, sp	8032	May be reactive
75-05-8	Acetonitrile	XACN	f1	8015B 8033	See Refs. 24 & 26.
98-86-2	Acetophenone	0010 0011	f1 f1	3542 8270C 8315A	See References 23 & 40 for 0011.
53-96-3	2-Acetylaminofluorene	0010?	f2, f4, l1	3542 8270C	
107-02-8	Acrolein	0011? PFBHA	f2, kp l4	8315A GC/MS or ECD	Stability/reactivity problems, even in DNPH See references 45 & 50 for PFBHA approach.
79-06-1	Acrylamide	0010	m, sp	GC/MS or 8316	Polar, water soluble. Poor GC, needs work.
79-10-7	Acrylic Acid	0010 sorbent	m, sp l4	8316 GC/FID	Suspect polymerization may be problem Ref 50&54, prototype needs to be isokinetic.
107-13-1	Acrylonitrile	XACN 0030 0031	s s l8	8015B 8033 5041A 8260B	See Refs. 24 & 26. Purges poorly, needs special attention.
107-05-1	Allyl Chloride	0030 kp 0031 kp 0040	f4, l1 f4 f1	5041A 8260B 5041A 8260B 8260B	0030 recoveries good in lab., 30% from field test (suspect reactivity)
92-67-1	4-Aminobiphenyl	0010 acid liquid	m, sp s	GC/MS HPLC/PDA	Ref 50&51.
62-53-3	Aniline	0010? kp acid liquid	f2, f4, l2 l4	3542 8270C HPLC/PDA	Extraction and reactivity problems. Ref 50&51, prototype needs to be isokinetic.
90-04-0	*o*-Anisidine	0010 kp acid liquid	f4, l2 s	3542 8270C HPLC/PDA	Ref 50&51, prototype needs to be isokinetic.
1332-21-4	Asbestos	-	-	microscopy	Separate S&A
71-43-2	Benzene	0030 0040	f1 f1	5041A 8260B 8260B	Make sure that the Tenax is clean.
92-87-5	Benzidine	0010? kp acid liquid	f2, f4, l3 s	3542 8270C HPLC/PDA	May react during sampling. Ref 50&51, prototype needs to be isokinetic.
98-07-7	Benzotrichloride	0010	f2	3542 8270C	
100-44-7	Benzyl Chloride	0010	f1, f2	3542 8270C	
92-52-4	Biphenyl	0010	f1	3542 8270C	
117-81-7	bis(2-Ethylhexyl)phthalate	0010	f2, f4, l1	3542 8270C	a.k.a. DEHP; common contaminant
542-88-1	bis(Chloromethyl)ether	n, kp 0010 kp 0030	f4, l1 l7	3542 8270C	Reacts quickly with water
75-25-2	Bromoform	0010	f1 f2	3542 8270C	
106-99-0	1,3-Butadiene	0040? kp	f4	8260B	Reactive, borderline results.

CAS No.	Chemical Name	Sampling Method	S. Code	Analysis Method	Comments
156-62-7	Calcium cyanamide	0010 M5	s	?	Should be able to collect salt as particulate. Analysis is problematic, low solubility without decomposition.
105-60-2	Caprolactam	0010?	f1, f4, l1	3542 8270C	Mixed results, suspect hydrolysis.
133-06-2	Captan	0010	m	3542 8270C HPLC	Can be reactive.
63-25-2	Carbaryl	0010?	f1, f4, l1	3542 8270C	Mixed results.
75-15-0	Carbon Disulfide	0030?	f2, f4, l2	5041A 8260B	Mixed results.
463-58-1	Carbon Tetrachloride	0030/0031	f1	5041A 8260B	
463-58-1	Carbonyl Sulfide	M15 0040	s	GC/FPD CG/FPD	
120-80-9	Catechol	0010	m	3542 8270C	Careful pH control during extraction mandatory. Recovery may be difficult.
133-90-4	Chloramben	acid liquid	l4	HPLC/PDA	Ref 50&51, prototype needs to be isokinetic
57-74-9	Chlordane	0010	f1	3542 8270C	
7782-50-5	Chlorine	M26/26A 0050 0051	f1	9056 9057	Halogens & halo-acids can be done simultaneously
79-11-8	Chloroacetic Acid	n, sp	n	HPLC	
532-27-4	2-Chloroacetophenone	0010	f1, f2	3542 8270C	
108-90-7	Chlorobenzene	0010 0030? 0031?	f1, f2 f1 f1	3542 8270C 5041A 8260B 5041B 8260B	Above recommended bp limit for 0030/0031, and for 0040.
510-15-6	Chlorobenzilate	0010	f1, f3, f4	3542 8270C	
67-66-3	Chloroform	0030 0031 0040	f1 f1 s	5041A 8260B 5041A 8260B 8260B	
107-30-2	Chloromethyl Methyl Ether	n kp 0030	l7	5041A 8260B	May decompose during s&a
126-99-8	Chloroprene	0030? 0031	f2, f4, l1 f1	5041A 8260B 5041A 8260B	Recoveries good in lab., mixed in field. Suspect reactivity.
1319-77-3	Cresols/Cresylic Acid	-	-	-	Determine as individual cresols by methods following.
95-48-7	*o*-Cresol	0010 NaOH	f1, f2 f1	3542 8270C HPLC	NaOH impinger collection for emissions in the 20-100 ppm range. Refs. 46, 64, & 65.
108-39-4	*m*-Cresol	0010 NaOH	f2 f1	3542 8270C HPLC	NaOH impinger collection for emissions in the 20-100 ppm range. Refs. 46, 64, & 65.

CAS No.	**Chemical Name**	**Sampling Method**	**S. Code**	**Analysis Method**	**Comments**
106-44-5	*p*-Cresol	0010 NaOH	f2 f1	3542 8270C HPLC	NaOH impinger collection for emissions in the 20-100 ppm range. Refs. 46, 64, & 65.
98-82-8	Cumene	0010	f1	3542 8270C	
94-75-7	2,4-D	0010	s	8151A, 8321A	
3547-04-4	DDE	0010	f1	3542 8270C	CAS #3547-04-4 is on CAAA, The large volume pesticide is 72-55-9. The two are similar (almost congeners) and should behave comparably.
334-88-3	Diazomethane	n, kp	-	-	Very reactive. Derivative method should be developed.
132-64-9	Dibenzofurans	0010	f1	3542 8270C	For PCDF, use Method 0023A or Method 23
84-74-2	1,2-Dibromo-3-Chloro-propane	0010	f1, f4	3542 8270C	
84-74-2	Dibutyl phthalate	0010	f1, f4	3542 8270C	Common contaminant
106-46-7	1,4-Dichlorobenzene(*p*)	0010	f1, f2	3542 8270C	
91-94-1	3,3'-Dichlorobenzidine	0010 acid liquid	f4, f5 s	3542 8270C HPLC/PDA	Reactive, no good with 0010. Ref 50&51, prototype needs to be isokinetic.
111-44-4	Dichloroethyl Ether	0010	f1, f2	3542 8270C	Same as bis(2-chloroethyl)ether
542-75-6	1,3-Dichloropropene	0030/0031 0010	f1, f2 f1, f2	5041A 8260B 3542 8270C	Mixed results. May be source sensitive.
62-73-7	Dichlorvos	0010	f1, f2	3542 8270C	
111-42-2	Diethanolamine	n, kp acid liquid	- s	8270 HPLC should work	The method of Ref. 50&51 should collect OK if made isokinetic. No benzene ring, so alternate detector may be needed
91-66-7	N,N-Diethyl aniline	0010 acid liquid	f1, f2 s	3542 8270C HPLC/PDA	Compound confused with Dimethylaniline on CAAA, wrong CAS number listed. Ref. 50&51, prototype needs to be isokinetic.
64-67-5	Diethyl Sulfate	n, kp	-	-	Probably special S&A. a.k.a. sulfuric acid, diethyl ester
119-90-4	3,3'-Dimethoxybenzidine	kp 0010 acid liquid	f4, l3 s	3542 8270C HPLC/PDA	Likely reactive. Ref 50&51, prototype needs to be isokinetic.
60-11-7	Dimethyl- aminoazobenzene	0010? acid liquid	f4, l1 s	3542 8270C HPLC/PDA	Suspect reactivity. Ref 50&51, prototype needs to be isokinetic.
121-69-7	N,N-Dimethylaniline	0010 acid liquid	f2, l1 l4	3542 8270C HPLC/PDA	Incorrectly called diethylaniline on CAAA Ref 50&51, prototype needs to be isokinetic
119-93-7	3,3-Dimethylbenzidine	0010? kp acid liquid	f1, f4, l3 l4	3542 8270C HPLC/PDA	Mixed results probably due to reactivity. Ref 50&51, prototype needs to be isokinetic
79-44-7	Dimethyl Carbamoyl Chloride	0010	m, sp	8321A	
68-12-2	N,N-Dimethylformamide	0010	m, sp	8260B, 8141A	

CAS No.	Chemical Name	Sampling Method	S. Code	Analysis Method	Comments
57-14-7	1,1-Dimethylhydrazine	0030?	kp, l7		Stability problems. Probably needs derivatization method.
131-11-3	Dimethyl Phthalate	0010	f1	3542 8270C	Common contaminant
77-78-1	Dimethyl Sulfate	special	s	special	
534-52-1	4,6-Dinitro-*o*-Cresol, and salts	0010	f1,f2, l3	3542 8270C	Bad lab results are puzzling. This test was for the cresol only, not salts.
51-28-5	2,4-Dinitrophenol	0010?	f1f4l3	3542 8270C	Mixed results, very good to very bad.
121-14-2	2,4-Dinitrotoluene	0010	f1	3542 8270C	
123-39-11	1,4-Dioxane	0010 0030	f1 l7	3542 8270C	a.k.a. 1,4-Diethyleneoxide. Easily lost during extraction and concentration. Labeled lab. recovery standard is mandatory. Water soluble.
122-66-7	1,2-Diphenylhydrazine	0010 acid liquid	m s	GC/MS HPLC/PDA	Reactive. Ref 50&51, prototype needs to be isokinetic.
106-89-8	Epichlorohydrin	0010 kp 0030 kp	f2, f4, l3 l7	3542 8270C	Mostly poor with 0010, worse with 0030. New method needed.
106-88-7	1,2-Epoxybutane	0030	m, sp	5040,(GCMS)	Suspect reactivity problems
140-88-5	Ethyl Acrylate	kp 0030? 0010 sorbent	l8 m, sp l4	GC/MS GC/FID	Polymerizes easily Ref 50&54.
100-41-4	Ethylbenzene	0010	f1	3542 8270C	
51-79-6	Ethyl Carbamate	0010?	f1, f4, l2	3542 8270C	a.k.a. urethane
75-00-3	Ethyl Chloride (Chloroethane)	0030?kp 0031?kp	f2, f4, l1 f4	5041A 8260B 5041A 8260B	Low bp, 0031 should have done better.
106-93-4	Ethylene Dibromide	0010 0030? 0031?	f1, f2 f1, f4, l1 f1	3542 8270C 5041A 8260B 5041A 8260B	a.k.a. dibromoethane. Above recommended bp for 0030/0031.
107-06-2	Ethylene Dichloride	0030 0031	f1, f2 f1	5041A 8260B 5041A 8260B	a.k.a. 1,2-Dichloroethane
107-21-1	Ethylene Glycol	0010	s	8015B, 8430	
151-56-4	Ethylene Imine (Aziridine)	n kp 0030	l7		Water soluble & polymerizes
75-21-8	Ethylene Oxide	Tedlar® bag CARB 431	f3	GC/MS GC/FID	Reactivity can cause problems in some matrices
96-45-7	Ethylene Thiourea	0010	m	HPLC/UV 8325	Reactive and water soluble. See Ref. 56 & 57 for HPLC/UV.

CAS No.	Chemical Name	Sampling Method	S. Code	Analysis Method	Comments
75-34-3	1,1-Dichloroethane (misnamed Ethylidene Dichloride on CAAA)	0030 0031 0040	f1, f2 f1 f1	5041A 8260B 5041A 8260B 8260B	75-34-3 is really 1,1-Dichloroethane. Ethylidene dichloride is 75-35-4
50-00-0	Formaldehyde	0011	f1	8315A	Simultaneous aldehydes possible, ref. 23&40
76-44-8	Heptachlor	0010	f1, f4, l1	3542 8270C	
118-74-1	Hexachlorobenzene	0010	f1, f2 f4	3542 8270C	Recovery increased greatly with each field test. Last one was 82.6%
87-68-3	Hexachlorobutadiene	0010	f1, f2	3542 8270C	
77-47-4	Hexachlorocyclopentadiene	0010	f2 f4	3542 8270C	Good to mediocre field tests, poor in the lab.
67-72-1	Hexachloroethane	0010	f1	3542 8270C	
822-06-0	Hexamethylene-1,6-diisocyanate	M207-1	f1	M207-2	Reactive, a.k.a. 1,6-Diisocyanatohexane a.k.a. HDI
680-31-9	Hexamethylphosphoramide	0010	f4 l3	3542 8270C	Suspect reactivity
110-54-3	Hexane	0030 0040	f1 f1	5041A 8260B 8260B	
302-01-2	Hydrazine	0010	kp	GC/MS	Water soluble & unstable, probably requires special S&A
7647-01-0	Hydrochloric Acid	M26/26A 0050 0051	f1	9056 9057	Halogens & halo-acids can be done simultaneously
7664-39-3	Hydrogen Fluoride	M26/26A	l4	9057	Methods 13A,13B,14 for total fluoride
123-31-9	Hydroquinone	0010	m, sp	GC/MS	Reactive, solubility problems.
78-59-1	Isophorone	0010 0011	f1 f1	3542 8270C 8315A	
58-89-9	Lindane (all isomers)	0010	f1	3542 8270C	a.k.a. hexachlorocyclohexane
108-31-6	Maleic Anhydride	0010	s, kp	HPLC	Reacts with water, must quantitate the acid & report as parent compound
67-56-1	Methanol	0030? M308 MST	m, sp f1 f1	5041A 8260B GC/FID GC/FID	Highly water soluble, may purge poorly See References 59, 60, & 61 for evaluation of M308 and MST.
72-43-5	Methoxychlor	0010	f2	3542 8270C	
74-83-9	Methyl Bromide	0030?kp 0031?kp 0040?kp	f2 f4 f4	5041A 8260B 5041A 8260B 8260B	a.k.a. bromomethane. 0030 barely met f2, 0031 should be better, but was worse. Low bp. 0040 results high.
74-87-3	Methyl Chloride (Chloromethane)	0030 kp 0031 kp 0040	f4 f4 f1	5041A 8260B 5041B 8260B 8260B	Artifact problems with Tenax®.
71-55-6	Methyl Chloroform	0030/0031 0040	f1 f1	5041A 8260B 8260B	a.k.a. 1,1,1-trichloroethane

CAS No.	**Chemical Name**	**Sampling Method**	**S. Code**	**Analysis Method**	**Comments**
78-93-3	Methyl Ethyl Ketone (2-Butanone)	0011 0030? PFHBA	f4 l8 l4	8315A 5041A 8260B GC/MSorECD	Water solubility causes problems with 5041A purge. See References 45 & 50 for PFBHA approach.
60-34-4	Methyl Hydrazine	0030	kp	5040	Reactive, probably requires special S&A
74-88-4	Methyl iodide	0030/0031	f1	5041A 8260B	a.k.a. Iodomethane
108-10-1	Methyl Isobutyl Ketone (Hexone)	0010 0011 PFBHA kp 0030?	f1 f4 l4 l8	3542 8270C 8315A GC/MSorECD	See references 45 & 50 for PFBHA approach, 23 & 40 for DNPH (0011).
624-83-9	Methyl Isocyanate	M 207-1	f1	M207-2	a.k.a. isocyanic acid, methyl ester, a.k.a. MI. See Ref. 18.
80-61-6	Methyl Methacrylate	0010 kp 0030? sorbent	m, sp l8 l4	5040,(GC/MS) GC/FID	May polymerize Ref 50&54.
1634-04-4	Methyl *Tert* Butyl Ether	kp 0030?	l8		a.k.a. *tert*-butyl methyl ether
101-14-4	4,4'-Methylene bis(2-Chloroaniline)	0010 acid liquid	m, sp s	GC/MS HPLC/PDA	Suspect reactivity problems during sampling. Ref 50&51, prototype needs to be isokinetic.
75-09-2	Methylene Chloride (dichloromethane)	0030/0031 0040	f1 f1	5041A 8260B 8260B	a.k.a. dichloromethane
101-68-8	Methylene Diphenyl Diisocyanate	M207-1	f1	M207-2	Reactive, See Ref. 18. a.k.a. MDI,a.k.a. 4,4'-bis(Carbonylamino)diphenylmethane.
101-77-9	4,4'-Methylenedianiline	0010 acid liquid	m, sp s	GC/MS HPLC/PDA	Reactive? Ref 50&51, prototype needs to be isokinetic.
91-20-3	Naphthalene	0010	f1	3542 8270C	
98-95-3	Nitrobenzene	0010	f1	3542 8270C	
92-93-3	4-Nitrobiphenyl	0010	f1	3542 8270C	
100-02-7	4-Nitrophenol	0010	f1, f2, l3	3542 8270C	Bad lab results are puzzling.
79-46-9	2-Nitropropane	0010,0030	s	GC/MS	
684-93-5	N-Nitroso-N-Methylurea	0010	m, sp	HPLC	Unstable
62-75-9	N-Nitrosodimethylamine	0010	f1	3542 8270C	
59-89-2	N-Nitrosomorpholine	0010	f1	3542 8270C	
56-38-2	Parathion	0010	f1, f2	3542 8270C	
82-68-8	Pentachloronitrobenzene	0010	f1, f3, f4	GC/MS	
87-86-5	Pentachlorophenol	0010	f1, f3, f4	3542 8270C	
108-95-2	Phenol	0010 NaOH	f1, f2 f1	3542 8270C HPLC	NaOH impinger collection for emissions in the 20-100 ppm range. Refs. 46, 64, & 65.

CAS No.	Chemical Name	Sampling Method	S. Code	Analysis Method	Comments
106-50-3	*p*-Phenylenediamine	0010 acid liquid	m, sp s	GC/MS HPLC/PDA	Reactive, polar, water soluble. Ref 50&51, prototype needs to be isokinetic.
75-44-5	Phosgene	XPHS	l1	GC/MS	Reactive, must be derivatized as collected. See Refs. 52 & 53.
7803-51-2	Phosphine	M29 0060	s	6010 6020 7000	Yields total P value
7723-14-0	Phosphorus	M29 0060	s	6010 6020 7000	Yields total P value
85-44-9	Phthalic anhydride	0010 0010 kp	s f4, l3	HPLC 3542 8270C	Reacts with water, must quantitate the acid & report as parent compound
1336-36-3	Polychlorinated Biphenyls (Aroclors)	0010 CARB 428	s	3542 GC/MS CARB 428	Combustion destroys Aroclor patterns. Determine isomer groups or individuals.
1120-71-4	1,3-Propane Sultone	0010	m	GC/MS	Polar and reactive.
57-57-8	â-Propiolactone	0010	m, sp	GC/MS	May be too reactive
123-38-6	Propionaldehyde	0011	f1	8315A	Simultaneous aldehydes possible. Ref.23&40
114-26-1	Propoxur	0010	f1, f2	3542 8270C	a.k.a. Baygon
78-87-5	Propylene Dichloride	0030 0031	f1, f2 f1	5041A 8260B 5041A 8260B	a.k.a. 1,2 dichloropropane
75-56-9	Propylene Oxide	kp 0030 0040	l7 m, sp		Reactive, water soluble, a.k.a. 1,2-Propylene oxide
75-55-8	1,2-Propylenimine	n kp 0030	l7		May be reactive
91-25-5	Quinoline	0010 acid liquid	f1 l4	3542 8270C HPLC/PDA	Ref 50&51, prototype needs to be isokinetic
106-51-4	Quinone	0010 0011?	f4, l3, kp f2,kp	3542 8270C 8315A	May be reactive,a.k.a. 1,4-benzoquinone,a.k.a. *p*-benzoquinone
100-42-5	Styrene	0010?	f1, f4, l1	3542 8270C	Low f4 results puzzling. Reactivity?
96-09-3	Styrene Oxide	0010 kp	f4, l3	3542 8270C	Reactive. a.k.a. 1,2-epoxyethylbenzene
1746-01-6	2,3,7,8-Tetrachlorodibenzo-*p*-Dioxin	M23 0023A	f1	M23 8290	Special care needed during recovery and analysis.
79-34-5	1,1,2,2-Tetrachloroethane	0010	f1	3542 8270C	
127-18-4	Tetrachloroethylene	0010 0030/0031	f2 f1, f2	3542 8270C 5041A 8260B	a.k.a. tetrachloroethene,.a.k.a perchloroethylene
7550-45-0	Titanium Tetrachloride	M29 0060	s	6010 6020 7000	For total titanium
108-88-3	Toluene	0010 0030 0040	f1, f2 f1 f1	3542 8270C 5041A 8260B 8260B	

CAS No.	**Chemical Name**	**Sampling Method**	**S. Code**	**Analysis Method**	**Comments**
95-80-7	2,4-Toluene Diamine	0010 acid liquid	m, sp l4	GC/MS HPLC/PDA	Reactive Ref 50&51, prototype needs to be isokinetic.
584-84-9	2,4-Toluene Diisocyanate	M207-1	f1	M207-2	Reacts with water,a.k.a. TDI
95-53-4	*o*-Toluidine	0010? acid liquid	f2, f4, l1 l4	3542 8270C HPLC/PDA	Mixed results, may be reactive. Ref 50&51, prototype needs to be isokinetic.
8001-35-2	Toxaphene (Chlorinated Camphene)	0010	s	GC/MS,8250	
120-82-1	1,2,4-Trichlorobenzene	0010	f1, f2	3542 8270C	
79-00-5	1,1,2-Trichloroethane	0010 0030/0031 0040	f1, f2 f1 f1	3542 8270C 5041A 8260B 8260B	
79-01-6	Trichloroethylene	0030/0031	f1	5041A 8260B	a.k.a. trichloroethene
95-95-4	2,4,5-Trichlorophenol	0010	f1	3542 8270C	
88-06-2	2,4,6-Trichlorophenol	0010	f1, f2	3542 8270C	
121-44-8	Triethylamine	n kp 0030 acid liquid	l7 s	HPLC should work	a.k.a. N,N-Diethylethanimine. Suspect reactivity. The method of Ref. 50&51 should collect OK. No benzene ring, so alternate detector may be needed
1582-09-8	Trifluralin	0010 acid liquid	f4, l2, kp m, kp	3542 8270C HPLC/PDA	Suspect reactivity, a.k.a. Treflan Ref 50&51, prototype needs to be isokinetic. Analysis method needs modification.
540-84-1	2,2,4-Trimethylpentane	0030 0040	f2 f1	5041A 8260B 8260B	a.k.a. isooctane
108-05-4	Vinyl Acetate	kp 0030? sorbent	l8 l4	GC/FID	Ref 50&54.
593-60-2	Vinyl Bromide	0030?kp 0031?kp 0040 M106	f2, f4, l1 f4 f1	5041A 8260B 5041A 8260B 8260B GC/MS	
75-01-4	Vinyl Chloride	0030 kp 0031? kp 0040 M106	f1, f4, l1 f4 l1 f1 l5	5041A 8260B 5041A 8260B 8260B GC/MS	Mixed results, 0030 is questionable. Poor field results for 0031 are puzzling, may be due to reactivity.
75-35-4	Vinylidene Chloride	0030/0031 0040 M106	f1/f1 f1 l5	5041A 8260B 8260B GC/MS	a.k.a. 1,1-dichloroethene. a.k.a. 1,1-dichloroethylene
1330-20-7	Xylenes(mixture)	0010	f1	3542 8270C	Determine individual xylenes, not total.
95-47-6	*o*-Xylene	0010	f1	3542 8270C	
108-38-3	*m*-Xylene	0010	f1	3542 8270C	
106-42-3	*p*-Xylene	0010	f1	3542 8270C	

CAS No.	Chemical Name	Sampling Method	S. Code	Analysis Method	Comments
-	Antimony Compounds	M29 0060	f1	6010 6020 7000	
-	Arsenic Compounds	M29 0060	f1	6010 6020 7000	Also Method 108 & 108A
-	Beryllium Compounds	M29 0060	f1	6010 6020 7000	Also Method 103 & 104
-	Cadmium Compounds	M29 0060	f1	6010 6020 7000	
-	Chromium Compounds	M29 0060	f1	6010 6020 7000	M29 or 0060 for total chromium, 0061 for hexavalent Cr.
-	Cobalt Compounds	M29 0060	s	6010 6020 7000	
-	Coke Oven Emissions	Method 109	-	-	
-	Cyanide Compounds	XHCN	l1	XHCN	XHCN for HCN, CARB426 for total cyanide.
-	Glycol Ethers	n 0010	- s	- 8430, 8015B	Category too general, however a method is possible for individual compounds. Should be isokinetic, probably 0010.
-	Lead Compounds	M29 0060	f1	6010 6020 7000	Also Method 12
-	Manganese Compounds	M29 0060	f1	6010 6020 7000	
-	Mercury Compounds	M29 0060	f1	7470	Also Methods 101,101A,102. For speciation research see references 50 & 55.
-	Mineral Fibers				
-	Nickel Compounds	M29 0060	f1	6010 6020 7000	
-	Polycyclic Organic Matter	0010 CARB 429	f3	3542 8270C CARB 429	Individual compounds are determined, not total POM, more or less synonymous with PNA, PAH, pac.
-	Radionuclides (including radon)	M111 M114 M115			
-	Selenium Compounds	M29 0060	f1	6010 7000	

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