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Risk Burn Guidance for Hazardous Waste Combustion Facilities

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RISK BURN GUIDANCE FOR HAZARDOUS WASTE COMBUSTION FACILITIES

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ACRONYM LIST

μg/dL	Micrograms per deciliter
$\mu g/m^3$	Micrograms per cubic meter
APCD	Air pollution control device
ASME	American Society of Mechanical Engineers
ATSDR	Agency for Toxic Substances and Disease Registry
AWFCO	Automatic waste feed cutoff
BIF	Boiler and industrial furnace
Btu	British thermal unit
CEMS	Continuous emissions monitoring system
CFR	Code of Federal Regulations
Cl_2	Molecular chlorine
COPC	Compound of potential concern
CSF	Carcinogenic slope factor
D/F	Dioxin and furan
DQO	Data quality objective
DRE	Destruction and removal efficiency
dscm	Dry standard cubic meter
EDL	Estimated detection limit
EER	Energy and Environmental Research Corporation
EMPC	Estimated maximum possible concentration
EPA	U.S. Environmental Protection Agency
ESP	Electrostatic precipitator
FGC	Field gas chromatography
GC	Gas chromatography
g/cm^3	Grams per cubic centimeter
grains/dscf	Grains per dry standard cubic foot
GRAV	Gravimetric
HCl	Hydrogen chloride

ACRONYM LIST (Continued)

HEAST	Health Effects Assessment Summary Tables
HEPA	High efficiency particulate air
HRA	Hourly rolling average
IRIS	Integrated Risk Information System
IWS	Ionizing wet scrubber
MACT	Maximum achievable control technology
MDL	Method detection limit
mg/dscm	Milligrams per dry standard cubic meter
mg/kg	Milligrams per kilogram
MS	Mass spectrometry
ng	Nanograms
NAAQS	National Ambient Air Quality Standard
OSW	Office of Solid Waste
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PCC	Primary combustion chamber
PIC	Product of incomplete combustion
POHC	Principal organic hazardous constituent
ppm	Parts per million
ppmv	Parts per million volume
QAPP	Quality assurance project plan
RAC	Reference air concentration
RCRA	Resource Conservation and Recovery Act
RDL	Reliable detection limit
RfC	Reference concentration
RfD	Reference dose
RME	Reasonable maximum exposure

ACRONYM LIST (Continued)

RTI	Research Triangle Institute
SCC	Secondary combustion chamber
SQL	Sample quantitation limit
SRE	System removal efficiency
TCO	Total chromatographable organics
TEQ	Toxic equivalents
TIC	Tentatively identified compound
TOE	Total organic emissions
U/BK	Uptake/biokinetic
WESP	Wet electrostatic precipitator

CHAPTER 1

INTRODUCTION

This document contains the U.S. Environmental Protection Agency (EPA) Office of Solid Waste's (OSW's) recommendations regarding stack emissions tests which may be performed at hazardous waste combustion facilities for the purpose of supporting multi-pathway, site-specific risk assessments, where such a risk assessment has been determined to be necessary by the permit authority. When a site-specific risk assessment will be performed as part of the Resource Conservation and Recovery Act (RCRA) permit decision for a hazardous waste combustion facility, the supporting emissions data may be collected in conjunction with a RCRA trial burn. The emissions data may also be collected during a test event separate from the RCRA trial burn, such as a Maximum Achievable Control Technology (MACT) performance test or other test. This guidance identifies the types of emissions data that EPA OSW recommends be collected to support site-specific risk assessments. The guidance recommends combustor operating and feed conditions that should generally be demonstrated during the testing, and identifies stack sampling and analytical techniques for collection of the emissions data. In addition, the relationship between test conditions and potential RCRA permit conditions is discussed.

Hazardous waste combustors include hazardous waste incinerators, as well as boilers and industrial furnaces (BIFs) that burn hazardous waste for energy or material recovery. Portions of this guidance may also be useful for emissions test efforts at thermal treatment facilities (other than incinerators and BIFs) conducting multi-pathway, site-specific risk assessments, as determined appropriate under 40 Code of Federal Regulations (CFR) Sections 264.601 and 264.602.

Multi-pathway human health and ecological risk assessments may be performed for hazardous waste combustion facilities to assess potential risks associated with direct and indirect exposures to:

- Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans, known collectively as dioxins and furans (D/Fs);
- Organic emissions (volatile, semivolatile, and nonvolatile) other than D/Fs, often referred to as products of incomplete combustion (PICs);
- Metals that are potentially toxic to human or ecological receptors;
- Hydrogen chloride (HCl) and molecular chlorine (Cl_2);

(EPA 1998a, 1999a and 1999b). Direct exposures include exposures via the inhalation pathway (EPA 1998a). Indirect exposures include exposures from contact of human and ecological receptors with soil, plants or waterbodies on which an emitted chemical has been deposited, resulting in bioaccumulation and food chain effects (EPA 1998a).

Performance of a site-specific risk assessment can provide the information necessary to determine what, if any, additional conditions in the RCRA permit may be necessary for each situation to ensure that operation of the combustion unit is protective of human health and the environment (EPA 1998a). These additional conditions may include, for example, emissions limits (such as limits on D/Fs, metals, or other site-specific compounds), process operating conditions, waste feed limitations, or expanded environmental monitoring (EPA 1998a).

1.1 USE OF THIS DOCUMENT

This document contains EPA OSW's recommendations regarding stack emissions tests which may be performed at hazardous waste combustion facilities for the purpose of supporting multi-pathway, site-specific risk assessments. This document does not provide recommendations regarding whether a site-specific risk assessment should be performed for a particular hazardous waste combustion facility, nor is it intended to provide guidance about how to conduct a site-specific risk assessment or make risk management decisions. It is recommended that users of this document consult other documents regarding risk assessment and risk management issues. The preamble to the hazardous waste combustion MACT rule published on September 30, 1999 (64 *Federal Register* 52828) contains EPA's most recent recommendations regarding when or if a site-specific risk assessment should be considered. EPA OSW

guidance for how to conduct a multi-pathway human health and ecological risk assessment is available in peer review draft form (EPA 1998a, 1999a, 1999b). And, EPA OSW's recommended risk and hazard targets that may be used when making risk management decisions are provided in an earlier guidance (EPA 1994a). Additional risk target information is also available (EPA 1998b). Many of the recommendations included in the MACT rule preamble and the human health/ecological risk assessment documents are also identified in this document for the convenience of the reader. However, this document is not intended to update, revise or replace the information contained in those documents. Revisions to the human health and ecological risk assessment documents are in progress, and more recent versions should be consulted when available. Other combustion risk assessment guidance (e.g., Research Triangle Institute [RTI] 1997) may also be consulted.

This document updates and replaces the following guidance documents related to emissions testing which may be performed for the purpose of supporting multi-pathway, site-specific risk assessments:

- U.S. EPA. *Guidance on Trial Burns.* June 2, 1994 Draft.
- U.S. EPA. *Guidance on Structuring RCRA Trial Burns for Collection of Risk Assessment Data.* May 2, 1997 and September 1997 Drafts.
- U.S. EPA. *Guidance on Collection of Emissions Data to Support Site-Specific Risk Assessments at Hazardous Waste Combustion Facilities.* Peer Review Draft. EPA530-D-98-002. August 1998.

This guidance is not intended to update, revise or replace any RCRA or MACT regulatory requirements pertaining to stack emissions testing, or the guidance documents which have been developed to support implementation of those requirements. Examples of guidance documents which are not superseded include:

- U.S. EPA. *Handbook: Guidance on Setting Permit Conditions and Reporting Trial Burn Results. Volume II of the Hazardous Waste Incineration Guidance Series.* Office of Research and Development. EPA/625/6-89/019. January 1989.
- 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.

- 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.

- U.S. EPA. *Technical Implementation Document for EPA's Boiler and Industrial Furnace Regulations.* Office of Solid Waste and Emergency Response. EPA-530-R-92-011. March 1992.

- U.S. EPA. *Final Technical Support Document for Hazardous Waste Combustor MACT Standards, Volume IV: Compliance with the MACT Standards.* Office of Solid Waste and Emergency Response. July 1999.

This document provides guidance to EPA regional and state permitting authorities on how best to implement statutory and regulatory provisions that concern permitting decisions for hazardous waste combustion facilities under the RCRA program. In particular, this document provides guidance regarding activities carried out pursuant to RCRA § 3005(c)(3), the "omnibus" authority, as codified in 40 CFR § 270.32(b)(2) and 40 CFR § 270.10(k). For EPA's explanation of the Agency's authority to carry out, or require, these activities, please refer to EPA OSW's guidance for how to conduct multi-pathway human health and ecological risk assessments (EPA 1998a and 1999a) and the preamble to the hazardous waste combustion MACT rule (EPA 1999c). This document is not intended to provide any new interpretations regarding the "omnibus" authority or any other statutory or regulatory authority, nor is it intended to reopen for consideration any statutory or regulatory interpretation in the risk assessment guidance documents (EPA 1998a and 1999a), the preamble to the MACT rule (EPA 1999c), or any other document.

This document describes statutory provisions and EPA regulations which are legally binding requirements. It does not substitute for those provisions or regulations, nor is it a regulation itself. Thus, it does not impose legally binding requirements on EPA, States, or the regulated community. Any decisions made regarding a particular facility will be made based on the statute and the regulations. EPA and State regulatory authorities retain the discretion to adopt approaches on a case-by-case basis that differ from this guidance. Therefore, interested parties are free to raise questions and objections about substance of this guidance and the appropriateness of any recommendations in the guidance with respect to a particular situation, and the regulatory authorities will consider whether or not the recommendations in the guidance are appropriate in that situation. This guidance is a living document, and may be updated without public

notice. EPA OSW welcomes public comments on this document at any time and will consider those comments in any future revision of this document.

1.2 OBJECTIVES

The objectives of this guidance are to:

1. **Provide recommendations to ensure the collection of adequate data to support completion of technically sound human health and ecological risk assessments.** Specific risk assessment data needs generally include: (1) D/F emission rates, (2) emission rates for organics other than D/Fs, (3) metals emission rates, (4) site-specific particle-size distribution data, and (5) emission rates for HCl and Cl_2. These data needs are discussed in detail in Chapter 2, and sampling and analytical procedures are discussed in Appendix B. Other risk assessment data needs can be addressed on a site-specific basis, and can include compounds such as radionuclides or other criteria pollutants not specifically addressed in this guidance. Additional discussion of these other compounds can be found in the EPA OSW risk assessment guidance (EPA1998a).

2. **Identify considerations associated with selection of appropriate test conditions for collection of emissions data supporting a site-specific risk assessment.** The emissions data to support a site-specific risk assessment may be collected in conjunction with a RCRA trial burn or a MACT performance test, where "worst-case" operating conditions are targeted to maximize emissions. It may also be appropriate to collect the emissions data during a separate test conducted exclusively for collection of risk assessment data, where the combustor might be operated under conditions representing long-term average, or normal, operations. Selection of appropriate test conditions for collection of risk assessment data is discussed in detail in Chapter 3.

3. **Identify key control parameters that may influence emissions of D/Fs, organics other than D/Fs, metals and HCl/Cl_2.** Feed and operating control parameters that should generally be demonstrated during the emissions testing and which may be limited by the final permit are identified and discussed. This guidance also identifies inherent design differences between hazardous waste burning incinerators, boilers, cement kilns, and lightweight aggregate kilns, and accounts for these differences in recommending control parameters to be limited under RCRA. Key control parameters related to emissions of D/Fs, organics other than D/Fs, metals, and HCl and Cl_2 emissions are discussed in Chapters 4, 5, 6, and 7, respectively. Particle-size distribution is discussed in Chapter 7.

4. **Provide recommendations regarding how to report emissions data and how to evaluate various emission scenarios in the risk assessment.** These issues are discussed in Chapter 8, and are illustrated by the examples in Appendix A.

5. **Identify additional permit terms that may be included in the final RCRA permit based upon evaluation of the risk burn results and risk assessment.** These issues are discussed in Chapters 3

through 9, and are illustrated by the examples in Appendix A.

Although general guidelines are provided, this guidance cannot encompass every potential situation. Permit writers are encouraged to consider facility-specific circumstances that may not be fully addressed.

1.3 REGULATORY REVIEW

This section provides summary information to explain how emissions tests and risk assessments factor into the RCRA regulatory framework for hazardous waste combustion facilities. First, background information on RCRA performance standards and trial burns is provided. Potential limitations of the RCRA regulations are identified, and the use of site-specific risk assessments to supplement those regulations is discussed. Finally, MACT standards for hazardous waste combustion facilities (EPA 1999c) are introduced briefly, and the relationship between the MACT standards and site-specific risk assessments is explained. This review is minimal and provided only for the convenience of the reader. Cited references should be consulted. Terms are defined in Section 1.4.

1.3.1 RCRA Performance Standards and Trial Burns

Performance standards for hazardous waste incinerators are described in Title 40 of the Code of Federal Regulations (CFR) Part 264, Subpart O. These standards were promulgated on January 23, 1981, and have been subsequently amended. The performance standards consist of the following: (1) a destruction and removal efficiency (DRE) of principal organic hazardous constituents (POHCs) of 99.99 percent, or 99.9999 percent for dioxin-listed wastes; (2) particulate matter emissions not to exceed 180 milligrams per dry standard cubic meter (mg/dscm) or 0.08 grains per dry standard cubic foot (grains/dscf), corrected to 7 percent oxygen; and (3) gaseous HCl emissions not to exceed 1.8 kilograms per hour or a removal efficiency of 99 percent. Compliance with these performance standards is generally established through a carefully designed trial burn (see 40 CFR § 270.62). Trial burns are typically conducted at extreme "worst-case" operating conditions of the unit in order to define the maximum operating range (or operating envelope) that assures compliance. Testing at "worst-case" conditions generally involves at least one

performance test condition conducted at a minimum combustion temperature to demonstrate DRE. Additional test conditions may be necessary to resolve potential conflicts between operating parameters. As long as the incinerator continues to operate within the operating envelope demonstrated during a successful trial burn, it is presumed to be in compliance with the regulatory performance standards.

Ongoing compliance with the three performance standards is generally assured by developing limits for the following control parameters, as specified in 40 CFR § 264.345:

- Minimum combustion temperature in the primary combustion chamber (PCC) and secondary combustion chamber (SCC), to assure sufficient temperatures for destruction of organics;
- Maximum flue gas flow rate (or velocity) and maximum waste feed rate, to assure sufficient residence time for destruction of organics and to prevent incomplete combustion due to waste overcharging;
- Carbon monoxide concentration in exhaust gas, as an ongoing indicator of combustion efficiency;
- Other operating requirements as necessary to ensure that performance standards are met.

Control parameters are important because performance measures, such as DRE, cannot be directly and continuously monitored after the trial burn. The control parameters provide a means for continuously assuring that operations remain within the range demonstrated during the trial burn. Guidance pertaining to these parameters has been provided previously (EPA 1983 and 1989) and is not repeated here. EPA's 1989 guidance also addresses the importance of establishing operating parameters for air pollution control devices (APCDs), including wet and dry scrubbers, fabric filters, and electrostatic precipitators (ESPs). APCD parameters include minimum and maximum pressure drops, temperatures, flow rates, pH, and power.

Standards for BIFs, including boilers, cement kilns and lightweight aggregate kilns that use hazardous waste as a fuel source, are found in 40 CFR Part 266, Subpart H. These standards were published on February 21, 1991. 40 CFR Part 266, Subpart H requires that BIFs comply with a DRE performance standard as well as emission standards for metals, HCl, Cl_2, particulate matter, carbon monoxide, and total

hydrocarbons. The February 21, 1991 rule also subjected BIFs to the general permitting provisions applicable to incinerators, including the requirement to submit a RCRA Part B permit application.

The BIF standards for 10 metals (antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium), as well as for HCl and Cl_2, were developed to limit risks from the inhalation exposure pathway. Standards for the carcinogenic metals arsenic, beryllium, cadmium, and hexavalent chromium are based on an aggregate (all carcinogenic metals) maximum potential excess lifetime carcinogenic risk for an individual of no greater than 1 in 100,000 (1E-5) from the direct inhalation exposure pathway. BIF standards for metals causing health effects other than cancer are based on oral reference doses (RfDs) converted to reference air concentrations (RACs) or published reference concentrations (RfCs) in air. Standards for lead are based on 10 percent of the National Ambient Air Quality Standard (NAAQS). HCl and Cl_2 emission rate limits are based on RfCs and RACs. RACs are also available for nickel and selenium, and these metals have sometimes been limited in addition to the BIF metals as necessary to protect human health and the environment (EPA 1992a).

Organic emissions from BIFs are controlled using a DRE standard (the same standard as for incinerators) and by limiting carbon monoxide (and in some cases total hydrocarbon) concentrations in stack gas (40 CFR Part 266 Subpart H; EPA 1992b). The BIF rule also recognizes that hazardous waste combustors equipped with dry APCDs operating between 450 and 750 °F may emit higher concentrations of D/Fs than units equipped with other types of APCDs. 40 CFR Part 266 Subpart H requires risk evaluations for BIFs equipped with dry APCDs operating at 450 to 750 °F to demonstrate that total cancer risk (including D/Fs) is less than 1E-5 for the inhalation exposure pathway.

The regulation of metals under the BIF rule led to the need for an additional performance test condition at some facilities, conducted at a high combustion temperature, in order to maximize metal volatility. Thus, under the BIF rule, the combustor operating envelope may be defined by a low-temperature test to demonstrate DRE and a high-temperature test to demonstrate system removal efficiency (SRE) for metals. Operating limits to control metals that are generally established based on the SRE test condition include maximum combustion temperature, maximum metals feed rates, and appropriate APCD operating parameters (e.g., temperature, pressure drop, flow rate, or power). The BIF rule requires that maximum

metal and chlorine feed rates be established using one of the following approaches: Tier I (assuming zero SRE without site-specific air dispersion modeling), Adjusted Tier I (assuming zero SRE with site-specific air dispersion modeling), Tier II (based on emissions data without site-specific air dispersion modeling), or Tier III (based on emissions data with site-specific air dispersion modeling). Owners and operators of BIFs may choose to spike the wastes used during the SRE test with metals and chlorine to demonstrate performance at maximum feed rates. Spiking helps to ensure that sufficiently flexible metal and chlorine feed rate limits are established. Similar provisions have been applied at hazardous waste incinerators as necessary to protect human health and the environment.

EPA trial burn and technical guidance documents for incinerators and BIFs (EPA 1983, 1989 and 1992b) describe control parameters typically monitored during trial burn testing. The 1989 document categorizes these control parameters (monitored during DRE or SRE conditions) as Group A, B, or C. Short-term limits, such as hourly rolling averages (HRAs) and instantaneous limits, are typically established for these parameters in the facility's RCRA permit. The Group A, B, and C designations are reviewed below.

Group A control parameters are generally continuously monitored while hazardous waste is being fed to the unit and are generally linked with automatic waste feed cutoff (AWFCO) limits to ensure that waste feed is automatically cut off when specified limits are exceeded. Examples of Group A parameters include maximum and minimum PCC and SCC temperatures, maximum combustion gas velocity, maximum waste feed rate, maximum carbon monoxide concentration, maximum combustion chamber pressure, minimum venturi scrubber differential pressure, minimum scrubber liquid-to-gas ratio and pH, minimum fabric filter differential pressure, minimum wet/dry ESP power input, and minimum wet electrostatic precipitator (WESP) liquid flow rate.

Group B control parameters generally do not involve continuous monitoring and may not be interlocked with the AWFCO system. However, detailed operating records are generally maintained to demonstrate compliance with permitted operating conditions. Examples of Group B parameters include maximum batch size for containerized waste and minimum scrubber blow-down. Some Group B operating parameters, including metal and chlorine feed rates, may be continuously monitored once the supporting analytical data have been entered into a data system.

Group C control parameters are generally set independently of trial burn conditions, and limits are typically based on manufacturers' recommendations and good operating practices. Examples of Group C parameters include maximum burner turndown and minimum scrubber nozzle pressure. Most Group C parameters do not involve continuous monitoring and interlocks with the AWFCO system; however, some may (for example, minimum atomization fluid pressure to a liquid injection burner). Similar to Group B parameters, detailed operating records for Group C parameters are generally maintained to demonstrate compliance with permitted operating conditions.

1.3.2 Site-Specific Risk Assessments

The RCRA performance standards described in Section 1.3.1 were promulgated in 1981 for incinerators and in 1991 for BIFs. Since that time, information has become available to suggest that the RCRA performance standards may not fully address potentially significant risks (EPA 1998a).

As documented in the Mercury Study Report to Congress (EPA 1997a), in technical background documents associated with the hazardous waste combustor MACT standards (RTI 1999), and in EPA OSW human health and ecological risk assessment guidance (EPA 1998a and 1999b), there can be potentially significant risks from the indirect exposure pathways (e.g., pathways other than direct inhalation), especially for bioaccumulative compounds such as D/Fs and mercury. Notable D/F and mercury emissions have been observed from hazardous waste combustion facilities (EPA 1996a and 1997b). The food chain pathway appears to be particularly important, and potential risks associated with indirect exposures often exceed potential risks from the direct inhalation pathway (EPA 1998a). Risks via the indirect exposure pathways were not directly taken into account when the RCRA regulations described in the previous section were developed (EPA 1998a).

Because the RCRA performance standards for hazardous waste combustors do not directly address indirect exposures, EPA recommended in 1993 and 1994 that site-specific risk assessments, including both direct and indirect exposure pathways, be conducted for each hazardous waste combustor seeking a RCRA permit (EPA 1993 and 1994b). Permitting authorities could then use the results of the site-specific risk assessments to determine, on a case-by-case basis, whether operation of the combustor in accordance with

the RCRA standards would be protective of human health and the environment (EPA 1998a). In those cases where a RCRA permitting authority identified a potentially significant risk, it could invoke Section 3005(c)(3) of RCRA (which is commonly referred to as the "omnibus authority" or "omnibus provision") to augment the RCRA permit with additional conditions as necessary to protect human health and the environment (EPA 1998a). As discussed in Section 1.3.3, EPA has recently revised its original recommendation in light of the new hazardous waste combustor MACT standards (EPA 1999c).

Section 3005(c)(3) of RCRA, codified in 40 CFR Section 270.32(b)(2), provides EPA with both the authority and responsibility to include additional terms and conditions in each RCRA facility permit as necessary to protect human health and the environment (EPA 1998a). Under 40 CFR Section 270.10(k), EPA may require a permit applicant to submit the information necessary to establish protective permit conditions under the omnibus authority (40 CFR Section 270.10(k); EPA 1998a). For hazardous waste combustors, the information required to establish permit conditions could include a site-specific risk assessment or the supporting information to conduct a site-specific risk assessment (EPA 1999c). Any decision to add permit conditions based on a site-specific risk assessment must be documented in the administrative record for each facility, and the implementing agency must explain the basis for the additional conditions (40 CFR Sections 124.7 through 124.9; EPA 1998a).

1.3.3 Hazardous Waste Combustor MACT Standards

Final MACT standards for certain hazardous waste combustion facilities were promulgated on September 30, 1999, and establish technology-based limits for D/Fs, mercury, semivolatile and low-volatile metals, HCl and Cl_2, hydrocarbons or carbon monoxide, particulate matter, and DRE (EPA 1999c). These standards were promulgated under joint authority of RCRA and the Clean Air Act. The MACT standards apply to several categories of hazardous waste combustion facilities including incinerators, hazardous waste burning cement kilns, and hazardous waste burning lightweight aggregate kilns. The MACT rule requires that these sources achieve compliance with the standards within three years of the rule effective date and begin performance testing for stack emissions within three years and six months of the rule effective date in accordance with 40 CFR §§63.1206(a) and 63.7(a)(2). MACT emission standards for hazardous waste burning boilers and additional industrial furnaces are anticipated in a future rulemaking.

The MACT standards are viewed as more stringent than RCRA Subpart O and Subpart H standards for incinerators and BIFs (EPA 1999c). A national risk assessment was performed to determine if the MACT standards satisfy the RCRA mandate to protect human health and the environment (RTI 1999). The national assessment was a multi-media, multi-pathway analysis addressing both human health and ecological risk. The assessment was predicated on the assumption that sources whose emissions were above the MACT standards would reduce their emissions to MACT levels, and that sources whose emissions were below the standards would maintain emissions at the existing levels. Based on this national assessment, EPA determined that sources complying with the MACT standards are *generally* not anticipated to pose an unacceptable risk to human health and the environment. However, a definitive finding could not be made (RTI 1999; EPA 1999c). Uncertainties remain, especially related to non-dioxin PICs (which were not evaluated in the national risk assessment), mercury (where bioaccumulation is very dependent on local conditions), and other site-specific factors that could vary from those evaluated in the national assessment. Given these uncertainties, EPA continues to believe that site-specific risk assessments may be warranted in some cases (EPA 1999c).

EPA recommends that permit writers evaluate the need for site-specific risk assessments on a case-by-case basis (EPA 1999c). The recommendation that the need for a site-specific risk assessment be evaluated on a case-by-case basis represents a modification to the site-specific risk assessment policy recommendation that EPA made prior to the publication of the MACT standards in 1993 and 1994, when EPA recommended that site-specific risk assessments be completed as part of the RCRA permitting process for all hazardous waste combustors (EPA 1993 and 1994b). The MACT rule preamble provides a list of qualitative factors to assist in the determination regarding the need for a site-specific risk assessment (EPA 1999c). EPA recommends that the decision be made prior to approval of the MACT comprehensive performance test protocol, to the extent possible (EPA 1999c). Therefore, if risk emissions data have not already been collected during a RCRA trial burn or other test, the necessary data can be collected during MACT performance testing (as appropriate).

In summary, promulgation of the MACT standards does not duplicate, supersede, or otherwise modify the omnibus authority or its applicability to hazardous waste combustors (EPA 1999c). Pursuant to the omnibus authority, the RCRA permitting authority has the responsibility to supplement the MACT

standards as necessary, on a site-specific basis, to ensure adequate protection under RCRA. Site-specific risk assessments provide a quantitative basis for making omnibus determinations at hazardous waste combustors (EPA 1999c). The results of site-specific risk assessments provide numerical information which can be compared to the MACT standards to determine whether risk-based limits are appropriate for a particular source in addition to the MACT requirements (EPA 1999c).

1.4 RISK BURN NOMENCLATURE

Key terms are summarized below. These terms are defined strictly for the purpose of supporting the concepts presented in this guidance and do not supersede regulatory definitions.

Control Parameters Combustor operations are defined by **control parameters** such as temperature, pressure, flow rates, and feed characteristics. The terms "control parameters" and "feed and operating parameters" are used interchangeably in this guidance.

Emissions Testing **Emissions testing** refers to the manual collection of stack gas sample(s), followed by chemical analysis to determine pollutant concentrations.

Normal Test A **normal test** can generally be described as a test where each **control parameter** is maintained either near the historical mean, or between the historical mean and the minimum or maximum (as appropriate) set point, while burning representative, but challenging, feeds. A normal test may be conducted for the purpose of generating emissions data for subsequent evaluation in a site-specific risk assessment and may be used as the basis for establishing permit terms. A normal test includes a minimum of one **test condition**, but may include more.

Operating Envelope The term **operating envelope** refers to the entire range of operation allowed for a combustor, as bounded by either physical or regulatory constraints.

Performance Test A **performance test** is a test performed for the purpose of demonstrating compliance with a specific regulatory emission limit or performance standard. Allowable operating limits are established based on the operation demonstrated during the performance test. Thus, the tests are usually conducted under **worst-case** operating conditions. RCRA trial burns and MACT performance tests are both performance tests. For hazardous waste combustors, performance testing may include a low-temperature **test condition** to demonstrate DRE for POHCs and a high-temperature **test**

condition to demonstrate SRE for metals. Additional test conditions may be necessary to resolve potential conflicts between targeted operating parameters.

Risk Burn — A **risk burn** is any **emissions testing** performed for the purpose of collecting emissions data for subsequent evaluation in a site-specific risk assessment. The testing may occur in conjunction with a RCRA trial burn or MACT performance test, or the risk burn may consist of a completely separate test effort. A risk burn includes a minimum of one **test condition**, but may include more.

Run — A **run** is the period of time needed to collect a stack gas sample of sufficient volume for subsequent analysis. During a run, control parameters are typically maintained at the same target set point. A minimum of three runs constitutes a **test condition**.

Test — The term **test** is used generically to refer to any **emissions testing**, without distinction as to the type of test or purpose of the testing.

Test Condition — A **test condition** is comprised of at least three **runs** where **control parameters** are maintained at the same target set point.

Trial Burn — The term **trial burn** refers specifically to **emissions testing** required by RCRA regulations. A trial burn is performed for the purpose of demonstrating compliance with a RCRA regulatory emission limit or performance standard and is used as the basis for establishing allowable operating limits. Trial burns may include a low-temperature **test condition** to demonstrate DRE for POHCs and a high-temperature **test condition** to demonstrate SRE for metals. Additional test conditions may be necessary to resolve potential conflicts between targeted operating parameters.

Worst-Case — The term **worst-case** is used to characterize **emissions testing** where a facility operates near the extreme edges of the **operating envelope**, and where emissions are likely to be maximized. The term "worst-case" is a general, not absolute, characterization. RCRA trial burns and MACT performance tests are generally considered to be worst-case tests.

CHAPTER 2

RISK ASSESSMENT STACK EMISSION DATA NEEDS

The categories of emissions data that are generally necessary for completing a site-specific risk assessment include: (1) D/F emission rates, (2) organic emission rates other than those for D/Fs, (3) metals emission rates, (4) particle-size distribution, and (5) emission rates of HCl and Cl_2. This chapter introduces these data needs and briefly summarizes their significance with respect to protection of human health and the environment.

EPA OSW recognizes that, for many compounds, only limited information is available regarding health effects (EPA 1998a). However, this does not imply that targeted sampling for a limited number of compounds should be conducted for the risk burn (EPA 1998a). Stack emissions should generally be characterized as completely as possible during a risk burn, regardless of availability of toxicological data. Although some compounds may eventually be eliminated from quantitative risk evaluation as suggested by the compound-of-potential-concern(COPC) selection process provided in the EPA OSW risk assessment guidance (EPA 1998a), it is important that all compounds initially be identified and quantified. New toxicological data may become available after the risk burn, or the risk assessor may consider provisional toxicity data or surrogate toxicity data from a similar compound in deciding whether to retain the compound as a COPC (EPA 1998a). Alternatively, a qualitative risk evaluation may be performed for any detected compound and presented as an uncertainty in the risk assessment (EPA 1998a).

2.1 DIOXINS AND FURANS

D/Fs are addressed in Chapter 4 of this guidance. D/Fs can pose significant risks through both direct and indirect exposure pathways. Their propensity to partition to adipose (fat) tissue and to bioaccumulate can

make potential food chain effects particularly significant. According to the dioxin reassessment review (EPA 1995a), the air-to-plant-to-animalexposure pathway is a primary exposure route for humans. Other significant exposure pathways include source-to-surface water-to-fish. Human exposures result from ingestion of contaminated milk, beef, fish, and other foods. D/Fs are believed to promote cancer and other harmful health effects in humans and other receptors, and the potential potency of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin as a carcinogen is currently being re-evaluated by EPA.

D/Fs are a group of anthropogenic chemical compounds created as unintended by-products during combustion and industrial activities (EPA 1995a). As described in Chapter 4, the formation of D/Fs in hazardous waste combustion units is highly dependent on post-combustion temperature, time, and the presence of a reaction surface. In general, D/Fs addressed in this document contain at least four chlorine atoms and can assume a planar configuration that allows for specific biological effects. D/Fs are generally quantified in terms of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin toxic equivalents (TEQ), as discussed in the EPA OSW risk assessment guidance (EPA 1998a). EPA OSW recommends that emissions testing for the tetra- through octa- D/F congeners be performed to support site-specific risk assessments.

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, analytical standards have been developed for certain mono- through tri-chloro D/F congeners. EPA encourages stack gas analysis for these mono- through tri-chloro 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 (EPA 1999c). Identification of an easily measurable surrogate may support future development of a continuous emissions monitoring system (CEMS) to indicate D/F emissions (see http://www.epa.gov/appcdwww/crb/empact/index.htm).

2.2 ORGANICS OTHER THAN DIOXINS AND FURANS

Organic compounds other than D/Fs are addressed in Chapter 5 of this guidance. Organics can result in increased risks from both direct and indirect exposures. Hazardous waste combustors can emit a variety of trace-level organics. As discussed in Chapter 5 of this document, organic emissions from hazardous waste combustion facilities typically include compounds such as volatile and semivolatile organics, aromatics, polyaromatics, D/Fs, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalates, nitrogenated and sulfonated organics, and short-chain alkanes (such as methane and propane). Both PAHs and PCBs are considered to be potential human carcinogens (EPA 2000), and are considered to be toxic, persistent, and bioaccumulative. PAHs are frequently associated with particulate matter emitted from combustion facilities. Combustion units have also been identified as major contributors to overall PCB emissions (Alcock and others 1999; EPA 1997b), and an increasing body of information supports the likelihood that PCBs may be formed in combustion systems regardless of PCB contamination in the feed (Lemieux and others 1999). PCBs may be formed by mechanisms similar to those described in Chapter 4 for D/Fs.

Target analyte lists for specific organics recommended for identification during a risk burn are provided in Appendix B. However, the total identification and quantification of all organics is frequently not possible, which adds to the uncertainty of the risk assessment process. Therefore, Chapter 5 and Appendix B of this document describe a method for Total Organic Emissions (TOE) analysis for quantifying the total mass of organics based on boiling point ranges. This information is useful in indicating the level of uncertainty associated with the risk assessment. To reduce uncertainty, stack gas analyses are also recommended for constituents that are not typically included on target analyte lists, such as tentatively identified compounds (TICs) and simple hydrocarbons.

2.3 METALS

Metals are addressed in Chapter 6 of this guidance. Metal emissions can pose potential human and ecological risks. EPA's BIF rule (40 CFR 266, Subpart H) identifies ten metals which may pose human health risks via the inhalation exposure pathway. These metals are antimony, arsenic, barium, beryllium,

cadmium, chromium, lead, mercury, silver, and thallium. A number of these metals also pose human health risks via the indirect pathways. Mercury, in particular, has significant potential to biotransfer up the food chain through water and sediments to fish and human receptors. Table A-1, "Information on Compounds of Potential Interest," of Appendix A of the EPA OSW human health risk assessment guidance (EPA1998a) and Table A-1, "Chemicals for Consideration as Compounds of Potential Concern," of Appendix A of the EPA OSW ecological assessment guidance (EPA1999b) identify eight additional metals as compounds of potential concern for evaluation of human and ecological risks. These eight additional metals are aluminum, copper, cobalt, manganese, nickel, selenium, vanadium, and zinc.

EPA OSW recommends that a facility conducting a site-specific risk assessment perform stack testing or develop emission estimates based on other information for the eighteen metals listed above. Although some metals may be subsequently eliminated from the risk assessment during the compound of potential concern (COPC) selection process, it is recommended that all eighteen metals be quantified during the test to prevent the need for additional testing later. Potential human cancer risks based on carcinogenic slope factors (CSFs) are typically evaluated for arsenic, beryllium, cadmium, hexavalent chromium, and certain species of nickel. Health effects other than cancer are based on RfDs and/or RfCs for antimony, barium, trivalent chromium, copper, manganese, mercury, certain species of nickel, selenium, silver, thallium, vanadium, and zinc. As explained in Section 2.3.2 of this document, EPA OSW has recommended that potential health effects from lead be modeled using an alternative approach (EPA 1998a).

EPA OSW's ecological risk assessment guidance (EPA 1999b) describes ecological toxicity reference values for a number of ecosystems and receptors including freshwater quality, freshwater sediment, marine and estuarine water quality, marine and estuarine sediment, and specific receptors including earthworms, terrestrial plants, mammals, and birds. Ecological toxicity reference values have been developed for aluminum, antimony, arsenic, barium, beryllium, cadmium, copper, hexavalent chromium, total chromium, lead, mercury, methyl mercury, nickel, selenium, silver, thallium, and zinc. EPA OSW has recommended that these metals be considered during the COPC selection process for ecological risk assessments (EPA 1999b).

EPA OSW's human health and ecological risk assessment guidance (EPA 1998a and 1999b) generally recommend addressing metals in the elemental form, with the exception of mercury, chromium, and nickel.

For mercury, chromium, and nickel, the guidance recommends assumptions regarding valence state or chemical form. Based on the conservative nature of the recommended assumptions, a facility may want to perform speciation sampling during the risk burn or present other information to replace the default assumptions with site-specific data. This is discussed further in Section 6.4 and Appendix B.

2.3.1 Human Health and Ecological Concerns for Specific Metals

The following paragraphs discuss human health and ecological significance of the metals aluminum, cobalt, copper, manganese, nickel, selenium, vanadium, and zinc. This information is provided in the EPA OSW risk assessment guidance, as well as other references, and is summarized here because these metals were not addressed in the original BIF rule (40 CFR 266, Subpart H). All of these metals (except aluminum and cobalt) have published toxicity values (CSFs, RfDs and/or RfCs) in EPA's Integrated Risk Information System (IRIS) (EPA 2000) and/or EPA's Health Effects Assessment Summary Tables (HEAST)(EPA 1997c). IRIS and HEAST do not currently identify toxicity values for aluminum and cobalt. However, an ecological toxicity reference value is available for aluminum, and provisional human health systemic toxicity data are available for cobalt. Since aluminum and cobalt can be readily sampled using the multiple metals sampling train, emissions determinations for both metals are recommended.

Aluminum, zinc, and copper are commonly occurring metals that bioaccumulate through the food chain in their ionic form (Paasivirta 1991). These metals can accumulate in soils and/or aquatic ecosystems. Selenium has been demonstrated to cause significant ecological impacts to wildlife, primarily because of the effects from irrigation return water. Nickel has caused both human health as well as ecological effects, and it is commonly associated with industrial operations such as plating.

Aluminum

Aluminum bioconcentrates in aquatic species and vegetation and can cause toxic effects (Agency for Toxic Substances and Disease Registry [ATSDR] 1999; Paasivirta 1991). In mammals, aluminum is poorly absorbed and is not readily metabolized (Ganrot 1986). From a human health perspective, toxicity values have not been established. Ecological toxicity reference values have been developed for aluminum.

Cobalt

Cobalt is a relatively rare metal that is produced primarily as a by-product during refining of other metals, primarily copper. Industrial exposure to airborne cobalt appears to result in sensitization followed by irritation and pronounced pulmonary effects (Doull and others 1991). Provisional human health systemic toxicity data are available for cobalt. Ecological toxicity reference values have not been developed.

Copper

Copper is an essential trace element required by numerous oxidative enzymes and is found in all mammals and several other classes of organisms; however, high doses can result in adverse effects to humans and ecological receptors (Doull and others 1991). In general, humans are less sensitive to copper toxicity than other mammals (such as sheep and cattle), and healthy adults usually are not affected by exposure to low, chronic doses of copper. Infants and children are susceptible to chronic copper toxicity. Once absorbed, copper is distributed to the liver and can bind to deoxyribonucleic acid or generate free radicals.

Organisms susceptible to absorption of contaminants are most vulnerable to copper toxicity. Aquatic organisms such as algae, fungi, certain invertebrates, and fish represent examples of these types of organisms. Thus, aquatic ecosystems would be the most sensitive to copper loading; however, copper released to surface waters generally precipitates out or adsorbs to sediments (ATSDR 1990). Ecological toxicity reference values have been developed for copper.

Manganese

Manganese is an essential trace element, is present in all living organisms, and is a cofactor in a number of enzymatic reactions. Industrial exposures to large doses of airborne manganese dioxide (or other forms of manganese) can result in manganese pneumonitis, which can result in permanent lung damage. Chronic exposure to airborne manganese can result in central nervous system effects including psychiatric disorders and a Parkinson-like syndrome. Liver cirrhosis has also been observed. It is significant that these effects have only been observed in higher primates such as humans and monkeys and not in experimental animals such as rats (Doull and others 1991). IRIS (EPA 2000) bases the chronic reference dose for inhalation on

data collected during occupational exposures to manganese dioxide; therefore, any potential risks from manganese will be driven by the direct inhalation exposure route. Ecological toxicity reference values for manganese have not been developed.

Nickel

Nickel is a commonly used industrial metal, and it is frequently associated with iron and copper ores. Significant loading of nickel to the atmosphere and surface waters has been observed over the past several decades (Doull and others 1991). EPA has identified certain forms of nickel, including nickel carbonyl, nickel subsulfide and nickel refinery dust, as potential human carcinogens (EPA 1998a and 2000). The BIF rule preamble indicates that nickel carbonyl and nickel subsulfide are not likely to be emitted from combustion devices, given their highly oxidizing conditions. Nickel oxide, which may be emitted from combustion devices, is not identified as a carcinogen by itself. However, the EPA OSW human health risk assessment guidance (EPA 1998a) points out that nickel oxide is a major component of nickel refinery dust, and the components responsible for the carcinogenicity of nickel refinery dust have not been conclusively established. Based on this information, EPA OSW has recommended that inhalation risks from nickel be evaluated using the CSF for nickel refinery dust, or that a facility present information indicating the absence of carcinogenic nickel refinery dust components (EPA 1998a). The approach recommended in the EPA OSW risk assessment guidance of evaluating inhalation risks using the CSF for nickel refinery dust is supported by the risk assessment methodology used in support of the MACT rule (RTI 1999; EPA 1999c) and represents a change in EPA OSW's previous policy (EPA 1992a) where it was recommended that nickel be evaluated as a noncarcinogen. Evaluating inhalation risks using the CSF for nickel refinery dust may result in lower allowable nickel feed rates. For exposure pathways other than inhalation, EPA OSW recommends that nickel be evaluated as a noncarcinogen (EPA 1998a). Additional information on nickel speciation is found in the EPA OSW risk assessment guidance (EPA 1998a) and in Section 6.4.3 of this document. Ecological toxicity reference values have been developed for nickel.

Selenium

Selenium occurs naturally in soils, is associated with copper refining and several industrial processes, and has been used in pesticides. It is an essential element, bioaccumulates in certain species of plants, and has

been associated with toxic effects in livestock (blind staggers syndrome). Soils containing high levels of selenium (seleniferous soils) can lead to high concentrations of selenium in certain plants, which then pose a hazard to livestock and other species. In humans, selenium partitions to the kidneys and liver and is excreted through the urine and feces. Toxic effects in humans include central nervous system and gastrointestinal effects (Doull and others 1991). Aquatic birds are extremely sensitive to selenium; toxic effects include teratogenesis. Ecological toxicity reference values have been developed for selenium.

Vanadium

Vanadium is found in several ores, is associated with petroleum products, and is commonly found in food oils. It is unclear whether or not vanadium has any essential role in human metabolism. Toxic effects of vanadium are usually associated with the inhalation exposure route. Effects of chronic exposure to airborne vanadium compounds in workers include bronchitis, bronchopneumonia, and kidney damage (Doull and others 1991). Animal experiments have confirmed effects on the lungs and kidneys. Ecological toxicity reference values for vanadium have not been developed.

Zinc

Zinc is an essential trace element that is involved with many enzymatic reactions in humans and other species (Doull and others 1991). It generally occurs in the divalent oxidation state. Zinc does bioaccumulate, specifically through the indirect soil-to-vegetable exposure pathway. The most common observed human health effect from zinc would be depression of enzyme production, resulting in copper deficiency. Ecological effects include a tendency to bioaccumulate and toxic effects to vegetation and aquatic organisms (Paasivirta 1991). Ecological toxicity reference values have been developed for zinc.

2.3.2 Risk Characterization for Lead

Information on estimating threshold levels of lead exposure is provided in the EPA OSW human health risk assessment guidance (EPA 1998a). Toxicity factors (CSFs and RfDs) are not available for lead. Therefore, EPA OSW has recommended that adverse health effects for lead be characterized through a direct comparison with media-specific health-based levels, adjusted for background exposure (EPA 1998a).

Under the BIF regulations, emissions and feed rate limits for lead are based on a RAC equivalent to 10 percent of the NAAQS for lead converted to an annual average, or 0.09 micrograms per cubic meter ($\mu g/m^3$). However, this standard only addresses the direct inhalation exposure pathway. Lead can also be deposited to soils, where it can be ingested. Therefore, EPA OSW has recommended that soil lead levels also be evaluated as part of a site-specific risk assessment (EPA 1998a). The fate and transport equations in the EPA OSW risk assessment guidance (EPA 1998a) can be used to estimate soil concentrations from stack emissions.

The neurobiological effects observed in children are used as the sensitive endpoint for evaluating lead toxicity from ingestion. EPA has recommended a maximum lead concentration in blood of 10 micrograms per deciliter (µg/dL), which is at the low end of the range of concern for adverse health effects in children (EPA 1998a). Potential risks from lead are evaluated based on the application of an uptake/biokinetic (U/BK) modeling approach that evaluates potential risks by predicting blood lead levels associated with exposure to lead. When run with standard recommended default values, the U/BK model can calculate a soil lead concentration in milligrams per kilogram (mg/kg) which corresponds to a prediction that no more than five percent of exposed children will have blood lead concentrations exceeding 10 µg/dL. In lieu of direct comparison to a target soil level, the EPA OSW risk assessment guidance (EPA 1998a) also describes the approach of running the U/BK model.

2.4 PARTICLE-SIZE DISTRIBUTION

Particle-size distribution is addressed in Section 7.2 of this guidance. Information on particle-size distribution (presented as particle diameters in micrometers, referred to as microns) is needed for the air dispersion and deposition modeling that supports the risk assessments (EPA 1998a). Because particle dispersion and subsequent deposition are directly related to particle size, potential risks are directly dependent on particle-size distribution. In general, most metals and a few organic COPCs with very low volatility are assumed to occur only in the particle phase. Mercury and more volatile organics are assumed to partition between the particle and vapor phases. Very volatile organics are modeled only in the vapor phase.

The EPA OSW risk assessment guidance (EPA 1998a) recommends that facilities perform site-specific

measurements to determine particle-size distribution. Measurements for particle-size distribution will reflect site-specific combustion characteristics and the efficiency of the APCD. Site-specific particle-size measurements are discussed in more detail in Chapter 7 and in Appendix B of this document.

2.5 HYDROGEN CHLORIDE AND CHLORINE

HCl and Cl_2 are addressed in Section 7.1 of this guidance. Potential risks from HCl and Cl_2 are limited to the inhalation pathway. 40 CFR Part 266 Subpart H already requires BIF facilities to sample stack emissions for HCl and Cl_2, and to limit emissions as necessary to meet direct inhalation RACs specified in the regulations. However, updated toxicological information (instead of the RACs specified in Subpart H) may be available and may need to be used for site-specific risk assessments at BIF facilities (EPA 1998a).

For incinerators, 40 CFR Part 264 Subpart O establishes a technology-based emissions limit and requires emissions sampling only for HCl. To support site-specific risk assessments, incinerators may also need to test their stack emissions for Cl_2.

CHAPTER 3

RISK BURNS

In this guidance, the term "risk burn" refers to any testing performed to collect emissions data for subsequent evaluation in a site-specific risk assessment. The testing may occur in conjunction with a RCRA trial burn or a MACT performance test, or the risk burn may consist of a completely separate test effort.

The objectives of a risk burn are to (1) collect appropriate emissions and feed characterization information for evaluation in a site-specific risk assessment, and (2) demonstrate the feed and operating conditions which correspond to measured emission levels. Feed and operating parameters (i.e., control parameters) may be limited and monitored after the risk burn to provide assurance on an ongoing basis that emissions remain at or below the measured levels.

Since EPA may consider the results of a risk assessment and use such information to establish risk-based permit limits under the omnibus authority of RCRA as described in 40 CFR § 270.32(b)(2), the risk burn should generally be integrated with trial burn or performance testing to the extent necessary to produce a consistent set of enforceable permit conditions. Planning is critical, and this chapter highlights key considerations. Terms are defined in Section 1.4.

3.1 RISK-BASED PERMITTING OVERVIEW

When a RCRA permit decision includes a site-specific risk assessment and risk burn, the following activities are generally involved.

PHASE 1: PLANNING

1. **The facility-specific risk burn plan and risk protocol are developed, reviewed, and approved**
   EPA OSW recommends that the risk burn plan and site-specific risk protocol be carefully coordinated to assure that the information generated during the risk burn will fully support the risk assessment and

final permit decision.

Collection of appropriate emissions and feed characterization information is a fundamental objective of the risk burn. EPA's recommended data quality objective (DQO) process (EPA 1998c) promotes collection of "the right data the first time." The EPA OSW risk assessment guidance (EPA 1998a) and this document support that objective by identifying and discussing data needs and measurement options. However, project-specific measurement goals should generally be established for each data collection effort. For example, some facilities may decide to achieve lower detection limits for certain constituents to demonstrate that risks are below target levels. Preliminary risk modeling can assist in determining the quantitative targets for the measurement design.

Advance planning is also important in choosing the risk burn operating mode. The risk burn operating mode affects the outcome of the risk assessment, and may also affect the final permit terms. Some hazardous waste combustors operate over a wide range of conditions and emission levels. However, the outcome of the risk assessment is linked to specific emission rates measured while operating under specific operating mode(s). To assure that the combustor continues to operate within the range where emissions have been found to be protective, the RCRA permit may limit control parameters based on the risk burn. Ultimately, the risk burn generally should strike a balance between operating modes which achieve desired permit flexibility, while also achieving protective emissions levels. Early communication between the permit writer and facility is important. A clear understanding of how the permit terms will be derived can assist in determining the risk burn operating modes. Preliminary risk modeling and preliminary emissions testing may also be helpful in planning the risk burn.

PHASE 2: DEMONSTRATION

2. **A risk burn is performed to gather stack emissions data and define the operating envelope that corresponds to the risk assessment.** The recommended control parameters for defining the operating envelope that corresponds to the risk burn and risk assessment are identified in Chapters 4 through 7 of this document. In some cases, these parameters may need to be limited in the permit to ensure (on an ongoing basis) that emissions remain below the levels that were measured during the risk burn and found to be protective. Many of the control parameters identified in Chapters 4 through 7 are identical to control parameters which are limited to ensure compliance with regulatory performance standards. Therefore, few (if any) additional permit limitations based on the risk burn may be necessary when the risk burn can be performed in conjunction with a RCRA trial burn or MACT performance test, and when emissions are already controlled to risk burn levels by regulatory limits on key control parameters. A greater number of permit limitations may be necessary when the risk burn and performance tests reflect different operating modes.

3. **A risk assessment is performed to verify that the demonstrated operation does not present significant risk to human health or the environment.** The site-specific risk assessment may either be performed using the actual data from the risk burn, or using a combination of risk burn data and other information. For example, a regulatory standard or allowable permit limit for metals might be evaluated in combination with actual emissions data for specific organics.

   Additional iterations of the risk assessment may be performed if the initial evaluation indicates

potentially unacceptable risks. Subsequent iterations might consider additional site-specific information that is more representative of the exposure setting, or reduced emissions (EPA 1998a). However, in most cases, the need for emissions reductions should generally be identified as part of the risk burn planning process, well in advance of performing the risk assessment.

4. **A permit decision is made, either to issue or deny.**

PHASE 3: VERIFICATION

5. **Conditions in addition to those specifically required by regulation may be included in the RCRA permit as necessary to protect human health and the environment** The final permit represents an important and integral conclusion to the risk-based permitting process. The risk burn and risk assessment are merely tools; it is the final permit that defines what operational conditions are necessary to protect human health and the environment and how that will be assured on an ongoing basis (i.e., risk-based permit limitations). Depending on site-specific considerations, risk-based permit limitations may be necessary to prevent operation at conditions which could result in higher emissions than those represented by the risk burn and risk assessment.

   Risk-based permit terms must be justified on a site-specific basis as limitations that are necessary to protect human health and the environment. EPA OSW recommends that the permitting authority consider a number of factors including, but not limited to, the operating mode(s) demonstrated during the risk burn, the emission levels evaluated in the risk assessment, the conservatism of the risk assessment assumptions, the outcome of the risk assessment, and the extent to which emissions are already controlled by regulatory standards or other limitations. Potential risk-based permit limitations include:

   - ***Emissions limits and stack testing.*** Specific emission limitations may be cited in the permit for certain pollutants. Since most emissions can only be verified by manual stack measurements, the permit may include a schedule for periodic stack testing to confirm that emissions remain below levels that may present a significant risk to human health and the environment.

   - ***Feed restrictions, operating limits and monitoring.*** Emission levels generally cannot be verified continuously. However, feed restrictions and operating limits may be established based on the risk burn as surrogate indicators of emissions. The feed and operating control parameters can then be continuously monitored to assure that emissions remain below the measured levels on an ongoing basis.

   - ***Other limitations.*** Other permit limitations may be established to control potential risks as necessary to protect human health and the environment. For example, environmental sampling may be specified to confirm that ambient concentrations of certain pollutants do not reach levels that may present a significant risk to human health and the environment.

As evident from this risk-based permitting overview, EPA OSW believes that the risk burn, risk assessment, and final permit terms will be closely linked for situations where the RCRA permitting authority has determined that a site-specific risk assessment is necessary. The risk burn plays a key role in the process. Operation during the risk burn may affect whether the measured emissions are found to present potential risk to human health and the environment. In addition, operation during the risk burn can define an operating envelope that establishes the working assumptions for the risk assessment and final permit terms. Within the bounds of the operating envelope demonstrated during the risk burn, emissions are characterized and evaluated for potential risk by the risk assessment. Outside of those bounds (unless additional information is available), emissions and risks may be unknown.

3.2 RISK BURN OBJECTIVES

This section discusses risk burn objectives in more detail. The objectives of the risk burn are to (1) collect appropriate emissions and feed characterization information for evaluation in a site-specific risk assessment, and (2) demonstrate the feed and operating conditions which correspond to emission levels that do not present a significant risk to human health or the environment.

3.2.1 Collection of Appropriate Emissions and Feed Characterization Information

As discussed in Chapters 1 and 2, collection of site-specific risk assessment data at hazardous waste combustion facilities generally involves stack sampling and analysis for D/Fs, non-D/F organics, metals, particle-size distribution, and HCl and Cl_2. Prior to data collection, EPA OSW recommends that specific measurement objectives be developed for the risk burn plan and associated quality assurance project plan (QAPP) to assure collection of complete and useable data.

EPA guidance on quality assurance project plans (EPA1998c and 1998d) describe recommended information to be included in a QAPP. The QAPP identifies a project's technical and quality objectives and documents how quality assurance and quality control will be applied to assure that the data support technically sound decision-making. In addition, the QAPP may identify potential limitations regarding use of the data.

EPA OSW recommends that, whenever possible, project-specific measurement objectives be defined considering information from a preliminary risk assessment. High detection or quantitation limits, presence of common laboratory contaminants, and sampling artifacts can artificially inflate risks. A preliminary risk assessment can provide information regarding the necessary detection or quantitation limits and constituent concentrations for demonstrating that risks are below levels of concern. If a proposed measurement option will not attain the quantitative objectives, the measurement design may need to be modified. For example, if lower detection or quantitation limits are needed, a longer sampling duration or use of a high resolution analytical finish might be considered. Conversely, if a facility can tolerate higher detection or quantitation limits, more economical measurement options might be selected. As an example, a single semivolatile sampling train might be used to sample for D/Fs, PCBs, PAHs and semivolatile organics (when a single train is used for multiple determinations, the train components are split and detection limits for the semivolatile organics increase). Detection and quantitation limits are discussed in more detail in Appendix B.

The recommended detection or quantitation limits that should generally be reported when constituents are not detected in a stack gas emissions sample are discussed in Section 8.1.1 of this document. It is also recommended that a facility inform the laboratory of preferred reporting conventions prior to development of the risk burn QAPP and analysis of the risk burn samples.

EPA OSW recommends that the risk burn plan and QAPP also address complete characterization of the feed materials to be burned during the risk burn, including wastes, fuels, raw materials, and spike materials. Data equivalent to the following should generally be generated for each feed material:

- 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 to determine approximate chemical properties including total organic carbon, total chlorine, total organic halogens, and elemental composition;
- Quantification of total metals feed rates for 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 quantities and types of organic compounds that are

present, as well as identification and quantitation of trace quantities of persistent, bioaccumulative, and toxic constituents based on analysis for volatile organics, semivolatile organics, PCBs, PAHs, and facility-specific compounds.

These data typically define a facility's baseline with respect to long-term impacts and potential effects on human health and the environment. When constituents are not detected in a feed matrix, it is recommended that the Sample Quantitation Limit (SQL) as described in *Guidance for Data Useability in Risk Assessment* (EPA 1992c) be reported, with appropriate consideration of the level of dilution necessary to perform the analysis.

EPA OSW recommends that the implications of different measurement options be fully considered during the initial planning stages of the risk burn. Risk burn measurement issues and data analysis are discussed further in the EPA OSW risk assessment guidance (EPA 1998a), and in Section 8.1 and Appendix B of this document.

3.2.2 Demonstration of Operating Modes

The second objective of a risk burn is to determine the feed and operating conditions which will ensure that emission levels do not present a significant risk to human health and the environment. The operating mode during the risk burn may affect the outcome of the risk assessment and, subsequently, the final permit decision. For this reason, EPA OSW recommends that preliminary information regarding potential emission rates and anticipated permit limitations be obtained early in the risk burn planning process.

Useful information regarding potential emissions and risks can be obtained by performing mini-burns and preliminary risk evaluations. Mini-burns involve stack sampling to collect limited emissions data prior to full scale testing. Emissions can also be estimated based upon data gathered at a similar facility, or by performing conservative engineering calculations. A preliminary risk evaluation indicates the degree of potential risk associated with the emissions levels that are anticipated for the risk burn. If the preliminary risk assessment indicates that anticipated emissions are likely to present a significant risk to human health and the environment, a facility may choose to reduce the emissions of certain compounds prior to

conducting the risk burn. Emissions reductions might involve simple refinements to the risk burn plan, such as lowering a target metals feed rate, or more complex measures, such as physically modifying the unit (subject to approval by the regulatory agency).

The risk burn operating mode may also be influenced by the permit limitations which are anticipated to be established based on the risk burn. Chapters 4 through 7 identify key control parameters associated with emissions of specific contaminants (D/Fs, non-D/F organics, metals and HCl/Cl_2) and specific types of hazardous waste combustion facilities (incinerators, boilers, cement kilns, and lightweight aggregate kilns). Depending on site-specific considerations, limitations for these parameters (or other parameters identified by the permit writer) may be established in the permit from the risk burn to provide assurance on an ongoing basis that emissions remain at or below levels which may pose a significant risk to human health and the environment. Communication between the permit writer and facility regarding the types of permit limitations to be established, as well as the manner in which the limits will be established, assists in targeting risk burn operating modes to achieve desired permit flexibility.

3.3 INTEGRATION OF RISK BURNS AND PERFORMANCE TESTING

In this guidance, the term "performance testing" refers to testing performed for the purpose of demonstrating compliance with a regulatory emission limit or performance standard. RCRA trial burns and MACT performance tests are both encompassed by this terminology. For hazardous waste combustors, performance testing usually includes low-temperature test condition(s) to demonstrate DRE for POHCs and may include a high-temperature test condition to demonstrate SRE for metals.

The risk burn may be associated with (1) low-temperature test conditions conducted to demonstrate DRE of POHCs, (2) a high-temperature SRE test condition conducted to establish metal feed rates and to account for metals emissions and partitioning, and/or (3) a separate test condition (which may be conducted at normal operating conditions) specifically for the collection of risk assessment data. Fewer permit limitations based on the risk burn may be necessary when the risk burn can be performed in conjunction with a RCRA trial burn or MACT performance test. A greater number of permit limitations may be necessary when the risk burn and performance tests reflect different operating modes.

Decisions regarding integration of the risk burn and DRE/SRE performance tests are not intuitive. The objectives and parameters for each potential test condition should be carefully evaluated, and the similarities and conflicts identified. Adjustments may be necessary in order to combine test conditions. The remainder of Chapter 3 presents information to guide permit writers and facility personnel through considerations which affect test design. A flow chart (Figure 3-1) provides an overview of the process.

3.3.1 Combined Testing

In deciding whether to perform the risk burn in conjunction with DRE/SRE performance testing, EPA OSW recommends that practical considerations, such as timing, be considered, as well as the following factors:

- emissions evaluation;
- waste selection and feed parameters;
- operating parameters.

3.3.1.1 Emissions Evaluation

Section 3.2.2 discusses EPA OSW's recommendation that a preliminary emissions and risk evaluation be conducted to assess the need for emissions reductions prior to the risk burn. An emissions evaluation also provides information that can be factored into the decision of whether to integrate the risk burn and DRE/SRE performance tests. As discussed in Section 1.3.1, DRE and SRE tests are generally conducted under "worst-case" conditions which tend to maximize emissions. For example, the SRE test may involve spiking to increase metal feed rates above normal levels, resulting in high metal emission rates. However, combustion risk assessments typically assess potential risks associated with operation over 30 or more years (EPA 1998a). Incorporating emissions data from DRE and/or SRE testing into the site-specific risk assessment could be overly conservative, given that a facility will not operate at the edges of its operating envelope or emit at maximum levels for the entire time. Under certain circumstances, it may be appropriate to consider emissions data generated during normal operation of the combustion unit in the risk assessment.

Emissions during normal operations (as compared to emissions during DRE or SRE conditions) may better represent the average emissions and risks posed by the combustion facility over its operating life.

When "worst-case" emissions from the DRE/SRE test conditions are not projected to pose a significant risk to human health and the environment, then a facility may choose to minimize the number of test conditions and resulting permit limitations by combining the risk burn and performance tests. Otherwise, the facility and permit authority might explore the possibility of performing the risk burn (or a portion of the risk burn) under normal operating conditions as a separate test effort. The option of collecting data under normal conditions is discussed further in Section 3.3.2.1.

It is important to keep in mind that different approaches may be chosen for different constituents (D/Fs, non-D/F organics, metals, etc.). In addition, the risk assessment can be performed using information other than actual test data for certain constituents. For example, emission rates for some metals can be calculated from metal feed rates and conservative zero SRE assumptions (i.e., no partitioning or removal). A facility may also choose to evaluate a regulatory emission limit for a particular constituent in the risk assessment instead of actual test data (in this case, testing simply confirms whether and under what conditions the regulatory standard can be met). EPA OSW recommends that the risk burn plan and risk protocol clearly designate which emissions levels for the risk assessment will be based on actual test data, and which emission values will be supplied from another source. These choices are discussed further in Sections 3.5 and 8.2.

3.3.1.2 Waste Selection and Feed Parameters

Waste selection and feed parameters may also influence the decision of whether to perform the risk burn in conjunction with a DRE or SRE performance test. As discussed later in Chapters 4 and 5, EPA OSW recommends that representative wastes generally be burned during collection of risk burn emissions data for D/Fs and non-D/F organics, and that actual wastes, and not surrogate wastes synthesized from pure compounds, be used to the extent possible.

In some cases, the preference for use of actual waste during the risk burn may be incompatible with the waste selection criteria for the DRE or SRE performance test. For example, synthetic "wastes" (wastes

mixed from pure compounds) are sometimes utilized during performance tests to achieve the worst-case conditions targeted for those tests. Synthetic wastes may be chosen for DRE or SRE performance tests because of analytical interferences between the designated POHCS and constituents present in actual wastes, because of incompatibilities between actual wastes and spiking materials, or because actual waste volumes are insufficient for completion of three runs per test condition. If circumstances preclude use of actual wastes (or actual waste spiked with POHCs or other compounds) during the DRE or SRE test conditions, then integration of risk-based data collection with performance testing may not be an appropriate option. Additional information on balancing the use of real wastes versus synthetic wastes is found in Section 5.2.2.

This document also identifies key feed parameters which may affect emissions of D/Fs (Chapter 4), non-D/F organics (Chapter 5), metals (Chapter 6), and HCl/Cl_2 (Section 7.1), and which EPA OSW recommends be demonstrated during the risk burn. Feed parameters associated with DRE and SRE testing are identified by regulations, and additional recommendations are discussed in other guidance (EPA 1983, 1989 and 1992b). If there is close overlap and little conflict between the risk burn and DRE/SRE feed targets, then a facility may prefer to integrate the risk burn and performance tests. Otherwise, it might be preferable to perform the risk burn (or a portion of the risk burn) as a separate test effort.

3.3.1.3 Operating Parameters

The operating parameters to be demonstrated during the risk burn may also influence whether the risk burn is performed in conjunction with a DRE or SRE performance test, or as a completely separate test effort. This document identifies key operating parameters which may affect emissions of D/Fs (Chapter 4), non-D/F organics (Chapter 5), metals (Chapter 6), and HCl/Cl_2 (Section 7.1), and which EPA OSW recommends be demonstrated during the risk burn. Operating parameters associated with DRE and SRE testing are identified by regulations, and additional recommendations are discussed in other guidance (EPA 1983, 1989 and 1992b). If there is close overlap and little conflict between the risk burn and DRE/SRE operating targets, then a facility may prefer to integrate the risk burn and performance tests. Otherwise, it might be preferable to perform the risk burn (or a portion of the risk burn) as a separate test effort.

3.3.2 Separate Testing

Section 3.3.2 identifies circumstances where it may be appropriate to perform the risk burn independently from the DRE/SRE performance tests. In some situations, a facility may prefer to perform all or part of the risk burn under normal operating conditions to better represent the average emission levels expected over the operating life of the unit. Testing at normal conditions is discussed in Sections 3.3.2.1 and 3.3.2.2. Alternatively, separate testing may be appropriate because of logistical conflicts, such as timing, or to resolve a conflict between the risk burn and DRE/SRE waste feed or operating targets. Separate testing to resolve a conflict is discussed in Section 3.3.2.3.

3.3.2.1 Testing at Normal Conditions

As explained in Section 3.3.1.1, it may be appropriate in certain circumstances to perform the risk assessment using emissions data generated during normal operation of the combustion unit. If a facility requests that emissions data collected under normal operating conditions be evaluated in the risk assessment, then an additional test condition (separate from the DRE/SRE test conditions) may be suggested in the risk burn plan. This additional condition is optional and is performed by the facility on a voluntary basis.

The permitting authority should generally consider proposals for use of emissions data generated under normal operating conditions in the risk assessment (in conjunction with or instead of data generated during a DRE or SRE test) on a case-by-case basis. Additional permit limitations may be needed to ensure that conditions represented as normal during the test are, in fact, normal over the long-term operation of the facility.

Some facilities may view the prospect of extra permit limitations as a disincentive to performing the risk burn (or a portion of the risk burn) under normal operating conditions. However, the "verification" phase of risk-based permitting has been explained in Section 3.1, and the logic is repeated here for emphasis. The permit endeavors to prevent operation at conditions which could result in higher emissions than those evaluated in the risk assessment and found to pose an insignificant risk to human health and the environment. If emissions data from testing at normal conditions are evaluated in the risk assessment (in

lieu of emissions data from "worst-case" DRE/SRE testing) and it is determined that such emissions do not present a significant risk to human health and the environment, then the permit should generally ensure that those emissions, on average, are not exceeded over the long term. Operating limitations from the DRE/SRE test conditions may not offer this assurance, because they represent operating extremes and elevated emissions. Thus, additional operating limitations may be needed to assure protection of human health and the environment. Although these extra permit limitations may indeed be viewed by some facilities as a disincentive to performing a risk burn under normal operating conditions, the decision to pursue testing at normal conditions rests completely with the facility.

It is important to mention that data from testing under normal conditions and data from testing under "worst-case" DRE/SRE conditions may sometimes be evaluated in a risk assessment as two completely separate risk scenarios (for example, to support a more informative risk communication strategy). Provided that "worst-case" emissions from DRE/SRE test conditions are evaluated in the risk assessment and it is determined that they do not present a significant risk to human health and the environment, then extra permit conditions to assure normal operation should not be necessary. Under these circumstances, the regulatory and permit limitations associated with the DRE/SRE testing would ensure that ongoing emissions remain below levels that may present a significant risk to human health and the environment.

3.3.2.2 Defining and Verifying Normal Conditions

Emissions data collected under normal operating conditions may reflect lower emission rates and lower, but more representative, potential risks. However, it may not be appropriate for every facility to use emissions data collected under normal conditions in the risk assessment. EPA OSW recommends that the following be considered when determining whether to test at normal conditions:

1. ***Can the facility provide sufficient information to define normal feed and operating conditions?***

   To use emissions data generated during testing at normal conditions in the risk assessment (in lieu of data generated during a DRE or SRE test), a facility should be able to characterize "normal" for their operations. This characterization could involve plotting control parameters over time, assessing typical variation, determining means and standard deviations, characterizing feed variability, or a combination of these and other approaches. For the feed characterization, EPA OSW recommends that both the hazardous and non-hazardous inputs (including fossil fuels, raw

materials, and non-hazardous wastes) be considered. For example, mercury in coal can contribute to potential risks and should be considered in the feed characterization.

Successful characterization of "normal" may be more probable when a facility burns wastes that have little temporal variation in chemical and physical properties, at relatively constant rates, and under operating conditions that do not fluctuate widely. Facilities that do not operate within these guidelines, including facilities that burn highly variable wastes, could experience more difficulty defining "normal." If a facility cannot define "normal" for their operation, collection of data for the risk assessment may need to be performed in conjunction with the DRE/SRE conditions.

Site-specific factors will inform what constitutes a "normal" test condition. However, a "normal" test can generally be characterized as a test where each control parameter is maintained either near the historical mean, or between the historical mean and the maximum or minimum set point (as appropriate), while burning representative, but challenging, feeds. The goal for burning representative, but challenging, feeds simply means that wastes which may cause elevated or more highly toxic emissions are preferred for the test. Examples include difficult-to-burn wastes, wastes that contain dioxin/furan precursors, or wastes that contain toxic or bioaccumulative constituents. For example, a hexachlorobenzene waste stream would be preferred over a methanol stream if both are routinely processed.

2. ***Can the facility identify additional permit limitations and record keeping provisions to ensure that the facility does not operate in excess of the normal conditions over the long term?***

Facilities choosing to use emissions data collected under normal operating conditions in the risk assessment (instead of data collected under "worst-case" DRE/SRE conditions) may be subject to additional permit limitations as necessary to protect human health and the environment. Additional limitations may be necessary to ensure that, on average and over the long term, emissions remain within the boundaries represented by a risk assessment. The permit terms may include long-term (monthly, quarterly, semiannual, and/or annual) average limits for certain control parameters, or use of control charts similar to those used for industrial quality control. For example, the control charts could be used to ensure that long-term variation does not exceed one or two standard deviations from the mean. Waste tracking and record keeping may also be specified. The permit may specify that significant changes be reported to the permitting authority. These changes may be subject to review and determination of the need for possible retesting.

Permitting approaches involving long-term averaging should generally be considered very carefully. In some cases, long-term averaging may not achieve the intended objective of maintaining ongoing emissions at levels that do not present a significant risk to human health and the environment. The main consideration, for a given control parameter, is whether high emissions caused by short-term perturbations outside of a certain operating range can be offset by lower emission rates during periods of more normal operations. A long-term averaging period may be utilized effectively when a control parameter exhibits a linear relationship with emissions. For example, elevated metals emissions from higher metals feed rates can generally be offset by commensurate periods of operation at lower metal feed rates. However, for other parameters, perturbations simply increase overall emissions. For example, when an interruption in caustic feed to a scrubber causes excess acid gas emissions, a facility cannot compensate by subsequently adding more caustic. In this situation, a long-term averaging approach may not be appropriate.

The facility should propose a permitting approach for ensuring that, over the long term, the unit does not operate in excess of the conditions represented as normal during the test. Most likely, the approach will closely mirror the approach used to define "normal" in the first place. It should generally not be necessary for the permit approach to be so conservative that operation during the "normal" test is driven towards the extreme edges of the operating envelope (thereby negating the point of the normal test). On the other hand, if testing near an operating extreme seems necessary to reflect variations in everyday operation, then it may be appropriate to reconsider whether "normal" can truly be defined for that operation.

3. ***Are there additional site-specific considerations?***

It may be appropriate to use emissions data collected under DRE and/or SRE conditions in the risk assessment because of other circumstances, such as acute risk concerns. For some constituents, direct inhalation may cause short-term or acute effects. In these situations, EPA OSW has recommended that a maximum, 1-hour emission rate be evaluated in the risk assessment (EPA 1998a). Maximum emission rates are generally achieved under DRE and/or SRE conditions.

One example of a situation where it may be appropriate to use emissions data collected under normal operating conditions in the risk assessment is a BIF facility that wishes to perform testing for metals at normal conditions. If the facility can provide historical data to characterize normal metal feed rates (consistent with the recommendations in Section 3.3.2.2) and if monthly-average metal feed rate permit limits could be established based on the risk burn to assure that ongoing operation remains within the range represented as normal during the test (consistent with the recommendations in Section 3.3.2.2), then it might be appropriate to use emissions data collected under normal operating conditions in the risk assessment. The recommended testing and permitting approach for this situation follows:

- ***SRE Test:*** The SRE test is conducted at *maximum metals feed rates*, and could involve metals spiking. Emissions from the SRE test are required to be below allowable BIF emission limits (which are based only on inhalation risks) pursuant to 40 CFR § 266.106. *Hourly rolling average metal feed rate limits* are established in the permit based upon this test.

- ***Normal Test:*** This test is conducted at *normal metals feed rates*, without metals spiking. Emissions data from the normal test are evaluated in the risk assessment to determine potential risks from both direct and indirect exposures. *Monthly-average metal feed rate limits* are established in the permit based upon this test.

An example of a situation where it may not be appropriate to use emissions data collected under normal

operating conditions in the risk assessment is a commercial facility with a diverse customer list that randomly burns any hazardous waste available on the test day. This facility may not be able to identify a specific waste that represents normal operations, or may not choose to commit to a waste inventory tracking scheme and long-term averaging to assess whether the test waste remains representative. In this case, it may be more appropriate to collect emissions data for the risk assessment during "worst-case" DRE/SRE performance tests.

In summary, emission rates (and related feed and operating conditions) that are evaluated in the risk assessment should clearly correspond to potential permit terms and conditions. The permit terms can ensure protection of human health and the environment by prohibiting operations outside of the operating boundaries represented by a risk burn and risk assessment that demonstrates emissions will not pose a significant risk. The permit writer should work closely with the facility to determine the appropriate test condition(s) for collection of risk burn data and a corresponding permit approach.

3.3.2.3 Separate Testing to Resolve a Conflict

Even if a facility does not choose to perform risk burn testing at normal conditions, it may be appropriate to perform the risk burn (or a portion of the risk burn) independently from the DRE/SRE performance tests to resolve a conflict. The risk burn may be performed independently because of logistical conflicts (for example, the DRE/SRE testing may have already been completed before the need for risk burn data was identified). The risk burn may also be performed independently to resolve a conflict between the risk burn and DRE/SRE waste feed or operating targets.

Conflicting parameters are key control parameters that cannot be demonstrated simultaneously (e.g., maximum combustion gas velocity and minimum fabric filter pressure differential). A facility may encounter conflicts when attempting to integrate the key control parameters for risk testing (identified in Chapters 4 through 7) with key control parameters associated with DRE/SRE performance testing. To overcome a conflict, it may be appropriate for a facility to perform duplicate tests as follows:

- A first set of operating conditions to set limits for all control parameters, excluding the ones in conflict;

- Additional operating condition(s) to set limits on the conflicting control parameters. To the maximum extent practicable, only the conflicting parameters should be varied from the first set of operating conditions. All non-conflicting parameters should be maintained as constant as possible during all operating conditions.

As discussed in Sections 3.3.1.2 and 3.3.1.3, it is recommended that the risk burn (or a portion of the risk burn) be performed independently of DRE/SRE testing when actual wastes are not utilized for the DRE/SRE test, or when there is a conflict between the risk burn and DRE/SRE feed or operating targets.

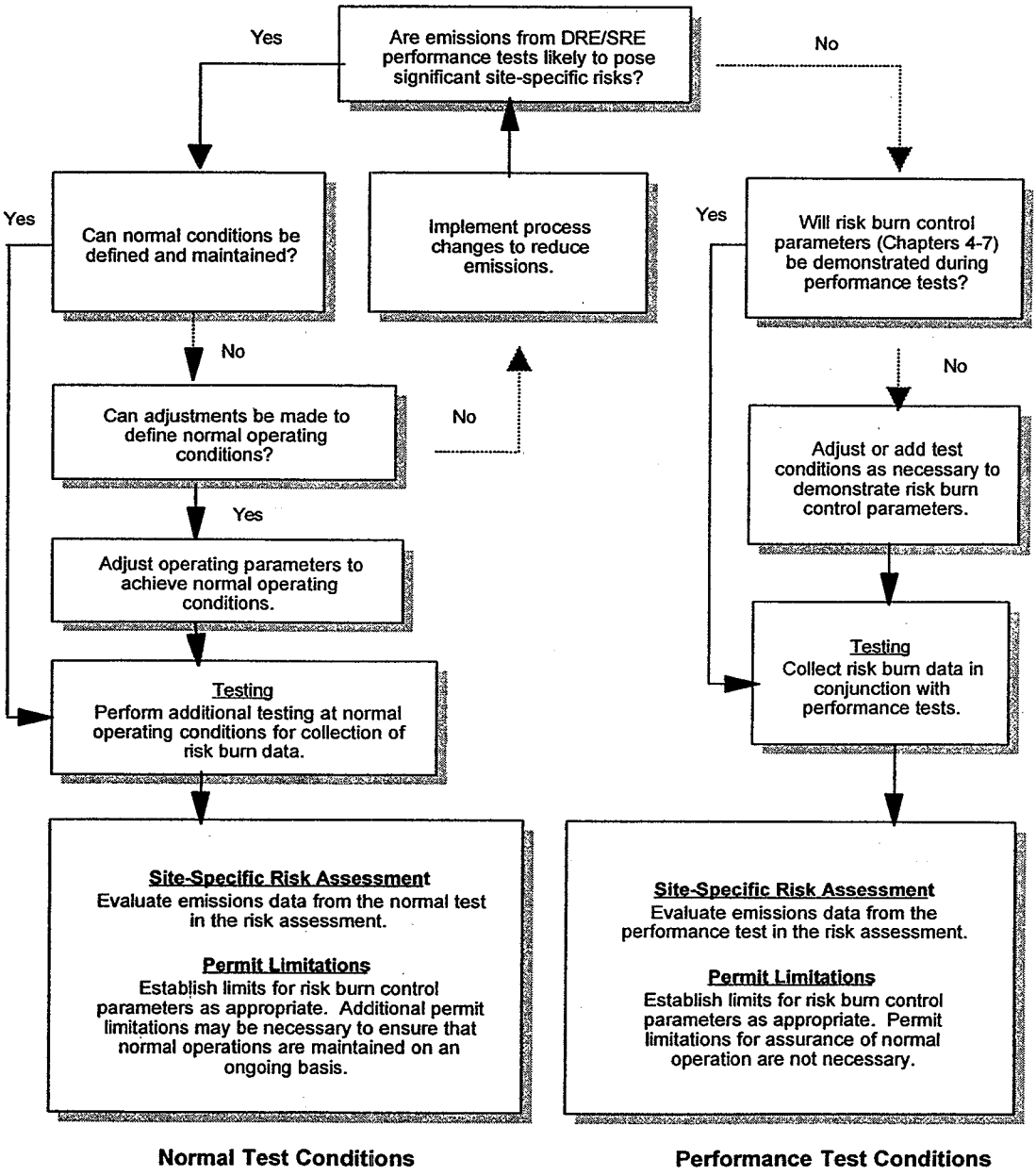
3.4 RISK-BASED DATA COLLECTION, EXAMPLE LOGIC

Figure 3-1 provides example logic (based on the recommendations discussed throughout this chapter) for permit writers and facility personnel to consider in determining appropriate test conditions for the risk burn. The first step involves determining whether emissions demonstrated under DRE and SRE conditions are anticipated to present a significant risk to human health and the environment, considering target risk levels as specified by the regulatory agency. EPA OSW recommends that this question be answered by evaluating existing emissions data, by conducting "mini-burns" (as allowed by existing permit or interim status conditions), or by evaluating data from similar facilities in a preliminary risk assessment.

Based on preliminary data analysis, a facility may anticipate that emissions data collected during performance testing (DRE and SRE conditions) will indicate that facility emissions do not pose a significant risk to human health and the environment. This situation is represented on the right-hand side of the flow chart. The permit writer would then work with the facility to determine whether the control parameters identified in Chapters 4 through 7 of this document can be demonstrated concurrently with parameters to be demonstrated during the DRE and SRE tests. If so, then it may be appropriate to perform the risk burn in conjunction with the DRE and SRE test conditions.

FIGURE 3-1

RECOMMENDED SITE-SPECIFIC RISK ASSESSMENT DATA COLLECTION FLOW CHART



In some cases, the control parameters identified in Chapters 4 through 7 of this document may not be targeted for demonstration during the DRE or SRE test conditions. In these circumstances, it may be appropriate to adjust the DRE/SRE test conditions to demonstrate appropriate control parameters from Chapters 4 through 7, or add extra test conditions as described in Section 3.3.2.3. An example is a hazardous waste boiler that is equipped with a dry APCD for particulate control, but whose waste feeds contain no metals. Since the waste feed does not contain metals at detectable levels, the facility is not required (pursuant to 40 CFR §§ 266.102 and 266.106) to perform a maximum temperature SRE test or to establish maximum inlet temperature limit for the dry APCD to control metals. However, Section 4.2.1.3 recommends maximum inlet temperature to a dry APCD as a primary control parameter related to D/F emissions. If the boiler cannot demonstrate maximum APCD inlet temperature during the DRE test (because of an inability to control APCD temperature independently of combustion temperature, which would be at a minimum), then it is recommended that an extra test condition be added to the test plan specifically to demonstrate maximum APCD temperature while sampling for D/Fs. [Note: The facility could also provide information to justify D/F testing while operating at normal APCD temperature. However, as explained in Section 4.2.1.3, the exponential relationship between D/F emissions and APCD temperature complicates the ability to assure that D/Fs will be maintained at normal levels on an ongoing basis.]

In some situations, the preliminary data analysis might suggest that a facility's worst-case emissions (as measured during performance testing under DRE and SRE conditions) may pose potential risk to human health and the environment if it is assumed that these emissions levels are present all of the time. This situation is represented on the left-hand side of the flow chart. In these circumstances, EPA OSW recommends two options: (1) demonstrate that normal operating conditions can be defined and maintained and perform additional testing at normal conditions; (2) implement process changes to reduce emissions and meet risk-based limits under DRE and SRE conditions. Process changes can include changes to improve combustion efficiency (including burner design and methods of feeding wastes), reductions in feed rates of certain toxic constituents (like metals), or the addition/modification of air pollution control systems.

Facilities that demonstrate the ability to define and maintain normal operating conditions may be subject to additional permit terms as necessary to protect human health and the environment to ensure that the conditions represented as normal during the test are, in fact, normal over the long-term operation of the

facility. These terms can include long-term average permit limitations for waste feed rates, temperatures, and other appropriate control parameters, use of control charts, and/or waste tracking and record keeping. These facilities may also be asked to submit a compliance monitoring plan to demonstrate how compliance with the permit terms will be maintained and documented.

3.5 TEST PLAN SUMMARY INFORMATION

A common understanding regarding how the final permit limits will be developed is integral to the design of the test protocol, and early communication and coordination between the permit writer and facility is essential. The permit writer is responsible for identifying control parameters which may be limited in the permit, and for explaining how specific permit terms may be established based on the test results. The permit writer should generally rely on the facility owner/operator to ensure that risk burn operating conditions are targeted in a manner that supports permit terms that are acceptable to the facility. EPA OSW recommends that the following specific types of information generally be included in the test plan to facilitate this process:

- For each type of emissions data to be evaluated in the risk assessment (D/Fs, non-D/F organics, metals and HCl/Cl_2), an explanation as to whether the facility expects for the risk assessment to be performed using: 1) emissions data from a trial burn or performance test; 2) emissions data from a normal test, or 3) other information, such as a regulatory standard or zero SRE assumptions for metals.

- For instances where the risk assessment will be performed using emissions data from a normal test, supporting narrative and historical information as necessary to characterize "normal" for the specific operations, as well as a proposed permit approach for assuring that conditions remain within those represented as normal on an ongoing basis.

- For each test condition, a narrative discussion explaining the overall objectives and approach, as well as a summary matrix listing:

  - The type of test condition (e.g., DRE, SRE, normal, etc.);

  - Emissions data to be collected and regulatory performance standards to be demonstrated;

  - The proposed feed characteristics and operating targets for each relevant control parameter. Control parameters include those listed in Chapters 4 through 7, as well as

the control parameters that will be demonstrated during trial burn or performance testing for DRE, SRE, particulate matter, and HCl and Cl_2.

- A list of conflicting parameters (key control parameters that cannot be maximized or minimized simultaneously), along with a detailed explanation of the reasons for the conflict. The two or more test conditions that will be performed to resolve the conflict should be described, and changes in other control parameters that may be necessary to resolve the conflict should be identified.

- A complete list of control parameters which are expected to be limited in the permit. This list should be consistent with the proposed test conditions and the following information should be included for each control parameter:

  - The anticipated permit limit, assuming that all test conditions are executed as planned;

  - An indication of whether the permit limit will be based on the trial burn or other information (such as a zero SRE assumption for metals);

  - Specific information on how each permit limit will be established based on trial burn results. This information includes specifying the test condition that will be used to establish the numerical limit and how the numerical limit will be calculated (such as the average over all test runs).

  - Specific information on how each control parameter will be monitored and recorded to demonstrate compliance with the permit limit (i.e., whether the control parameter will be continuously monitored, the type of record to be maintained and the recording frequency, and what averaging period will be used for the compliance determination).

  - Statements as to whether the parameter will be interlocked with the AWFCO system, and the corresponding proposed set point.

EPA OSW recommends that the risk burn be integrated with DRE/SRE performance testing as necessary to produce a consistent set of enforceable permit conditions. When permit terms will be established from multiple test conditions, the complete list of anticipated limitations should be reviewed for internal consistency and potential conflicts.

CHAPTER 4

DIOXIN AND FURAN EMISSIONS

D/Fs can pose significant risks through both direct and indirect exposure pathways. This chapter reviews EPA OSW's recommendations for specific operating and feed parameters to be considered for demonstration during collection of D/F emissions data for risk burns. Depending on site-specific considerations, it may be necessary to limit certain of these control parameters in the RCRA permit to protect human health and the environment by ensuring that D/F emissions remain within the levels measured during the risk burn on an ongoing basis.

D/F formation is an extensive and complex subject. This chapter starts with general information and becomes progressively more specific. Background information regarding formation mechanisms is provided in Section 4.1. Key control parameters are reviewed and summarized in Section 4.2, and the relevance of the parameters for each industry category (incinerators, boilers, cement kilns, and lightweight aggregate kilns) is discussed in Sections 4.3 through 4.6. Tables 4-1 and 4-2 summarize the recommendations by industry category.

This guidance relies on available research and emissions databases to draw general conclusions and provide recommendations. However, it is important to note that this guidance cannot encompass every situation. Permit writers should evaluate facility-specific operating trends and information in conjunction with the principles summarized in this document in order to make their facility-specific permit decisions.

4.1 DIOXIN AND FURAN FORMATION MECHANISMS

D/Fs can result from a combination of formation mechanisms, depending on design, combustion conditions, feed characteristics, and type and operation of APCD equipment. D/F formation mechanisms have been studied since the late 1970s when D/Fs were found in municipal waste combustor emissions.

Lustenhouwer originally advanced three theories to explain the presence of D/Fs (Lustenhouwer and others 1980). The theories may now be described as:

1. Survival of trace D/Fs in the fuel.

2. D/F formation from gas-phase precursors which are chemically similar to D/Fs, such as chloro-aromatics, via

   a. homogeneous (gas-gas phase) reactions, or
   b. heterogeneous (gas-solid phase) condensation reactions between gas-phase precursors and a catalytic particle surface.

3. *De novo* synthesis of D/Fs from carbon sources that are chemically quite different from the dioxin and furan ring structures. *De novo* synthesis involves heterogeneous, surface-catalyzed reactions between carbonaceous particulate and an organic or inorganic chlorine donor.

It is now generally accepted that Theory (1) cannot explain the levels of D/F emissions which have been measured from combustors. Most combustion units do not burn D/F contaminated wastes, and Schaub and Tsang have noted that the gas-phase thermal destruction efficiency for D/Fs is high at the flame temperatures typically achieved in a combustion unit (Schaub and Tsang 1983). D/Fs have been found to decompose rapidly at temperatures above 1700 °F (Schaub and Tsang 1983).

Theory (2a) is also believed to play a relatively minor role in the D/F emissions from combustion facilities. An early kinetic model developed by Schaub and Tsang suggested that the homogeneous gas-phase rate of formation could not account for observed yields of D/Fs (Schaub and Tsang 1983). At the high temperatures in a combustion zone, the multi-step process necessary for D/F formation cannot compete with destruction. Although Sidhu and others have subsequently demonstrated pure gas-phase formation of D/Fs (Sidhu and others 1994), the minor role of homogeneous gas-phase formation is evidenced by numerous field measurements which show higher D/Fs downstream of the combustion chamber than in the flue gases immediately exiting the combustion chamber (Gullett and Lemieux 1994).

D/F emissions from combustion devices are now believed to result primarily from heterogeneous, surface-catalyzed reactions in the post-furnace regions of the unit (Theories 2b and 3). Experimental evidence suggests that these reactions occur within a temperature range of approximately 390 to 750 °F (200 to

400 °C) or wider, with maximum formation occurring near 570 °F (300 °C) (Kilgroe and others 1990).

Theories (2b) and (3) are both characterized by heterogeneous, surface-catalyzed reactions. Dickson summarizes the distinctions between the two heterogeneous formation pathways (Dickson and others 1992). Theory (2b) can be distinguished by reactions involving gas-phase chloro-aromatic precursors which might already be present in the fuel, or which could be formed as products of incomplete combustion (Karasek and Dickson 1987; Dickson and Karasek 1987). Theory 3 does not require that chloro-aromatic precursors be present on fly ash or in the gas stream. Instead, both the chloro-aromatic precursors and D/Fs may be synthesized *de novo* from gas-solid and solid-solid reactions between carbon particulates, air, moisture and inorganic chlorides in the presence of a metal catalyst, primarily divalent copper (Stieglitz and others 1989a and 1989b). Activated carbon has also been implicated as a catalyst (Dickson and others 1992).

Dickson has performed studies to quantitatively determine the relative predominance of the two heterogeneous formation pathways (Dickson and others 1992). Yields of polychlorinated dibenzo-*p*-dioxin from the precursor compound pentachlorophenol were 72-99,000 times greater than yields formed from reactions of activated charcoal, air, inorganic chloride and divalent copper catalyst under identical reaction conditions. Citing the kinetic work of Altwicker (Altwicker and others 1990a), Dickson postulated the following:

- fast reactions involving chloro-aromatic precursors may be expected to predominate in the post-combustion and heat exchanger sections of a combustor, where the temperatures range from 600 to 250 °C and the residence time of the gas stream and entrained particulates is on the order of 1 second, and
- slower processes such as *de novo* synthesis may influence D/F emissions in dry pollution control equipment, where particulate residence times vary from 1 to about 1000 seconds.

Although both mechanisms may contribute to observed D/F emissions, Gullett and Lemieux have shown that "in flight" formation alone (at residence times less than 5 seconds) is sufficiently rapid to explain the D/F concentrations measured in the field (Gullett and Lemieux 1994).

Molecular chlorine (Cl_2) appears to play a role in D/F formation by chlorinating aromatic D/F precursors through substitution reactions. Chlorination of phenol has been shown to be three orders of magnitude

greater with Cl_2 than with HCl (Gullett and others 1990). Although HCl does not directly participate in precursor chlorination to a significant degree, it can produce molecular chlorine via the Deacon reaction (Griffin 1986; Gullett and others1990):

$$2HCl + \frac{1}{2} O_2 \Longleftrightarrow Cl_2 + H_2O, \text{ with copper or other metals serving as catalysts} \qquad \text{(Equation 1)}$$

where:

HCl	=	hydrogen chloride
O_2	=	oxygen
Cl_2	=	chlorine
H_2O	=	water

The Deacon reaction depends on the presence of a metal catalyst to overcome kinetic limitations which would otherwise limit the production of Cl_2 from HCl (Griffin 1986). However, the metal catalyst also serves another important function. Once the aromatic rings have been chlorinated, the metal catalyst supports condensation reactions to form the D/F dual ring structure (Bruce and others 1991; Gullett and others 1992). Gullett has shown that formation of the dual ring structure (biaryl synthesis) is enhanced up to three orders of magnitude in the presence of metal catalysts, such as divalent copper (Gullett and others 1992). Based upon testing with nine different metals and oxidation states, divalent copper appears to demonstrate the strongest catalytic activity (Gullett and others 1992; Stieglitz and others 1989a).

Radical Cl also appears to play a role in D/F formation. Recent work by Gullett shows that radical Cl persists to temperatures where hydrocarbon chlorination occurs (Gullett and others 2000a). This mechanism is a likely chlorination route, and is influenced by combustion conditions and their effect on Cl radical persistence.

Sulfur has been shown to decrease D/F emissions. Substantially lower D/F emissions have been observed from coal-fired power plants than from municipal waste combustors, even though coal-fired utilities operate under conditions that should generally be conducive to D/F formation. The sulfur/chlorine ratio of the fuel may explain the difference. The typical S/Cl ratio in a municipal waste combustor is about 0.2, which is approximately an order of magnitude lower than that found in coal combustion (Raghunathan and

Gullett 1996). Raghunathan and Gullett have demonstrated significant D/F reduction at S/Cl ratios as low as 0.64 in a natural-gas-fired furnace, and as low as 0.8 in a coal-fired furnace (expressed as uncorrected furnace concentrations of parts per million SO_2 /HCl). Additional work has shown that D/F formation is substantially inhibited when the S/Cl ratio is greater than about 1:1 (Gullett and Raghunathan 1997).

Researchers have concluded that sulfur may interfere with D/F formation by (1) SO_2 depletion of Cl_2 (Equation 2), and (2) SO_2 poisoning of copper catalysts (Equation 3) to prevent biaryl synthesis (Griffin 1986; Gullett and others 1992; Bruce 1993; Raghunathan and Gullett 1996):

$$Cl_2 + SO_2 + H_2O \Longleftrightarrow 2HCl + SO_3 \qquad \text{(Equation 2)}$$

where:

Cl_2	=	chlorine
SO_2	=	sulfur dioxide
H_2O	=	water
HCl	=	hydrogen chloride
SO_3	=	sulfur trioxide

and:

$$CuO + SO_2 + \tfrac{1}{2} O_2 \Longleftrightarrow CuSO4 \qquad \text{(Equation 3)}$$

where:

CuO	=	cupric oxide
SO_2	=	sulfur dioxide
H_2O	=	water
$CuSO_4$	=	cupric sulfate

It is also possible that poisoning of the copper catalyst may interfere with the Deacon reaction.

From this background, it is clear that D/F formation involves many complex reactions. A complete understanding of the reaction chemistry may never be possible. However, for units achieving good combustion, the most important reactions appear to depend on gas/solid chemistry in cooler zones

downstream of the combustion chamber. Conditions conducive to downstream formation include (1) presence of particulates, which allow for solid-catalyzed reactions, (2) post-furnace particulate residence time in the critical temperature window (approximately 400 to 750 °F), (3) presence of Cl and organic precursors, including chloro-aromatics, and (4) a shortage of formation inhibitors, such as sulfur. Poor combustion can substantially increase D/F formation, possibly through increased soot formation (providing more catalytic reaction sites for D/F formation), increased formation of PICs (which can serve as D/F precursors), and increased gas-phase formation of D/Fs, although sufficient oxygen also appears to be necessary (Gullett and others, in press). Approaches that have been successfully demonstrated in full scale systems for controlling D/F emissions include:

- Maintenance of good combustion conditions to limit organic precursors and soot;
- Rapid flue gas quenching or other measures to minimize post-furnace particulate residence time in the critical temperature zone;
- Use of formation inhibitors;
- End-of-pipe flue gas cleaning techniques for D/F removal or catalytic decomposition.

4.2 CONTROL PARAMETERS TO BE CONSIDERED FOR RISK BURNS

As explained in Section 4.1, researchers have concluded that D/F formation mechanisms in combustion systems are extremely complex. D/F emissions cannot be predicted accurately with kinetic models or surrogate monitoring parameters such as carbon monoxide or total hydrocarbons (Santoleri 1995). Even in systems achieving good combustion (with low carbon monoxide concentrations), D/F formation may occur in cooler zones downstream of the combustion chamber (Santoleri 1995). Almost any combination of carbon, hydrogen, oxygen, and chlorine can yield some D/Fs, given the proper time and temperature (Altwicker and others 1990b; Santoleri 1995). Factors such as non-detect levels of chlorine in feed streams, lack of dry APCD systems, presence of D/F inhibitors (such as sulfur), lack of D/F catalysts (such as copper), and lack of D/F precursors (such as chloro-aromatics) may lead to reduced or low emissions of D/Fs. However, because mechanisms of D/F formation are extremely complex and are not well understood, it is not possible to predict with certainty whether a given facility will have significant D/F

emissions.

Since D/F emissions cannot be predicted, it is recommended that D/F emissions testing be performed to develop the emissions data for site-specific risk assessments. This section recommends key control parameters to be considered in establishing D/F test conditions. After the risk burn, these parameters may need to be limited in the permit to protect human health and the environment by ensuring that D/F emissions remain below measured levels on an ongoing basis.

Several of the control parameters identified in this section may already be limited in association with the DRE standard, and a number of the control parameters will be limited pursuant to the requirements of the hazardous waste combustor MACT rule. To the extent that risks from D/Fs are already adequately controlled by regulatory limits on key control parameters, then fewer risk-based limits may be needed in the RCRA permit. However, if regulatory controls are not applicable or sufficiently comprehensive, then additional risk-based limits may be warranted. A greater number of risk-based permit limitations may be necessary when the risk burn and RCRA or MACT performance tests reflect different operating modes.

In formulating the recommendations in Section 4.2, a conservative approach has been taken. It is important that D/F emissions not be underestimated for risk assessments. However, a facility is not precluded from showing, on a site-specific basis, why a less conservative approach may be warranted, or from following the procedures in Section 3.3.2.1 to show that D/F testing should be performed at normal conditions to better represent the risk over the facility's operating life. Conservative recommendations are appropriate for this guidance because the option of testing at normal conditions may not be appropriate for every facility. EPA OSW recommends that conditions conducive to D/F formation first be reviewed to ensure that high-emitting operating modes at a facility are not under-represented by the risk assessment. In addition, the option of testing at normal conditions depends on whether a permit approach can be developed to ensure that emissions remain at or below measured levels. It may be difficult to ensure that "normal" D/F emissions will be maintained on an ongoing basis after the risk burn because of the non-linear relationship between D/F emissions and certain control parameters, such as particulate hold-up temperature (i.e., short-term perturbations outside of a certain operating range can cause high emissions which cannot be offset during periods of more normal operations). Finally, some level of conservatism in the D/F testing and permitting approach may be warranted to compensate for the continuing uncertainty regarding D/F

formation mechanisms in general.

Although Section 4.2 presents each control parameter individually, the relative importance of the parameters with respect to one another should generally also be considered. When one or two control parameters are clearly dominant for a particular system, there may be little benefit to demonstrating and limiting additional parameters. The hierarchical ranking at the end of this section (Section 4.2.6) provides information to be considered in addressing this issue.

Control parameters are categorized according to post-combustion conditions (Section 4.2.1), combustion conditions (Section 4.2.2), feed composition (Section 4.2.3), hysteresis/memory effects (Section 4.2.4), and D/F control technologies (Section 4.2.5). All parameters may not be relevant for all systems, and the information in Section 4.2 should be considered in conjunction with the industry-specific information provided in Sections 4.3 through 4.6, as appropriate, as well as facility-specific information.

4.2.1 Post-Combustion Conditions

The flue gas temperature profile through the D/F formation region (approximately 400 to 750 °F) downstream of the combustion chamber is a critical factor influencing D/F emissions. Even for advanced combustor systems where CO levels are nearly zero (indicating complete combustion), downstream formation of D/Fs may still be significant (Buekens and Huang 1998). Post-combustion situations that should generally be considered during risk burn planning include:

- rapid wet quench systems;
- partial wet quench temperatures;
- dry particulate hold-up temperatures.

4.2.1.1 Rapid Wet Quench Systems

Recommendation *– EPA OSW recommends that facilities with rapid wet quench systems and "wet"*

APCD systems perform risk burn testing for D/Fs in conjunction with the DRE test conditions, whenever possible. If D/F testing during the DRE test is not feasible (for example, due to timing) consideration may be given to testing at normal conditions, where appropriate (see Section 3.3.2.2).

During the risk burn, demonstration of specific control parameters associated with the rapid quench system should generally not be necessary. Consequently, permit limits for the rapid wet quench system based on the test are not expected to be needed. However, controls based on design specifications may be appropriate in some cases to assure that the quench continues to function properly.

A rapid quench system involves rapid liquid quenching (on the order of milliseconds) from combustion temperatures to saturation temperatures. Facilities with "wet" APCD trains, such as venturi and packed bed scrubbers, utilize rapid wet quench. Wet scrubbers by design operate at stack gas dew point temperatures, which typically range from 170 to 200 °F. Thus, a flue gas exit temperature limit for the quench column or wet scrubbing device is not necessary to ensure that particulates are not held up in the critical 400 to 750 °F temperature window. (Note: This discussion applies to facilities with completely "wet" APCD trains. Temperature limits may be needed for facilities with "dry" APCD components that only perform a partial wet quench prior to a dry APCD, or that initially perform a full quench, but then reheat flue gases downstream of the wet scrubbing system and prior to a dry APCD. Sections 4.2.1.2 and 4.2.1.3 address these situations.)

In systems that perform rapid flue gas cooling from combustion temperatures to saturation (below 200 °F), surface-catalyzed D/F formation reactions are effectively precluded. Hazardous waste combustion facilities utilizing wet APCD systems are among the lowest-emitting sources of D/Fs (EPA 1999d; Santoleri 1998). A database containing more than 40 test conditions indicates that D/F emissions from these facilities are almost always less than 0.4 nanograms (ng) TEQ per dry standard cubic meter (dscm), and are often less than 0.1 ng TEQ/dscm (EPA 1999d). Ullrich describes reductions in D/F emissions which can be achieved through the use of a rapid liquid quench (Ullrich and others 1996).

A notable exception to the low D/F emissions trend for rapid wet quench systems is documented for one source (Source ID No. 330) where two test conditions showed average D/F emissions of 33 and 39 ng

TEQ/dscm, and an individual test run reached a maximum of 76 ng TEQ/dscm (EPA 1999d; Santoleri 1998). This source was burning waste oils with high levels of PCBs (30%). Although other PCB-burning sources have demonstrated low D/F emissions (EPA 1999d), it is possible that the PCBs or PCB combustion breakdown products could be responsible for significant gas-phase precursor formation of D/Fs at Source ID No.330.

The anomalous nature of the high D/F emissions at Source ID No. 330 emphasizes the inherent uncertainty in attempting to predict D/F emissions trends in lieu of actual emissions testing. Even in rapid wet quench systems where post-furnace D/F formation reactions are effectively precluded, the possibility of high D/F emissions cannot be ruled out. Incomplete combustion due to mixing inhomogeneities or cold pockets may generate D/F precursors, and D/Fs may be formed via gas-phase precursor formation mechanisms in regions of the combustion chamber where temperatures are below flame temperatures. These concerns lead to the recommendation for performing D/F testing at DRE test conditions (which usually represent challenging combustion conditions) for rapid wet quench systems whenever possible. Further information regarding the relationship between combustion conditions and D/F emissions is provided in Section 4.2.2.

4.2.1.2 Partial Wet Quench Temperatures

Recommendation *– EPA OSW recommends that facilities that partially quench flue gases to between 570 and 800 °F prior to a dry air pollution control device perform risk burn testing for D/Fs at a maximum post-partial quench flue gas temperature (i.e., at the highest temperature within the 570 to 800 °F range that the facility wishes to achieve during post-risk burn operation). For some facilities, this condition may occur in conjunction with the high temperature SRE test. Unless historical operating data are provided to indicate little variation in post-partial quench temperature, EPA OSW recommends against performing D/F testing at normal or average hold-up temperatures. A permit limit on maximum post-partial quench temperature based on the risk burn may be necessary to protect human health and the environment by assuring that the measured D/F emissions are maintained on an ongoing basis.*

Facilities with "dry" APCD components, such as fabric filters and ESPs, often utilize a wet quench for flue gas cooling prior to the APCD. However, unlike the rapid wet quench situation where flue gases are

quenched to saturation, the flue gas upstream of a dry APCD is only partially quenched, and APCD inlet temperatures are maintained well above the dew point.

As explained in Section 4.2.1.1, facilities that rapidly quench flue gases to below saturation temperatures generally have low D/F emissions. However, this may not necessarily be the case for facilities that perform only a partial quench. Waterland and Ghorishi observed significant increases in D/F levels in the flue gas (more than 2 orders of magnitude) as post-partial-quench temperatures increased from 711 to 795 °F (Waterland and Ghorishi 1997). The observed residence time was approximately 0.5 seconds. This phenomenon, termed rapid high-temperature D/F formation, appears to be active in a post-partial-quench temperature range of 570 to 800 °F (Waterland and Ghorishi 1997).

Based on this information, it appears that post-quench temperatures from partial quench systems can be important. Therefore, risk burn testing for D/Fs should generally be performed during a maximum post-partial quench flue gas temperature condition. For some facilities, this condition may occur in conjunction with the maximum temperature SRE test. A permit limit on post-partial quench temperature based on the risk burn may be necessary to protect human health and the environment by assuring that measured D/F emissions are maintained on an ongoing basis.

Unless historical operating data are provided to indicate little variation in post-partial quench temperature, EPA OSW recommends against performing D/F testing at normal or average hold-up temperatures. The exponential relationship observed between the quench temperature and D/F emissions makes it difficult to ensure that "normal" D/F emissions will be maintained on a ongoing basis after the risk burn (i.e., the D/F emissions from one minute of operation at 100 °F above normal cannot be offset by one minute of operation at 100 °F below normal). It is important that D/F emissions not be underestimated for risk assessments. However, a facility is not precluded from showing, on a site-specific basis, why a less conservative approach may be warranted, or from following the procedures in Section 3.3.2.2 to show why D/F testing should be performed at "normal" quench temperatures. If testing at normal temperatures is proposed, the facility should be prepared to explain how a monitoring scheme can be developed to reliably ensure that D/Fs will be maintained at "normal" levels on an ongoing basis.

4.2.1.3 Dry Particulate Hold-Up Temperatures

Recommendation *– EPA OSW recommends that facilities with "dry" particulate hold-up areas between 400 and 750 °F downstream of the combustion chamber perform risk burn testing for D/Fs at a maximum particulate hold-up temperature (i.e., at the highest temperature within the 400 to 750 °F range that the facility wishes to achieve during post-risk burn operation). For some facilities, this condition may occur in conjunction with the maximum temperature SRE test. Unless historical operating data are provided to indicate little variation in the inlet (or outlet, as appropriate) temperature to a particulate hold-up device, EPA OSW recommends against performing D/F testing at normal or average hold-up temperatures.*

The locations where temperatures should generally be maximized include: 1) the inlet to dry APCD equipment; 2) the outlet of heat exchangers; and 3) the inlet to extensive runs of un-insulated ductwork at lightweight aggregate kilns where substantial convective cooling occurs. Permit limits on maximum temperatures at these locations based on the risk burn may be necessary to protect human health and the environment by ensuring that D/F emissions are maintained at or below the measured levels on an ongoing basis.

Unless a facility utilizes a completely "wet" APCD system and performs rapid liquid quenching (on the order of milliseconds) to saturation, as discussed in Section 4.2.1.1, there may be one or more "dry" system components downstream of the combustion chamber which are conducive to surface-catalyzed D/F formation via precursor condensation and *de novo* synthesis mechanisms. Downstream components conducive to D/F formation include any devices which preclude rapid quench to below 400 °F, as well as devices where particulates are physically held up in the critical temperature window (approximately 400 to 750 °F). Specific devices include heat exchangers, extensive runs of un-insulated ductwork at lightweight aggregate kilns where substantial convective cooling occurs, and dry APCDs (such as ESPs, fabric filters, and possibly high efficiency particulate air [HEPA] filters).

Data described in numerous literature sources highlight the importance of inlet temperatures for dry APCDs, such as ESPs and fabric filters (Harris and others 1994; Lanier and others 1996; Kilgroe 1996; EPA 1999d and 1999e). In general, these data indicate that, within the D/F formation window of

approximately 400 to 750 °F, D/F formation can increase exponentially with increases in APCD inlet temperature. Thus, dry APCD inlet temperature is a critical control parameter.

Heat exchangers also provide the conditions necessary for surface-catalyzed D/F formation. When flue gas cooling involves a heat exchanger (a waste heat boiler is a type of heat exchanger), the gas is cooled slowly through the catalytic D/F formation temperature region. In addition, particulates may be held up on the heat exchanger tubes. Outlet temperatures from waste heat boilers typically range from 400 to 600 °F (EPA 1999d). Santoleri, citing numerous studies in Germany and the United States, notes that facilities with heat recovery boilers have been found to have higher emissions of D/Fs than facilities without heat recovery (Santoleri 1995). The D/F emissions trend for waste heat recovery boilers is further supported by data collected in support of the hazardous waste combustor MACT rule which indicates that incinerators equipped with recovery boilers have significantly higher D/F emissions than other incinerators (EPA 1997d and 1999d). Acharya has hypothesized that D/Fs in a boiler may be minimized by only cooling combustion gases to about 800 °F (Acharya and others 1991). Although energy recovery might be reduced, the gas temperatures would be maintained outside of the 400 to 750 °F range. Based on this information, the outlet temperature of a heat exchanger is a critical control parameter.

Data collected in support of the hazardous waste combustor MACT rule also document elevated D/F emission rates at some lightweight aggregate kilns, where formation apparently occurred in extensive runs of un-insulated ductwork connecting the kilns to the fabric filters (EPA 1997d and 1999d). Convective cooling in un-insulated ductwork can result in slow gas cooling through the catalytic D/F formation temperature region, and the ductwork provides surface area for particulate hold-up. EPA noted that reductions of D/F emission rates could likely be achieved simply by rapidly quenching gases at the exit of the kiln to less than 400 °F and insulating the ductwork to maintain gas temperatures above the dew point prior to the fabric filter. This information indicates that the temperature at the inlet to extensive runs of un-insulated ductwork at lightweight aggregate kilns (where flue gas can cool through the 400 to 750 °F temperature range) is a critical control parameter.

In summary, the relatively low temperature (approximately 400 to 750 °F) "dry" areas of particulate hold-up downstream of the combustion zone should generally be emphasized for D/F testing. These areas are conducive to surface-catalyzed D/F formation via precursor condensation and *de novo* synthesis

mechanisms. Available data indicate that particulate matter provides the substrate to act as a chemical reactor, given the appropriate temperature, time, and presence of Cl. Thus, any particulate hold-up area (including fabric filters, ESPs, HEPA filters, heat exchangers, and extensive runs of ductwork at aggregate kilns) operating in the critical temperature range can promote D/F formation.

Particulate hold-up temperatures should be considered very carefully in determining the appropriate test condition for D/F testing. In most instances, it is recommended that facilities perform risk burn testing for D/Fs at a maximum particulate hold-up temperature (i.e., at the highest temperature within the 400 to 750 °F range that the facility wishes to achieve during post-risk burn operation). For some facilities, this condition may occur in conjunction with the high temperature SRE test. The locations where temperatures should generally be maximized include: 1) the inlet to dry APCD equipment; 2) the outlet of a heat exchanger; and 3) the inlet to an extensive run of un-insulated ductwork at lightweight aggregate kilns where substantial convective cooling occurs. Permit limits on maximum temperatures at these locations based on the risk burn may be necessary to protect human health and the environment by ensuring that D/F emissions are maintained at or below the measured levels on an ongoing basis. (Note: If the device is maintained *above* the critical temperature range to prevent D/F formation, for example, above 800 °F, a minimum temperature limit may be appropriate instead.)

Unless historical operating data are provided to indicate little variation in the inlet (or outlet, as appropriate) temperature to a particulate hold-up device, EPA OSW recommends against performing D/F testing at normal or average hold-up temperatures. D/F formation has been observed to increase exponentially with increases in temperature over the range of approximately 400 to 750 °F (Harris and others 1994; Lanier and others 1996; Kilgroe 1996; EPA 1999e). This non-linear relationship makes it difficult to ensure that "normal" D/F emissions will be maintained on a ongoing basis after the risk burn (i.e., the D/F emissions from one minute of operation at 100 °F above normal cannot be offset by one minute of operation at 100 °F below normal). It is important that D/F emissions not be underestimated for risk assessments. However, a facility is not precluded from showing, on a site-specific basis, why a less conservative approach may be warranted, or from following the procedures in Section 3.3.2.2 to show why D/F testing should be performed at "normal" temperatures. If testing at normal temperatures is proposed, the facility should be prepared to explain how a monitoring scheme can be developed to reliably ensure that D/Fs will be maintained at "normal" levels on an ongoing basis.

A final consideration involves the use of a reheater in a flue gas cleaning train. One source utilizing a rapid wet quench and wet scrubbing system (EPA 1999d, Source ID No. 602) has reported somewhat higher D/F emissions than those observed from most rapid wet quench systems. This source uses a coil-tube reheater downstream of the wet scrubbing system to reheat flue gases to above saturation temperatures prior to HEPA filtration. The gases are reheated to approximately 250 °F. Although this flue gas temperature is outside of the 400-750 °F range, the reheater tubes provide surface area for particulate hold-up and are estimated to be about 500 °F (EPA 1999d). These tube surface temperatures may promote surface-catalyzed D/F formation. During a risk burn, specific temperature targets for a reheater should generally not be necessary (operation of a reheater is expected to be fairly constant). However, it is recommended that the permit writer ensure that emissions sampling for D/Fs occurs downstream (rather than upstream) of the reheater.

4.2.2 Combustion Conditions

Although D/Fs are primarily formed in the post-combustion zone of combustion systems, the reactants or precursors for D/F formation originate in the combustion chamber itself (Buekens and Huang 1998). This section provides general information regarding the affect of combustion conditions on D/F emissions. Since the general discussion may not be entirely relevant for all systems, the industry-specific discussions provided in Sections 4.3 through 4.6 should also be consulted. In addition, some information may not be relevant to units that operate in a sub-stoichiometric mode. The discussions and recommendations in this section are based on the underlying assumption that all hazardous waste combustors are required by regulation to operate under combustion conditions that meet or exceed 99.99 percent DRE.

4.2.2.1 Target Test Conditions

Recommendation *– The complex, multi-variate nature of combustion parameters and their influence on D/F emissions makes it difficult to isolate effects, and thus to conclusively ascertain the relationship between individual parameters and D/F emissions. The difficulty in isolating effects complicates the task of targeting test conditions to ensure that D/F emissions are not under-represented in the risk assessment. To capture the potential range of D/F emissions, it is recommended that facilities perform testing for D/Fs during* <u>*all*</u> *planned test conditions (including*

both DRE and SRE conditions) whenever possible.

EPA OSW recommends that the challenging combustion scenarios discussed later in Section 4.2.2.3 be represented during D/F testing (if applicable to a particular system). The challenging combustion situations described in Section 4.2.2.3 include: 1) transient conditions; 2) operation with containerized or batch waste feeds; and 3) high carbon monoxide situations.

The combustion parameters identified later in Section 4.2.2.2 should automatically be addressed when D/F testing is performed during all planned test conditions, since these parameters are typically demonstrated and limited as part of the DRE determination. The combustion parameters listed in Section 4.2.2.2 include: 1) minimum primary and secondary combustion chamber exit temperatures; 2) maximum combustion gas velocity; 3) maximum waste feed rate at each feed location; 4) limitations on waste feed composition and batch feeds; and 5) maximum flue gas carbon monoxide and/or total hydrocarbon concentrations.

The general recommendation for D/F testing during all test conditions may be less appropriate for situations where downstream formation is of little or no concern (i.e., the rapid wet quench/wet APCD configurations discussed in Section 4.2.1.1). When there is minimal potential for downstream formation, D/F emissions will either be low, or are likely to be driven by poor combustion situations (see Section 4.2.1.1). Under these circumstances, D/F testing during only the DRE test conditions may be appropriate instead of testing during every test condition. Even under such circumstances, EPA OSW recommends that the challenging combustion scenarios discussed in Section 4.2.2.3 be emphasized, if applicable. The combustion parameters listed in Section 4.2.2.2 should automatically be addressed, since they are typically demonstrated and limited as part of the DRE determination. D/F testing during only the DRE test conditions should be less burdensome than testing during all conditions, but still conservative.

The recommendation for D/F sampling during all test conditions (or during the DRE conditions for rapid wet quench/wet APCD configurations) is a general guideline. However, some facilities and permit writers may be faced with situations that are not addressed by this general guideline. For example, DRE and SRE testing may already have been conducted in advance of the risk burn, or

simultaneous stack determinations for consolidated testing may not be possible. These and other situations call for decisions regarding the specific combustion conditions to be demonstrated (in addition to the conditions which are conducive to downstream formation discussed in Section 4.2.1). Therefore, this guidance recommends that the challenging combustion scenarios described in Section 4.2.2.3 (if applicable) be preferentially targeted for D/F testing and that, as appropriate, permit limits for the Section 4.2.2.2 combustion parameters be established based on D/F testing conducted under these challenging combustion scenarios. In addition, EPA OSW recommends that a facility-specific review of trial burn and historical operating data be performed to determine whether the challenging combustion scenarios correlate with other operating or feed parameters. If so, it is recommended that the correlating parameters be demonstrated during the testing, and it may be appropriate to limit those parameters in the permit in addition to, or possibly in lieu of, the combustion parameters listed in Section 4.2.2.2. Caution should be exercised to ensure that targets during the D/F testing for the Section 4.2.2.2 combustion parameters are not substantially different from those demonstrated during the DRE test.

Finally, it is important to recognize that some combustion units operate under extremely steady-state conditions, at temperatures and residence times that should routinely ensure good combustion. Challenging combustion situations, such as those described in Section 4.2.2.3, do not occur. For example, a liquid injection incinerator feeding a single high-British thermal unit (Btu) waste stream may sustain very constant, high temperatures. Combustion conditions may not fluctuate at all, and carbon monoxide may be near zero. Ideally, logistics will favor combining the D/F testing with the DRE conditions (in addition to performing D/F testing during the conditions conducive to downstream formation per Section 4.2.1, if applicable). If so, then the combustion parameters listed in Section 4.2.2.2 should automatically be addressed, since they are typically demonstrated and limited as part of the DRE determination. However, if combined testing is not possible, then consideration may be given to limiting the D/F testing to only those test conditions which are conducive to downstream formation (if applicable), and/or testing under normal combustion conditions, where appropriate (see Section 3.3.2.2). EPA OSW also recommends that historical operating data for the appropriate combustion parameters be reviewed to verify that the facility maintains steady-state operations with very few fluctuations. Demonstration of absolute maximum or minimum values for the combustion parameters listed in Section 4.2.2.2 during D/F testing may

be less critical for steady-state operations. In lieu of specific permit limits for the parameters listed in Section 4.2.2.2, periodic reporting to confirm continued absence of transients may be appropriate. When D/F testing cannot be performed in conjunction with the DRE test, caution should be exercised to ensure that targets during the D/F testing for the combustion parameters listed in Section 4.2.2.2 are not substantially different from the levels demonstrated during the DRE test.

Combustion conditions can play a key role in minimizing the formation of D/F precursors, and thus, in potentially minimizing D/F emissions. Maintenance of good combustion conditions to limit organic precursors and soot is repeatedly cited as a prerequisite necessary for achieving low D/Fs (Hasselriis 1987; Kilgroe and others 1990; Kilgroe 1996; Prescott 1996; Berger and others 1996; Gullett and Raghunathan 1997; EPA 1999e).

Substantial information exists to indicate that D/F emissions can be quite high when combustion parameters are not optimized. A majority of the work documenting the influence of combustion quality has been performed on municipal waste combustor systems. Gullett and Raghunathan observed substantial increases in D/F emissions under conditions of poor combustion and carbon monoxide levels greater than 2,000 parts per million (ppm) (Gullett and Raghunathan 1997). Buekens and Huang cite studies where poor combustion situations caused order-of-magnitude D/F increases over those observed during normal combustion (Buekens and Huang 1998). Berger describes a correlation between high D/F emissions and high total hydrocarbon emissions (Berger and others 1996). Prescott documents order-of-magnitude reductions in D/Fs through the use of good combustion control (Prescott 1996), and Hasselriis found that the optimum combustion conditions for minimizing dioxins and furans are closely related to those which minimize carbon monoxide emissions (Hasselriis1987).

Because order-of-magnitude increases in D/F emissions have been observed under certain combustion situations, it is important to ensure that potentially high-emitting operating modes are not overlooked when planning the risk burn. Therefore, the recommendations in this section focus on identifying and demonstrating challenging combustion situations for D/F testing. However, a facility is not precluded from showing, on a site-specific basis, why a less conservative approach may be warranted, or from following the procedures in Section 3.3.2.2 to show that D/F testing should be performed at normal conditions to

better represent the risk over a facility's operating life.

Targeting specific combustion conditions for D/F testing can be extremely challenging, because the relationship between individual combustion parameters and D/F emissions is not necessarily intuitive or readily demonstrated. Buekens and Huang explain that D/F formation in combustion processes is influenced by a number of combustion parameters simultaneously, and is therefore regarded as a multi-variate process (Buekens and Huang 1998). Key parameters are likely to vary by facility, and the key parameters may or may not be those identified in this guidance. For example, oxygen concentration is not specifically addressed during many trial burns, and often varies considerably between test conditions if excess air is used to simultaneously achieve minimum combustion temperature and maximum combustion gas velocity. Although studies show that D/F emissions may be affected by oxygen levels, contradictory conclusions have been reached regarding the specific relationship (Buekens and Huang 1998). Buekens and Huang postulate that different combustors may exhibit different behaviors with varying oxygen, and that there may not be a universally applicable correlation. The uncertain relationship between oxygen and D/Fs is just one example of the difficulty in predicting how different operating scenarios may affect D/F emissions.

Because of the inherent uncertainties involved in correlating D/F emissions and individual combustion parameters, it is recommended that D/F emissions be determined during *all* planned test conditions (e.g., DRE and SRE conditions) whenever possible. By characterizing D/Fs over the entire range of combustion conditions, a facility can minimize the possibility of inadvertently omitting combustion situations that may play a key role in D/F formation. In addition, the data collected during multiple conditions can be analyzed for trends to determine which combustion parameters may need to be limited in the RCRA permit to control D/F emissions. EPA OSW recommends that the challenging combustion scenarios discussed later in Section 4.2.2.3 be represented during the testing (if applicable). The challenging combustion situations described in Section 4.2.2.3 include: 1) transient conditions; 2) operation with containerized or batch feeds; and 3) high carbon monoxide situations. The combustion parameters identified in Section 4.2.2.2 should automatically be addressed when D/F testing is performed during all planned test conditions, since these parameters are typically demonstrated and limited as part of the DRE determination. The combustion parameters listed in Section 4.2.2.2 include: 1) minimum primary and secondary combustion chamber exit temperatures; 2) maximum combustion gas velocity; 3) maximum waste feed rate at each feed location; 4)

limitations on waste feed composition and batch feeds; and 5) maximum flue gas carbon monoxide and/or total hydrocarbon concentrations.

At the beginning of Section 4.2.2.1, several situations were identified where it may not be possible (or even necessary) to perform D/F sampling during every test condition. For example, DRE and SRE testing may have already been conducted in advance of the risk burn. In these situations, EPA OSW recommends that the challenging combustion scenarios described in Section 4.2.2.3 be preferentially targeted for D/F testing (if applicable). Again, these scenarios include: 1) transient conditions; 2) operation with containerized or batch waste feeds; and 3) high carbon monoxide (greater than 100 ppm) situations. These scenarios are appropriate to target because of the increased potential for localized oxygen deficiencies and carbon monoxide/total hydrocarbon spikes. Numerous test programs have established that D/Fs can be high when oxygen is insufficient or when carbon monoxide/total hydrocarbon concentrations are high (Hasselriis 1987; Kilgroe and others 1990; Harris and others 1994; Kilgroe 1996; Berger and others 1996; Gullett and Raghunathan 1997; Buekens and Huang 1998). As appropriate, EPA OSW recommends that permit limits for the Section 4.2.2.2 combustion parameters be established based on D/F testing conducted under these challenging combustion scenarios. In addition, it is recommended that a facility-specific review of trial burn and historical operating data be performed to determine whether the challenging combustion scenarios correlate with other operating or feed parameters. If so, then EPA OSW recommends that the correlating parameters be demonstrated during the testing, and it may be appropriate to limit them in the permit in addition to, or possibly in lieu of, the combustion parameters listed in Section 4.2.2.2.

At some facilities, the challenging combustion scenarios identified in Section 4.2.2.3 may not occur. Although challenging combustion situations can clearly increase D/Fs, there is little information regarding the difference between "better" and "best" combustion. One study shows that stack concentrations of D/Fs may be somewhat independent of combustion conditions (except in instances of very poor combustion) provided that downstream formation of D/Fs is limited or controlled (Kilgroe 1996). This study would seem to indicate that, for steady-state systems, demonstration of absolute minimum or maximum values for the Section 4.2.2.2 combustion parameters during the D/F testing may be less critical. Although demonstration of these control parameters can ideally be accomplished by combining the D/F testing with the DRE demonstration (which is preferred whenever possible), consideration may be given for some steady-state systems to limiting the D/F testing to only those test conditions which are conducive to

downstream formation per Section 4.2.1 (if applicable), and/or testing under normal conditions provided the facility meets the criteria in Section 3.3.2.2. Periodic reporting to confirm the continued absence of transients may be appropriate in lieu of establishing specific permit limits for the Section 4.2.2.2 combustion parameters.

4.2.2.2 Combustion Parameters

Recommendation *– To assure combustion quality and minimize D/F precursors, EPA OSW recommends that the following combustion parameters be demonstrated during D/F testing and controlled during subsequent facility operation, consistent with the recommendations in Section 4.2.2.1:*

- *Minimum PCC and SCC combustion temperatures;*
- *Maximum combustion gas velocity as an indicator of residence time;*
- *Maximum waste feed rate for each feed location;*
- *Limitations on waste feed composition and batch /containerized feeds;*
- *Maximum flue gas carbon monoxide and/or total hydrocarbon concentrations.*

If other potentially significant parameters are identified based on a facility-specific review, then it is recommended that those parameters be demonstrated during D/F testing and possibly limited in the permit in addition to, or possibly in lieu of, the parameters listed above.

The relationship between these parameters and combustion quality has been discussed at length in other EPA documents (EPA 1989 and 1999e), and is not repeated here. Further discussion on waste feed composition, as well as on limitations for batch or containerized feeds, can be found in Section 4.2.2.3.1, Section 4.2.2.3.2, and Section 4.2.3 of this document. Controls may also be established on the waste firing system to ensure that burners are operated efficiently and in a manner consistent with manufacturer specifications (EPA 1989 and 1999e).

It is important to keep in mind that the most influential combustion parameters may not always be the ones listed above. EPA OSW recommends that a facility-specific review of test burn and historical operating data be performed to determine the potential significance of other operating or feed parameters, especially for the challenging combustion scenarios described in Section 4.2.2.3. If other potentially significant parameters are identified, then it is recommended that they be demonstrated during D/F testing and possibly limited in the permit in addition to, or possibly in lieu of, the parameters listed in this section as necessary to protect human health and the environment.

The importance of a facility-specific review to determine the significant parameters affecting combustion quality is illustrated by a situation documented by Branter (Branter and others 1999). In an initial test effort involving containerized waste feeds, the facility did not adequately control downstream D/F formation (i.e., the heat exchanger outlet temperature was not maintained as low as possible). For the two test conditions conducted at a high heat exchanger outlet temperature, the D/F yields were substantially greater at *maximum* PCC combustion temperatures than at minimum PCC combustion temperatures. This result seems counter-intuitive at first, and illustrates the importance of analyzing trial burn or historical operating data on a case-by-case basis.

Although the phenomenon described by Branter initially seems counter-intuitive, it may be explained by the work of Lemieux (Lemieux and others 1990). Lemieux showed that containers may be more rapidly heated and ruptured at higher PCC temperatures and higher kiln rotation speeds. Evolution of waste gases from the containers can exceed the rate at which stoichiometric oxygen can be supplied, resulting in increased organic emissions, or "puffs." Lower temperatures may lead to more gradual rupture of waste containers, and less disruptive organic puffs. This situation is discussed further in Section 4.2.2.3.2. In the situation documented by Branter (Branter and others 1999), the higher PCC temperature test may have been associated with more rapid container heating and larger organic puffs, providing more organic precursors for downstream D/F formation at the high quench outlet temperature. Despite the higher PCC temperature and CO below 100 ppm (hourly rolling average corrected to 7% oxygen), this unit operating at a high PCC temperature also failed DRE. The unit passed DRE and experienced reduced D/F emissions during the lower PCC temperature run. It is interesting to note that, once downstream quench temperatures were lowered, D/F emissions were reduced and appeared to be independent of PCC temperature.

Section 4.2.2.3 Challenging Combustion Scenarios

Section 4.2.2.1 recommends D/F sampling during *all* test conditions whenever possible (or during the DRE conditions for rapid wet quench/wet APCD configurations). However, some facilities and permit writers may be faced with situations that are not addressed by these general guidelines. DRE and SRE testing may have already been conducted in advance of the risk burn, or simultaneous stack determinations for consolidated testing may not be possible. These and other situations call for decisions regarding the specific combustion conditions to be demonstrated. Therefore, this guidance recommends that the following combustion situations (if applicable) be preferentially targeted for D/F testing:

- Transient conditions;
- Combustion of containerized or batch wastes;
- Operation at high carbon monoxide levels, for units with carbon monoxide limits greater than 100 ppm.

In all of these situations, there may be an increased potential for incomplete combustion products to act as D/F precursors and increase D/F emissions. The remainder of this section provides additional information on these scenarios.

4.2.2.3.1 Transient Conditions

Recommendation *– If a combustion unit normally operates under transient conditions, then EPA OSW recommends that this form of operation be represented during D/F testing. It is recommended that the facility-specific feed or operating conditions causing the transients be identified and targeted for the risk burn. The need for permit conditions to limit transients after the risk burn may be necessary to protect human health and the environment and should generally be considered taking into account the risk burn emissions data and the facility's operating history.*

Transient combustion conditions are usually indicated by recurring spikes in combustion parameters, especially combustion temperatures, combustion chamber pressure, carbon monoxide, or total

hydrocarbons. Routine spikes should generally be emphasized for the risk burn (i.e., spikes which may occur as often as several times per hour on an ongoing basis). Upsets are not encompassed by the term "transient," and are generally not represented during the risk burn unless there is a specific agreement reached between the facility and permit writer.

Transient spikes indicate potential changes in combustion quality that may increase D/F emissions. Raghunathan documented an order-of-magnitude D/F increase during a test run where a few significant CO spikes occurred, even though the average CO concentration for the 3-hour test run was maintained well below 100 ppm (Raghunathan and others 1997a). Berger describes a correlation between high D/F emissions and total hydrocarbon spikes (Berger and others 1996).

If a combustion unit normally operates under transient conditions, then it is recommended that this form of operation be represented during D/F testing. The permit writer should review historical operating data to determine whether a facility experiences routine transients. If so, EPA OSW recommends that the waste feed or operating conditions that cause the transients be determined. The feeds or operating conditions causing transients represent candidate conditions for D/F testing. Particular attention should generally be given to data indicating transients for combustion temperatures, combustion chamber pressure, carbon monoxide, and total hydrocarbons. Instantaneous data will be more useful in identifying transients than rolling average data, which inherently dampens spikes.

Batch feeds can cause transients, and are discussed separately in Section 4.2.2.3.2. However, other wastes can cause transients if they are not blended properly, or if they are treated in a unit that is not designed to accommodate particular waste types. Adequate blending or mixing of waste to minimize variations in heating value, volatility and moisture content can reduce combustion transients associated with improper feed conditions (Kilgroe 1996). Examples of wastes that can cause transients if handled improperly include:

- Stratified or highly viscous liquids and sludges;
- Aqueous or low heating value liquids;
- Liquids with a high percentage of solids;

- Highly chlorinated wastes;
- Low heating value solids and sludges;
- Wastes with a high moisture content; and
- Batch feeds with high moisture, volatility, or instantaneous oxygen demand.

During D/F testing, EPA OSW recommends that the facility treat actual wastes (and not surrogate wastes synthesized from pure compounds) whenever possible. Candidate wastes should generally be selected based upon a review of the wastes handled at a particular facility, with special consideration given to those wastes burned at commercial facilities due to their variation and complexity.

4.2.2.3.2 Containerized or Batch Wastes

Recommendation *– When a facility feeds containerized or batch wastes, EPA OSW recommends that D/F testing be performed while operating under simulated "worst-case" containerized or batch feeding conditions. It may be appropriate to spike actual wastes to maximize the volatility and oxygen demand of each batch charge.*

EPA OSW recommends that maximum total waste feed rate to the batch feed system (e.g., lb/hr) be maintained as part of the "worst-case" test demonstration. The individual batch size and feeding frequency will depend on the feeding practices at a particular facility.

During the risk burn, EPA OSW recommends that the air flow to the combustion unit generally be adjusted to minimize excess oxygen at the location in the combustion chamber where the batch is fed. In addition, the testing should generally be performed at higher kiln temperatures and higher kiln rotation speeds.

In most cases, permit limits for maximum total waste feed rate to the batch feed system (e.g., lb/hr) and maximum flue gas carbon monoxide/total hydrocarbon concentrations will be established to meet regulatory requirements (see Section 1.3). Additional permit limits may be necessary to protect human health and the environment, taking into account whether preventive controls are

necessary to assure that good combustion practice is maintained. Preventive controls may be needed if operating extremes for the batch feed system cannot be adequately represented during the risk burn, or if the facility has historically experienced frequent operational upsets or waste cutoffs due to batch feeds.

If preventive controls are needed, other permit limitations which might be considered include: 1) maximum batch size; 2) maximum batch charge heat content; 3) maximum batch feeding frequency; 4) minimum oxygen concentration at the location where the batch is fed; 5) maximum kiln temperature; 6) maximum kiln rotational speed; and 7) limitations on waste volatility, composition, or heat content.

Overcharging conditions can occur when containerized or batch wastes are fed to a combustion unit, especially if waste parameters and feeding practices are not closely matched to the unit design. When highly combustible or volatile wastes are exposed to the high temperatures in a combustion chamber, a surge of waste vapors rapidly evolves from the batch. This surge can deplete local oxygen, causing formation of fuel rich gas pockets that may escape the combustor without being adequately oxidized. This situation is often described as "puffing." Stack emissions may be affected, depending on whether the organics are destroyed elsewhere (such as in an afterburner).

Transient puffs arising from batch feed operations are well documented based on measurements conducted at the PCC exit of both pilot scale and full scale incinerators (Linak and others 1987; Cundy and others 1991; Lemieux and others 1990). At a pilot-scale facility, Linak documented PCC exit total hydrocarbon levels in excess of 10,000 ppm during very intense puffs, and performed chemical analysis to show that the puffs can contain numerous hazardous compounds, even though adequate DREs (>99.99%) may be achieved (Linak and others 1987). In several of the measurements, D/Fs were also formed at part-per-trillion levels. Both D/Fs and other chlorinated hazardous organics were formed most readily when chlorinated compounds were fed together with high heating value materials, such as toluene, which caused high magnitude, high intensity puffs. Linak observed that higher kiln temperatures and rotation speeds adversely affect puff intensity, because de-volatilization rates are enhanced by the increased temperatures and bed mixing. This observation has been confirmed by Lemieux (Lemieux and others 1990), and Branter (Branter and others 1999) has documented higher D/F emissions at higher PCC temperatures for a full-

scale facility (see the discussion in Section 4.2.2.2).

Because the soot and chlorinated organic precursors from transient puffs can affect D/F emissions, this guidance recommends that the risk burn be performed while operating under simulated "worst-case" batch feeding conditions (i.e., conditions that maximize precursor generation) to ensure that D/F emissions are not under-estimated for the risk assessment. Historical information on operating trends and AWFCO events should generally be reviewed in an effort to determine which batch characteristics are most likely to cause transients for a particular facility. Some batch-charged and containerized wastes can volatilize rapidly, causing an instantaneous release of heat and gases that completely consume the available oxygen. This rapid volatilization results in a momentary oxygen-deficient condition that can result in poor combustion. Conversely, if too large a batch of aqueous waste or wet soil is fed, there is danger that the batch can instantaneously quench temperature.

During the risk burn, EPA OSW recommends that actual wastes be spiked as necessary to maximize the volatility and oxygen demand of each batch charge. This maximization can be achieved by spiking with low boiling point/low latent heat of vaporization organics (preferably chlorinated), together with high heating value organics that have a high stoichiometric oxygen demand (Linak and others 1987; Wendt and others 1990; Cundy and others 1991). In rotary kilns, spiking compounds may be fed in bottles placed within the batch (instead of sorbed onto a solid matrix) to maximize the rate of volatilization.

The individual batch size and feeding frequency to be targeted for the risk burn should generally be based on the feeding practices at a particular facility. The "total waste feed rate" for the batch feed system (e.g., lb/hr) is a target combustion parameter (see Section 4.2.2.2) and should generally be maximized anyway. However, risk burn goals for individual batch size and feeding frequency may conflict (i.e., a facility may not be able to simultaneously feed their largest batch at their highest frequency). For the most part, the work of Lemieux suggests that larger batches fed less frequently will be worse than smaller batches fed more frequently at a given total feed rate (Lemieux and others 1991). In defining maximum batch size, the "maximum batch charge heat content" (maximum Btu/charge) is just as important as (and perhaps more important than) total mass.

The test plan for a batch-fed facility should generally include a description of the procedures used to

maintain adequate oxygen while feeding batch or containerized wastes. During the risk burn, the air flow to the combustion unit should generally be adjusted to minimize excess oxygen at the location in the combustion chamber where the batch is fed. In addition, the testing should generally be performed at higher kiln temperatures and rotation speeds, since these parameters have been shown to exhibit a strong correlation with puff intensity. Demonstration of high kiln rotation speed may be less imperative if spiking compounds are added in bottles to the batch instead of sorbed to a solid matrix, since this spiking method should generally assure a high volatilization rate. Multiple test conditions may be necessary to demonstrate high kiln temperatures, as well as the minimum temperatures recommended in Section 4.2.2.2. For some incinerators, a worst-case test may involve maximum PCC temperatures demonstrated in conjunction with minimum SCC temperatures.

The effect of transient puffs on stack emissions may vary substantially from facility to facility. Variations may depend on: 1) unit design and operation (including size, presence of an afterburner or SCC, and fuel-to-air controls); 2) waste characteristics (including volatility, instantaneous oxygen demand, heating value, and moisture content); and 3) feeding practices (including batch size, feeding frequency, feed location, excess oxygen, and the oxygen demand of batch feeds versus the oxygen demand of other fuels). Historically, batch feed practices at some facilities have caused DRE failures, upset conditions, carbon monoxide spikes, and excessive waste feed cutoffs. At other facilities, batch feeds do not appear to significantly affect either emissions or day-to-day operations.

The variable effect of batch feeds on emissions and day-to-day operations suggests that a facility-specific evaluation may be necessary to determine appropriate permit restrictions after the risk burn. In most cases, permit limits for maximum total waste feed rate to the batch feed system (e.g., lb/hr) and maximum flue gas carbon monoxide/total hydrocarbon concentrations will be established anyway to ensure compliance with RCRA and MACT regulatory performance standards (see Section 1.3). These parameters also assure combustion quality and minimization of D/F precursors, as discussed in Section 4.2.2.2.

Although total waste feed rate to the batch feed system (e.g., lb/hr) will be limited to meet specific RCRA or MACT regulatory requirements, this limitation may not be adequate for all situations because a facility can theoretically feed a very large batch on a very infrequent basis. A batch feed rate limit may be sufficient when it is based on a worst-case test, and when other system constraints are present (for example,

maximum batch size may be limited by the physical constraints of the batch feed system). However, in some cases, it may be preferable to augment a pound-per-hour feed rate limit with additional restrictions on maximum batch size or maximum batch charge heat content.

Carbon monoxide/total hydrocarbon levels have routinely been used to characterize combustion perturbations associated with batch feeds (Linak and others 1987; Cundy and others 1991; Lemieux and others 1991). Establishing limits for these parameters in conjunction with a "worst-case" batch feed test may be sufficient for assuring that ongoing operations are protective at some facilities. However, carbon monoxide or total hydrocarbon monitoring alone may not be adequate for all batch feed operations. Because oxygen depletion can occur very rapidly due to batch overcharging, carbon monoxide/total hydrocarbon levels may exceed the permit limit before corrective action can be initiated. For some operations, additional preventive measures may be necessary to protect human health and the environment by assuring that good combustion practice is maintained.

Other permit limitations which might be considered if preventive measures are needed include: 1) maximum batch size; 2) maximum batch charge heat content; 3) maximum batch feeding frequency; 4) minimum oxygen concentration at the location where the batch is fed; 5) maximum kiln temperature; 6) maximum kiln rotation speed; and 7) limitations on waste volatility, composition or heat content. Implementation of minimum oxygen limits for rotary kilns can sometimes be difficult, due to potentially significant gas-phase stratification (Cundy and others 1991). If gas-phase stratification is a problem, alternative monitoring locations may need to be considered.

The need for preventive controls should generally be determined based on a review of test conditions, emissions data, and the facility's operating history. There may be less need for preventive controls if operating extremes for the batch feed system can be adequately represented during the risk burn (or if emissions appear to be unrelated to batch feed operations), and if the facility routinely operates with few operational upsets or waste cutoffs related to batch feeds. Conversely, there may be more justification for establishing preventive controls on the batch feed system if operating extremes for the batch feed system cannot be adequately represented during the risk burn, or if the facility experiences frequent operational upsets or waste cutoffs due to batch feeds.

4.2.2.3.3 High Carbon Monoxide

Recommendation *– EPA OSW recommends that units with carbon monoxide limits greater than 100 ppm perform D/F emissions testing while carbon monoxide levels are maximized.*

When D/F emissions data are evaluated by normalizing the data based on APCD inlet temperature and carbon monoxide, low carbon monoxide levels (less than 100 ppm) are found to be associated with very low D/F emissions (less than 1 ng/dscm on a total basis) (EPA 1994c; Harris and others 1994). For carbon monoxide levels greater than 100 ppm, temperature-normalized dioxin emissions are found to be significantly higher (in the range of 10 to 100 ng/dscm on a total basis). This observation suggests that units with carbon monoxide limits *greater than* 100 ppm should generally perform D/F testing under conditions that maximize carbon monoxide levels.

4.2.3 Feed Composition

In addition to the physical waste characteristics described in Sections 4.2.2.3.1 and 4.2.2.3.2 that may contribute to poor combustion, there are several chemical feed characteristics that have been evaluated with respect to their potential influence on D/F emissions. These characteristics include chlorine concentration, the presence of metals (such as copper, iron, and nickel) that can act as catalysts for D/F formation, the presence of D/F precursors (such as chlorobenzenes and chlorophenols), and the presence of D/F inhibitors (such as sulfur, calcium hydroxide, and ammonia). Each of these is discussed below.

4.2.3.1 Chlorine

Recommendation *– For D/F testing, EPA OSW recommends that chlorine feed rates be maintained at normal levels (i.e., chlorine should not be biased low). Permit limits on total chlorine feed rate generally should not need to be established based on the risk burn.*

While the presence of chlorine is a necessary prerequisite for D/F formation, there does not appear to be a direct correlation between the level of chlorine in the feed and the level of D/Fs in the flue gas at full-scale combustion facilities. The American Society of Mechanical Engineers (ASME) (Rigo and others 1995)

analyzed over 1,700 test results with chlorine feed concentrations ranging from less than 0.1 percent up to 80 percent, and found no statistically significant relationship between D/F emission rates and chlorine concentration. Gullett provides a possible explanation for the poor correlation (Gullett and others 2000a). Obviously, no D/Fs can be formed in the complete absence of chlorine. However, extremely low concentrations of chlorine may be sufficient to form D/Fs at the trace levels of concern. An excess of chlorine does not necessarily yield greater quantities of D/Fs, and other parameters, such as APCD inlet temperature, appear to have a more significant influence on D/F yields.

Based on this information, there does not appear to be a need to demonstrate maximum chlorine feed rates during the risk burn, or to establish specific feed rate limits on total chlorine in the permit based upon the D/F testing. However, it is reasonable to expect that facilities will maintain normal levels of chlorine for the D/F testing (i.e., chlorine should generally not be biased low). Chlorinated wastes are preferred over non-chlorinated wastes for the risk burn, where the choice exists. In this guidance, the term "chlorine" refers to total chlorine from all sources, including both organic and inorganic forms.

4.2.3.2 Metal Catalysts

Recommendation *– EPA OSW recommends the use of wastes or other feed materials containing copper over feeds without copper during the D/F testing, where the choice exists. However, specific permit limits on copper (or other catalytic metal) feed rates based upon the D/F testing are generally not anticipated to be necessary to protect human health and the environment.*

Abundant pilot-scale and fundamental research has shown that certain metals, such as copper, may catalyze the formation of D/Fs (see Section 4.1). However, there does not appear to be a direct correlation between the level of copper in the feed and the level of D/Fs in the flue gas at full-scale combustion facilities. Copper spiking during full-scale testing of a cement kiln showed little or no influence on D/F emissions (Lanier and others 1996), although the testing may have been conducted in a system that was influenced by other, more dominant factors.

Luijk has shown that copper plays a competing role in both the formation *and destruction* of D/Fs (Luijk and others 1994). Copper contributes to *de novo* synthesis of D/Fs, but it also catalyzes their oxidative

destruction. Luijk and others hypothesize that $CuCl_2$ levels in the ppm range (no greater than the levels normally observed in municipal waste combustion fly ash) may offer optimum conditions for the formation of D/Fs.

Based on this information, there does not appear to be a need to spike copper during the D/F testing, or to establish specific permit limits on copper (or other catalytic metals). However, EPA OSW recommends the use of wastes or other feed materials containing copper over feeds without copper, where the choice exists.

4.2.3.3 D/F Precursors

Recommendation *– If a facility burns wastes containing significant quantities of D/F precursors, EPA OSW recommends that these wastes be used for D/F testing, rather than wastes without precursors. Although specific D/F precursor feed rate limits in the permit are not anticipated to be necessary to protect human health and the environment, it may be appropriate to consider a permit condition requiring waste profile tracking to determine whether increased quantities of precursor wastes warrant retesting.*

The role of organic precursors with respect to D/F formation is discussed in Section 4.1. Some waste combustors that burn wastes containing D/F precursors, including chlorobenzenes, chlorophenols, and PCBs, have been shown to have high D/F emissions (for example, see the discussion regarding Source ID No. 330 in Section 4.2.1.1). EPA has compared a limited number of facilities that feed known D/F precursors to those that do not feed D/F precursors (EPA 1996a). This limited comparison suggested no strong correlation between the level of precursors and D/F formation; however, the issue has not been examined in detail.

Since higher D/F emissions have been observed at some facilities burning D/F precursors, wastes containing significant quantities of D/F precursors are generally preferred over wastes without precursors for D/F testing. Specific feed rate limits on D/F precursors in the permit generally should not be necessary. However, it may be necessary for protection of human health and the environment to include a permit condition requiring waste profile tracking to determine whether increased quantities of precursor wastes warrant retesting.

4.2.3.4 D/F Inhibitors

Recommendation *– In reviewing the D/F test protocol, EPA OSW recommends that the permit writer verify that the facility will not burn a high sulfur waste or fuel in quantities that bias the S/Cl feed ratio above normal. At S/Cl molar feed ratios approaching 0.3 or greater, it may be appropriate for protection of human health and the environment after the risk burn to require waste and fossil fuel tracking to ensure that a minimum S/Cl ratio is maintained on an ongoing basis. If sulfur or other D/F inhibitors are intentionally added to the system to achieve D/F control, then EPA OSW suggests that the recommendations in Section 4.2.5 be followed.*

The role of SO_2 in suppressing D/F formation is discussed in Section 4.1. D/F inhibitors, such as sulfur, have been commercially marketed as feed stream additives to control D/F emissions. These same compounds may naturally be present in fossil fuels (such as coal) or hazardous waste fuels.

Numerous pilot-scale and full-scale tests on municipal solid waste combustors have proven that D/F emissions reductions can be achieved via coal co-firing to increase SO_2 or SO_2 injection (Raghunathan and Gullett 1996; Gullett and Raghunathan 1997; Raghunathan and others 1997a; Buekens and Huang 1998; Gullett and others 2000b). The suppression effect is well documented when sulfur is present at levels nearly stoichiometric to the chlorine in the feed (i.e., S/Cl molar feed ratio of approximately 1:1). Ullrich has also shown that sulfur levels well below stoichiometric ratios with chlorine can reduce dioxin formation measurably in a full-scale hazardous waste incinerator (Ullrich and others 1996). Significant decreases in D/F emission rates were observed at sulfur-to-chlorine molar ratios as low as 0.3 in the feed (Ullrich and others 1996).

In reviewing the D/F test protocol, EPA OSW recommends that the permit writer verify that the facility will not burn a high sulfur waste or fuel in quantities that bias the S/Cl feed ratio above normal. The particular S/Cl ratio that begins to cause a D/F suppression effect is likely to be system specific, and D/F suppression may be influenced by other, more significant facility-specific variables (Gullett and others, 2000b). However, the results from Ullrich suggest that S/Cl molar feed ratios above approximately 0.3, considering both waste and fossil fuel inputs, should generally be viewed with caution (Ullrich and others 1996). If S/Cl molar ratios approach 0.3 or greater during the risk burn, then waste and fossil fuel tracking

conditions in the permit may be necessary to protect human health and the environment by ensuring that a minimum S/Cl ratio is maintained on an ongoing basis.

This discussion primarily applies to situations where naturally-occurring sulfur may be introduced to the combustor with fossil fuels, or when sulfur is normally present in the waste fuel. In some cases, sulfur or other D/F inhibitors are intentionally added to the combustion system to achieve D/F control. For these situations, EPA OSW suggests that the recommendations in Section 4.2.5 be followed.

4.2.3.5 Dioxin-Containing Wastes

Recommendation *– If a facility burns dioxin-containing wastes (such as F020, F021, F022, F023, F026, F027, F032, F039 or K099), EPA OSW recommends that those wastes be represented during D/F testing. Specific permit limits on D/F contributions from these wastes may be necessary to protect human health and the environment by ensuring that dioxin/furans are not being burned in higher amounts than those represented during the risk burn and found to be protective.*

For many combustion units, D/F emissions are primarily influenced by formation within the combustion system. However, a few hazardous waste combustors burn dioxin-containing wastes (such as F020, F021, F022, F023, F026, F027, F032, F039 or K099), and D/F emissions from those units may be significantly affected by survival of trace D/Fs introduced with the waste feed (even at an adequate level of DRE). When a facility burns these dioxin-containing wastes, the potential waste feed D/F contribution to total D/F emissions should generally be accounted for in the risk burn and risk assessment.

Ideally, the waste feed D/F contribution to total D/F emissions can be accounted for by feeding dioxin-containing wastes during the risk burn to achieve a maximum D/F input. After the risk burn, specific permit limits on waste feed D/F contributions from F020, F021, F022, F023, F026, F027, F032, F039 or K099 wastes may be necessary to protect human health and the environment by ensuring that D/Fs are not subsequently burned in higher amounts than those represented during the risk burn and found to be protective.

If dioxin-containing wastes are not available for the risk burn, then the D/F emissions measured during the

risk burn will only represent the D/Fs formed within the combustion system. In this case, it may be necessary to approximate a potential waste feed D/F contribution based on the maximum anticipated D/F feed input and the applicable DRE. Dioxin-listed wastes, including F020, F021, F022, F023, F026, and F027, are required by the RCRA and MACT regulations to be burned in a 99.9999% DRE combustion unit. Other dioxin-containing wastes, such as F032, may be burned in a 99.99% DRE combustion unit. A total D/F emissions estimate may be developed for the risk assessment by calculating the residual D/F remaining after 99.99% or 99.9999% DRE, and then adding that value to the D/F emissions measured during the risk burn (i.e., the D/Fs formed within the combustion system).

When waste feed D/F contributions are approximated, it is recommended that follow-up testing to confirm D/F emission levels be planned to coincide with receipt of an appropriate dioxin-containing waste shipment. A D/F emissions approximation is uncertain in that it cannot reflect potential differences between the congener profile (the TEQ) of the waste and resulting emissions, or the potential for waste D/F contributions to overload D/F control systems, or the potential for partial combustion products from dioxin-containing wastes to exacerbate downstream D/F formation.

4.2.3.6 Other Factors

Other waste feed components may potentially affect D/F emissions. The presence of bromine, in particular, has been found to affect emissions of chlorinated organic PICs and D/Fs in pilot-scale experiments (Lemieux and Ryan 1998a and 1998b). Lemieux and Ryan have observed that D/F emissions can be enhanced by the addition of bromine, although there appears to be a threshold below which minimal enhancement occurs and above which significant enhancement occurs (Lemieux and Ryan 1998a). For the particular study showing these effects, this threshold appeared to lie in a range of Br/Cl molar feed ratios between 0.1 and 0.5.

Although the effects of bromine have not been clearly established during full-scale testing, permit writers should be aware of this issue when selecting waste feeds for trial burns, particularly if the facility burns brominated waste during normal operations. Very little brominated waste is generated and few facilities burn it, but some do.

4.2.4 Hysteresis/Memory Effects

Recommendation *– EPA OSW recommends that the recent operating history at a facility be considered in planning the risk burn. The risk burn generally should not be performed immediately after refractory replacement or other maintenance activity involving soot removal from boiler tubes, ductwork, or other locations where soot and catalytic metals may have deposited. In addition, the risk burn generally should not be performed immediately after a period of firing high sulfur fuel or injecting sulfur additives.*

D/F emissions in full-scale combustion units can be influenced by hysteresis, or "memory effects" (Buekens and Huang 1998). Hysteresis means that deposits or residual contaminants remaining within the unit from previous operations can have an ongoing effect on emissions, even after operating or feed conditions have changed. Raghunathan has shown that soot deposits from periods of inefficient combustion can enhance subsequent D/F yields, with the yields decaying over time (Raghunathan and others 1996). Combined soot-copper deposits cause more D/F formation than a deposit of soot or copper alone, and D/F formation from soot deposits is inhibited in the presence of sulfur dioxide (Raghunathan and others 1996 and 1997b).

Recent work by Gullett provides further insight regarding the influence of past operating conditions on D/F emissions (Gullett and others 2000b; in press). Gullett examined the effect of co-firing coal with municipal waste in a field-scale unit to determine whether sulfur in the coal would inhibit D/F formation (Gullett and others 2000b). D/F concentrations were in fact reduced up to 80 percent from co-firing coal, and past operating conditions were found to have a lingering and significant effect on D/F concentrations. Gullett concluded that the influence of past conditions on D/F levels was consistent with a D/F formation mechanism involving combustor wall deposits as sites for formation, and proposed that the effect of higher sulfur dioxide concentration from co-firing coal was to alter the deposits in a way that either reduced chlorine contact with active sites or reduced the catalytic activity of the deposits (thereby reducing ongoing D/F formation). In research involving a hazardous waste fired boiler, Gullett and others (in press) found that boiler tube deposits became a sink and source for D/F reactants (copper and chlorine), resulting in continued D/F formation and emissions long after waste co-firing ceased. From these two studies, it appears that deposits can have both a negative and positive effect on ongoing D/F emissions. Deposits

affected by sulfur dioxide can act to suppress ongoing D/F emissions, whereas deposits that serve as a sink for D/F reactants may enhance ongoing emissions.

These data suggest that the recent operating history at a facility should be considered in planning the risk burn. The risk burn should generally not be performed immediately after refractory replacement or other maintenance activity involving soot removal from boiler tubes, ductwork, or other locations where soot and catalytic metals may have deposited. In addition, memory effects can persist for at least a day, and a given test condition may continue to reflect, in part, what happened during the previous operation (Gullett 1999). Therefore, for example, EPA OSW does not recommend performing the risk burn immediately after a period of firing high sulfur fuel or injecting sulfur additives.

4.2.5 D/F Control Technologies

Some facilities may install specific D/F control technologies such as carbon injection, carbon beds, catalytic oxidizers, and D/F inhibitor technologies. If a facility uses one of these technologies, then EPA OSW recommends that key control parameters related to performance of these technologies be demonstrated during the D/F test conditions of the risk burn and limited in the permit as necessary for protection of human health and the environment. Relevant control parameters are identified in a technical support document for the hazardous waste combustor MACT standards (EPA 1999e), and are not addressed further here.

Although control technologies involving carbon can achieve reductions in stack emissions of D/Fs, permit writers should be aware that the use of carbon may sometimes *increase* total D/F synthesis when D/Fs in the solid residues are considered. Carbon has been used successfully in a variety of applications. However, carbon injection at higher temperature locations downstream of the combustor can be problematic. Schreiber reported that dioxin concentrations in cement kiln dust increased by approximately 2 orders of magnitude when carbon was injected between the kiln and ESP at operating temperatures in excess of 500 °F (Schreiber and others 1995). A similar result is documented by Ullrich, where D/F levels in the fabric filter dust increased by a factor of 100 over levels without carbon injection when carbon was injected directly to the fabric filter (instead of at a lower temperature location downstream of the fabric filter) (Ullrich and others 1996). The quantities of D/Fs in the fabric filter dust exceeded the quantities

removed in the stack gas by a factor of 50.

4.2.6 Control Parameter Summary

Although Section 4.2 presents each control parameter individually, EPA OSW recommends that the relative importance of the parameters with respect to one another also be considered. When one or two control parameters are clearly dominant for a particular system, there may be little benefit to limiting additional parameters in the permit.

Based on a review of existing information, this guidance prioritizes control parameters and conditions associated with D/F formation as primary, secondary, or tertiary. These hierarchical designations should not be considered absolute, but are intended to emphasize the relative importance of demonstrating various control parameters during D/F testing and limiting those parameters in the final RCRA permit. A summary of primary, secondary, and tertiary control parameters follows.

1. Primary control parameters are those which have shown the highest correlation with D/F emissions in full-scale tests, and which are therefore expected to dominate D/F formation and removal. EPA OSW recommends that these parameters be demonstrated during the D/F testing, and that permit writers consider whether specific quantitative limits on these parameters are necessary to protect human health and the environment. The primary control parameters are focused on surface-catalyzed D/F formation downstream of the combustion chamber, survival of trace D/Fs from waste feeds, and the use of specific D/F control technologies. Primary control parameters include:

    - Partial wet quench temperatures;
    - Dry particulate hold-up temperatures;
    - Combustion parameters listed in Section 4.2.2.2, for systems that operate under the challenging combustion scenarios discussed in Section 4.2.2.3;
    - Sulfur-to-chlorine molar feed ratio, unless the S/Cl ratio is well below 0.3;
    - D/F contributions from dioxin-containing wastes;
    - Key control parameters for specific D/F control technologies, including the intentional addition of sulfur as a D/F inhibitor.

2. Secondary control parameters are those that may influence D/F emissions under certain circumstances. However, there is less information indicating a direct correlation between these parameters and D/F emission rates. These parameters may or may not be appropriate to demonstrate during the D/F test, and corresponding permit terms may or may not be necessary to protect human health and the environment, depending on the significance of these parameters for a given system configuration and the presence or absence of dominant primary parameters. Secondary control

parameters include:

- Combustion parameters listed in Section 4.2.2.2, for steady-state systems that routinely maintain good combustion and are equipped with rapid wet quench/wet APCDs;
- Conditions other than combustion quality that may produce organic precursors (such as organics from raw materials in cement kilns and lightweight aggregate kilns, as discussed later in Section 4.5).

3. Tertiary control parameters pertain to feed composition. These control parameters have been the subject of fundamental and pilot-scale research on D/F formation, but have not routinely been correlated with D/F emissions during full-scale testing. These parameters may influence the selection of feeds for D/F testing and subsequent waste profile tracking, but it is generally not expected that specific feed rate limits in the permit will be necessary to protect human health and the environment. Tertiary control parameters include:

- Chlorine feed rates;
- Presence of D/F catalysts (such as copper);
- Presence of D/F precursors (such as chlorinated aromatics);
- Presence of naturally-occurring D/F inhibitors (such as sulfur), provided that the S/Cl molar feed ratio is well below 0.3.

4.3 D/F EMISSIONS FROM INCINERATORS

Hazardous waste incinerator designs include rotary kiln, liquid injection, fluidized bed, and fixed hearth. Incinerator designs are described in detail in a technical support document to the hazardous waste combustor MACT rule (EPA 1999f). Commercial incineration facilities typically accept hazardous wastes from a variety of generators, and the wastes fed to commercial units can be highly variable. Wastes may range from low- and high-Btu liquids, to laboratory packs, to soils contaminated with low levels of RCRA hazardous wastes. Large chemical facilities sometimes operate "captive" incinerators that treat on-site wastes, as well as wastes generated off-site by corporate affiliates. Wastes fed to a captive unit may also be highly variable, especially if the facility burns a number of wastes from different production operations without the capability to blend the wastes to a consistent specification. Some facilities operate small on-site incinerators that treat only one or two waste streams. The wastes fed to small on-site incinerators can sometimes be more predictable and/or homogeneous than those fed to commercial or captive units.

Air pollution control for hazardous waste incinerators typically involves an exhaust gas cooling step, followed by particulate matter and acid gas control. A few incinerators treat low-ash, low-halogen wastes and do not utilize any air pollution control. Exhaust gas cooling can be performed using a waste heat boiler or heat exchanger, mixing with ambient air, or injection of water into the exhaust gas. As discussed in Section 4.2.1 of this document, the procedures used for exhaust gas cooling can have a significant affect on D/F emissions.

Particulate matter and acid gas control systems for hazardous waste incinerators can generally be grouped into three categories: 1) "wet" systems; 2) "dry" systems; and 3) "hybrid wet/dry" systems (EPA 1999f). In wet systems, wet scrubbers are used for both particulate and acid gas control. These scrubbers may include venturi scrubbers, packed bed scrubbers, ionizing wet scrubbers, wet ESPs, innovative high efficiency scrubbers, or some combination of these. In dry systems, a fabric filter or ESP is used for particulate matter control. Dry scrubbing may also be utilized upstream of the dry APCD to achieve acid gas control. In hybrid systems, a dry technique (i.e., ESP or fabric filter) is used to control particulate matter (possibly in combination with dry scrubbing for acid gas control), followed by wet scrubbing for acid gas control. Some new technologies are being developed, and several facilities are injecting activated carbon for control of D/Fs, non-D/F organics, and mercury.

D/F emissions data are available from a variety of hazardous waste incinerators. Units equipped with rapid wet quench and wet APCD systems are among the lowest-emitting sources and generally have D/F emissions below 0.4 ng TEQ/dscm. D/F emissions from units equipped with dry air pollution control components range from 0.15 to 20 ng TEQ/dscm. Systems equipped with waste heat boilers or other types of heat exchangers have D/F emissions ranging from about 1 to 40 ng TEQ/dscm (EPA 1999d).

The level of D/F emissions from incinerators may be dependent on incinerator design, APCD type, particulate hold-up temperatures, type of quench or presence of a heat recovery unit, combustion conditions, and feed composition. In summary, all of the considerations discussed previously in Section 4.2 apply to hazardous waste incinerators. The most predominant factors influencing D/F emissions from incinerators seem to be the presence of a heat recovery unit and the temperature profile of dry APCD systems.

Table 4-1 summarizes potential control parameters associated with D/F emissions from incinerators. If dry APCD equipment or heat recovery devices are present in the downstream control system, the temperature profile across these devices is recognized as a primary control parameter directly related to D/F formation (see Section 4.2.1). Demonstration of maximum post-combustion temperature is likely to coincide with SRE testing (unless the facility can adjust inlet temperature to obtain the requisite temperature profiles during DRE testing). Combustion efficiency is also a primary control parameter for D/F formation, especially for transient operations, units burning containerized wastes, or high carbon monoxide situations as discussed in Section 4.2.2. Demonstration of control parameters affecting combustion efficiency will most likely coincide with the DRE test conditions.

Facilities with more predictable, homogeneous waste feeds, few operating fluctuations, and no particulate hold-up devices may prefer to collect D/F emissions data during a risk burn conducted under normal operating conditions, as appropriate (see Section 3.3.2.2). Waste feed selection should generally be based on representative waste streams, with a preference for D/F precursors such as chlorophenols and minimal amounts of D/F inhibitors (such as sulfur).

TABLE 4-1

POTENTIAL CONTROL PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM INCINERATORS AND BOILERS

	Control Parameter	Most Likely Achieved During	Parameter Type/Example Averaging Period*	How Limit May Be Established*	Other Considerations
PRIMARY CONTROL PARAMETERS					
Post-Combustion Conditions: See Section 4.2.1	Maximum post-partial wet quench temperature (within the range of 570-800 °F)	SRE test, unless a variable quench is used	Group A: 1 hour rolling average	Average of the test run averages	See Section 4.2.1.2
	Maximum dry ESP inlet temperature (within the range of 400-750 °F)	SRE test, unless a variable quench is used	Group A: 1 hour rolling average	Average of the test run averages	See Section 4.2.1.3
	Maximum fabric filter inlet temperature (within the range of 400-750 °F)				
	Maximum HEPA filter inlet temperature (within the range of 400-750 °F)				
	Maximum heat exchanger exit temperature (within the range of 400-750 °F)	Any test that achieves the critical temperature window	Group A: 1 hour rolling average	Average of the test run averages	See Section 4.2.1.3 Establish a *minimum* limit if the device is operated *above* the critical temperature range to prevent formation

TABLE 4-1 (continued)

POTENTIAL CONTROL PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM INCINERATORS AND BOILERS

	Control Parameter	Most Likely Achieved During	Parameter Type/Example Averaging Period*	How Limit May Be Established*	Other Considerations
PRIMARY CONTROL PARAMETERS (Continued)					
Combustion Conditions: *(It is recommended that these parameters also be limited to control non-D/F organics, see Section 5.3)* See Sections 4.2.2 and 4.2.6 Combustion parameters are most critical for challenging combustion scenarios including: - transient operations - batch operations - high carbon monoxide operations Combustion parameters may be less critical for steady-state systems. Although demonstration of these control parameters during DRE conditions is preferred whenever possible, D/F testing at normal combustion conditions may be considered for some steady-state units.	Minimum combustion temperature, each chamber	DRE	Group A: 1 hour rolling average Record keeping and periodic reporting to confirm continued absence of transients may be appropriate in lieu of hourly average limits for some steady-state systems.	Average of the test run averages	See Section 4.2.2.2
	Maximum combustion gas velocity	DRE/SRE			
	Maximum waste feed rate, each location	DRE			Consider limits for: - maximum organic liquids to PCC - maximum aqueous liquids to PCC - maximum sludges to PCC - maximum solids to PCC - maximum batch feeds to PCC - maximum organic liquids to SCC - maximum aqueous liquids to SCC

TABLE 4-1 (continued)

POTENTIAL CONTROL PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM INCINERATORS AND BOILERS

	Control Parameter	Most Likely Achieved During	Parameter Type/Example Averaging Period*	How Limit May Be Established*	Other Considerations
PRIMARY CONTROL PARAMETERS (Continued)					
Combustion Conditions: (Continued):	Waste variability that could cause transients	DRE	This is not a continuously monitored parameter, but pertains to selection of wastes for testing. Conditions for waste profile tracking may be specified by the permit writer.		See Section 4.2.2.3.1 Wastes with physical properties that can cause combustion transients should be selected.
	Batch feed conditions: - see "Maximum waste feed rate, each location" - see "Maximum carbon monoxide and/or total hydrocarbons"	DRE			See Section 4.2.2.3.2 Test wastes with high volatility and oxygen demand. Other parameters that may be necessary to limit are listed in Section 4.2.2.3.2
	Maximum carbon monoxide and/or total hydrocarbons	DRE	Group A: 1 hour rolling average	Establish per applicable regulations	See Section 4.2.2.3.3
Feed Composition: See Section 4.2.3	Minimum sulfur-to-chlorine feed ratio (unless the S/Cl molar feed ratio during the test is well below 0.3)	Any test condition where a S/Cl feed ratio $\geq$ 0.3 is used	Group B: Feed stream analyses may be specified to monitor sulfur-to-chlorine feed ratios	Average of the test run averages	See Section 4.2.3.4
	D/F contributions from dioxin-containing wastes	Any test with dioxin-containing wastes	Group B: Feed stream analyses may be specified to monitor dioxin input	Average of the test run averages	See Section 4.2.3.5

TABLE 4-1 (continued)

POTENTIAL CONTROL PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM INCINERATORS AND BOILERS

	Control Parameter	Most Likely Achieved During	Parameter Type/Example Averaging Period*	How Limit May Be Established*	Other Considerations
PRIMARY CONTROL PARAMETERS (Continued)					
D/F Control Technologies: See Section 4.2.5	D/F-specific control technologies include carbon injection, carbon bed, catalytic oxidizers and D/F inhibitor technologies. If one of these control technologies is used to limit D/F emissions, permit limits on key control parameters as described in a technical support document to the hazardous waste combustor MACT rule (EPA 1999e) may be appropriate.				
TERTIARY CONTROL PARAMETERS					
Feed Composition: See Section 4.2.3	Total Chlorine D/F Catalysts D/F Precursors D/F Inhibitors	These are not continuously monitored parameters, but pertain to selection of wastes and fuels for testing. Conditions for waste profile tracking may be specified by the permit writer.			Considerations are discussed in Section 4.2.3

Notes: D/F = dioxins and furans
DRE = destruction and removal efficiency
EPA = U.S. Environmental Protection Agency
ESP = electrostatic precipitator
HEPA = high efficiency particulate air
PCC = primary combustion chamber
SCC = secondary combustion chamber
SRE = system removal efficiency

* = See Section 1.3.1 for a description of the Group A, B and C designations. Hourly rolling averaging periods are specified as examples, but other averaging periods and techniques may be considered. By establishing operating limits from the test as "the average of the test run averages," the permit writer can better ensure consistency between the manual emissions measurements and the permit. It is less desirable to establish an operating limit as "the average of the minimum (or maximum) hourly rolling averages from the three test runs," because the minimum or maximum operating extremes may only be demonstrated during a minor portion of the total stack sampling period.

4.4 D/F EMISSIONS FROM BOILERS

Boilers recover thermal energy from combustion of hazardous waste and export the energy in the form of steam, heated fluids, or heated gases. General boiler designs are discussed in *Combustion Emissions Technical Resource Document* (EPA 1994c), and requirements for boilers burning hazardous waste are defined in 40 CFR Part 266.100 et seq. The following characteristics of a boiler are prescribed by 40 CFR Part 260 for RCRA regulatory purposes: 1) the combustion chamber and primary energy recovery section must be of integral design; 2) thermal recovery efficiency must be at least 60%; and 3) at least 75% of the recovered energy must be exported (i.e., not for internal boiler use). Hazardous waste is most commonly burned in firetube boilers, although watertube boilers are used in some cases. Most boilers treating hazardous waste are on-site units at chemical production facilities. Many oil- and gas-fired boilers burn low-ash, low-halogen wastes and are not equipped with any air pollution control. Some boilers utilize wet scrubbing or fabric filtration, and a few units (primarily coal-fired devices) are equipped with ESPs.

The database of D/F emissions from hazardous waste burning boilers is not as extensive as for incinerators and cement kilns (EPA 1994c). EPA provides data on two boilers equipped with ESPs indicating average D/F emissions less than 0.03 ng TEQ/dscm (EPA1994c). Handrich summarizes data from testing at 21 boilers in Louisiana (Handrich 1999). D/F emissions range from less than 0.008 ng TEQ/dscm to as high as 0.88 ng TEQ/dscm for a unit equipped with a fabric filter. Finally, Gullett and others (in press) provide data from a firetube boiler where the boiler was intentionally operated under poor combustion conditions to assess the maximum potential for D/F formation. After a period of flame wall impingement and soot formation on the boiler tubes, combustion conditions were improved and D/F emissions increased to as high as 49 ng TEQ/dscm.

D/F emissions from boilers are expected to be dependent on boiler design, APCD type, particulate hold-up temperatures, combustion conditions, and feed composition. Table 4-1 summarizes control parameters associated with D/F and other organic emissions from boilers. Depending on the system configuration, demonstration of control parameters associated with D/F formation in boilers may coincide with both the DRE and SRE test conditions.

As explained in Section 4.2.1.3, boiler tubes may serve as particulate hold-up areas and lead to D/F

emissions. Because boilers typically have no rapid quench, the flue gas time and temperature window may be suitable for D/F formation. This premise is supported by data for incineration systems equipped with waste heat boilers or other types of heat exchangers, where D/F emissions ranging from about 1 to 40 ng TEQ/dscm have been measured (EPA 1999d). Heat exchanger exit temperature (measured at the exit of the last heat exchanger section) is considered a primary control parameter for D/F formation and control. Collection of D/F emissions data for boilers is recommended during conditions that achieve heat exchanger exit temperatures in the upper end of (but well within) the 400 to 750 °F range. For example, for a facility with heat exchanger exit temperatures ranging from 350 to 550 °F, D/F testing at the exit temperature of 550 °F would be preferred over testing at the exit temperature of 350 °F. Heat exchanger exit temperatures may fall in the upper end of the D/F formation window during either DRE or SRE conditions, depending on the facility-specific operating envelope. (Note: If the heat exchanger outlet temperature is maintained *above* the critical temperature range to prevent D/F formation, for example, above 800 °F, a *minimum* temperature limit may be appropriate instead. However, this situation is not expected to be likely, since the thermal recovery efficiency for the boiler would be compromised.) For boilers equipped with a dry APCD, the inlet temperature to the dry APCD is also considered a primary control parameter.

Demonstration of parameters related to combustion quality (see Section 4.2.2) can also be a consideration, especially for boilers that burn wastes resulting in combustion transients. Some boilers at chemical facilities burn different production run wastes in campaigns. These conditions should generally be evaluated by the permit writer prior to trial burn to determine the potential for transients. Demonstration of control parameters affecting combustion efficiency will most likely coincide with the DRE test condition.

Demonstrating key control parameters related to combustion quality may be problematic for some boilers based on potential test condition conflicts (Schofield and others 1997). For example, depending on the capacity of the forced draft fan, a facility burning a single high-Btu waste stream may be unable to add enough excess combustion air to demonstrate minimum combustion temperature and maximum feed rate simultaneously. Thus, two test conditions may be appropriate in some cases to demonstrate all of the key control parameters related to combustion.

Conducting D/F emissions testing during the DRE condition may not always be possible for reasons discussed in Section 4.2.2 (e.g., because simultaneous stack determinations for consolidated testing may

not be possible, or because the risk testing is being performed separately from performance testing). In these situations, it may be appropriate for a facility with predictable, homogeneous waste feeds and few combustion transients to conduct testing under normal combustion conditions (see Section 3.3.2.2). It is recommended that the facility still demonstrate heat exchanger exit temperatures (as well as inlet temperatures to a dry APCD device) in the upper end of the 400 to 750 °F range.

In summary, boilers with highly variable operations should generally collect D/F emission samples during DRE-like test conditions, as well as any other condition necessary to achieve heat exchanger exit temperatures (and inlet temperatures to a dry APCD device) in the upper end of the 400 to 750 °F window. This objective could result in multiple test conditions. Facilities with more predictable, homogeneous waste feeds and few combustion transients may opt to test only during the test condition achieving the requisite heat exchanger exit temperatures and APCD inlet temperatures, as appropriate (see Section 3.3.2.2).

Finally, EPA OSW recommends that normal soot blowing practices at a boiler generally be reflected during the D/F testing. Buekens and Huang summarize measurements showing that D/F emissions during soot-blowing can increase as much as 30-fold over normal operations (Buekens and Huang 1998). However, data for long operating periods are not available, and it is possible that more frequent cleaning of heat surfaces could lead to lower D/F formation overall on a long term basis (Buekens and Huang 1998). This guidance recommends that normal soot blowing procedures be determined from the facility's operating record and reflected during the D/F testing according to the methodology specified in *Technical Implementation Document for EPA's Boiler and Industrial Furnace Regulations* (EPA 1992b). Prior to the test, soot blowing should generally not be performed on a more rapid cycle than normal.

4.5 D/F EMISSIONS FROM CEMENT KILNS

Cement kiln designs are described in detail in a report sponsored by the Portland cement kiln industry (Dellinger and others 1993). The majority of hazardous waste burning cement kilns utilize a long wet kiln design. A few hazardous waste burning kilns are long dry or preheater/precalciner dry units, and several facilities are beginning to replace long wet units with dry preheater/precalciner or semi-dry preheater/precalciner designs (Yonley 2000).

Cement kilns burn hazardous waste commercially (i.e., they accept waste from off-site generators) for use

as a fuel supplement in the production of Portland cement. Liquid wastes are typically injected into the hot end of the kiln. Solid wastes may be introduced into the calcining zone at some facilities. For long kilns, this means that the solid waste is introduced mid-kiln, and for preheater/precalciner kilns it is introduced onto the feed shelf. Containerized solid wastes may also be projected into the calcining zone by an air cannon mounted to the kiln hood. According to a technical support document to the hazardous waste combustor MACT rule (EPA 1999f), all cement kilns are equipped with either ESPs or fabric filters for particulate matter control. In some cases, the flue gases are cooled prior to the dry APCD. Add-on acid gas pollution control devices are not used at cement kilns, since the raw materials are highly alkaline and provide some degree of acid gas control.

D/F emissions data are available for most hazardous waste burning cement kilns. Test condition averages are highly variable, ranging from 0.004 to nearly 50 ng TEQ/dscm (EPA 1999d). The level of D/F emissions from a cement kiln may potentially be affected by a number of factors. However, the inlet temperature to the particulate matter control device is one factor that has been shown to consistently affect D/F formation (EPA 1999d).

Table 4-2 summarizes potential control parameters associated with D/F and other organic emissions from cement kilns. Data presented in numerous documents (Harris and others 1994; Lanier and others 1996; EPA 1999d and 1999e) demonstrate that D/F emissions from cement kilns increase exponentially with increases in inlet temperatures to the dry APCD within the D/F formation window (400 to 750 °F). A number of kilns have recently added flue gas quenching units upstream of the APCD to reduce inlet APCD temperature, and these additions have significantly reduced D/F emissions (EPA 1999d). This information suggests that maximum inlet temperature to the dry APCD system, as discussed previously in Section 4.2.1.3, is the primary control parameter related to D/F emissions for cement kilns. Collection of D/F emissions data should generally occur during a test condition that achieves maximum APCD inlet temperatures (for example, the SRE test condition, which is performed at a maximum APCD inlet temperature).

Parameters related to combustion quality (as described in Section 4.2.2) are generally less relevant for cement kilns than for incinerators and boilers. The operating envelope of cement kilns is dictated largely by the American Society for Testing and Materials specifications for their final product. Cement kilns operate

TABLE 4-2

POTENTIAL CONTROL PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM CEMENT KILNS AND AGGREGATE KILNS

	Control Parameter	Most Likely Achieved During	Parameter Type/Example Averaging Period*	How Limit May Be Established*	Other Considerations
PRIMARY CONTROL PARAMETERS					
Post-Combustion Conditions: See Sections 4.2.1, 4.5 and 4.6	Maximum dry ESP inlet temperature (within the range of 400-750 °F)	SRE	Group A: 1 hour rolling average	Average of the test run averages	See Section 4.2.1.3
	Maximum fabric filter inlet temperature (within the range of 400-750 °F)				
	Aggregate Kilns: Maximum inlet temperature to extensive runs of ductwork (where cooling through the 400-750 °F temperature range occurs)				
Combustion Conditions: *(It is also recommended that these parameters be limited to control non-D/F organics, see Section 5.4)* See Sections 4.2.2, 4.2.6, 4.5 and 4.6	Batch feed conditions: - maximum batch waste feed rate at the location where the batch is fed - maximum carbon monoxide and/or total hydrocarbons	Any test where the post-combustion parameters identified in Section 4.2.1 are also demonstrated	Group A: 1 hour rolling average	Average of test run averages For carbon monoxide and/or total hydrocarbons, establish per applicable regulations	See Section 4.2.2.3.2 Test wastes with high volatility and oxygen demand. Other batch feed parameters that may be necessary to limit are listed in Section 4.2.2.3.2
	Aggregate Kilns: Consider Section 4.2.2.2 parameters on a case-by-case basis				

TABLE 4-2

POTENTIAL CONTROL PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM CEMENT KILNS AND AGGREGATE KILNS (Continued)

	Control Parameter	Most Likely Achieved During	Parameter Type/Example Averaging Period*	How Limit May Be Established*	Other Considerations
PRIMARY CONTROL PARAMETERS (Continued)					
Feed Composition: See Sections 4.2.3, 4.5 and 4.6	Minimum sulfur-to-chlorine ratio at the stack (unless the S/Cl molar ratio during the test is well below 0.3)	Any test condition where a S/Cl ratio $\geq$ 0.3 is used	Group B: Feed stream analyses may be specified to monitor sulfur input	Average of the test run averages	See Sections 4.2.3.4, 4.5 and 4.6
	D/F contributions from dioxin-containing wastes	Any test with dioxin-containing wastes	Group B: Feed stream analyses may be specified to monitor dioxin input	Average of the test run averages	See Section 4.2.3.5
D/F Control Technologies: See Section 4.2.5	D/F-specific control technologies include carbon injection, carbon bed, catalytic oxidizers and D/F inhibitor technologies. If one of these control technologies is used to limit D/F emissions, permit limits on key control parameters as described in a technical suppor document to the hazardous waste combustor MACT rule (EPA 1999e) may be appropriate .				
SECONDARY CONTROL PARAMETERS					
Control of Precursors from Raw Material Organics: *(It is recommended that these parameters also be limited to control non-D/F organics, see Section 5.4)* See Sections 4.5 and 4.6	Maximum total hydrocarbons, as measured at both the main and bypass stacks, not to exceed regulatory limits	SRE	Group A: 1 hour rolling average	Establish per applicable regulations. Limits in addition to those specifically prescribed by regulation may be considered based on the results of the risk assessment.	Temporary total hydrocarbon monitors may be needed if the facility does not normally measure total hydrocarbons in both stacks.

TABLE 4-2

POTENTIAL CONTROL PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM CEMENT KILNS AND AGGREGATE KILNS (Continued)

	Control Parameter	Most Likely Achieved During	Parameter Type/Example Averaging Period*	How Limit May Be Established*	Other Considerations
TERTIARY CONTROL PARAMETERS					
Feed Composition: See Sections 4.2.3, 4.5 and 4.6	Total Chlorine D/F Inhibitors	These are not continuously monitored parameters, but pertain to selection of wastes and fuels for testing. Conditions for waste profile tracking may be specified by the permit writer.			Considerations are discussed in Sections 4.2.3, 4.5 and 4.6

Notes: D/F = dioxins and furans
EPA = U.S. Environmental Protection Agency
ESP = electrostatic precipitator
SRE = system removal efficiency

* = See Section 1.3.1 for a description of the Group A, B and C designations. Hourly rolling averaging periods are specified as examples, but other averaging periods and techniques may be considered. By establishing operating limits from the test as "the average of the test run averages," the permit writer can better ensure consistency between the manual emissions measurements and the permit. It is less desirable to establish an operating limit as "the average of the minimum (or maximum) hourly rolling averages from the three test runs," because the minimum or maximum operating extremes may only be demonstrated during a minor portion of the total stack sampling period.

at high temperatures (approaching 3,500 °F) to achieve material temperatures of at least 2,700 °F, with typical gas residence times from 4 seconds to as high as 16 seconds. These conditions are conducive to highly efficient organic destruction. Although some cement kilns operate at elevated carbon monoxide levels, these levels are not necessarily indicative of poor combustion. A portion of the carbon monoxide in cement kilns is due to the calcination process. The calcination process releases large quantities of carbon dioxide, which can subsequently decompose into carbon monoxide at the extremely high temperatures in the kiln. In addition, carbon monoxide may be formed at the kiln exit where total hydrocarbons are volatilized from the raw materials and are partially oxidized.

Results from both kinetic modeling and field studies suggest that organics are efficiently destroyed when fed at the hot end of cement kilns (Dellinger and others 1993). DRE results seem to confirm this. DRE failures at cement kilns are extremely limited, and can generally be explained by high blank or baseline (non-hazardous waste) levels of POHCs. In one instance, DRE failure has been attributed to poor atomizer design (Dellinger and others 1993). However, facility-specific DRE testing should generally be sufficient to reveal design problems. For these reasons, Table 4-2 does not recommend control parameters related to combustion of liquid hazardous wastes introduced to the hot end of cement kilns.

Table 4-2 does recommend limiting combustion control parameters when kilns feed batch waste at mid- or feed-end locations. Batch wastes injected at mid- or feed-end locations may not experience the same elevated temperatures and long residence times as liquid wastes introduced at the hot end. In a worst-case scenario, volatile compounds may be released from the charge so rapidly that they are not able to mix with oxygen and ignite before they cool below a critical temperature, forming PICs (Dellinger and others 1993). Increased PICs, or precursor organics, may enhance formation of D/Fs. To ensure that D/F emissions are not under-estimated for the risk assessment, EPA OSW recommends that batch wastes be fed under simulated "worst-case" feeding conditions during the risk burn as discussed in Section 4.2.2.3.2. The recommended permit limits in Table 4-2 are also discussed in Section 4.2.2.3.2, together with a listing of other batch feed parameters that may be limited on a case-by-case basis, as necessary to protect human health and the environment. Some cement kilns self-restrict individual batch size to less than 1% of the total hourly fuel feed, and this practice may be considered in determining appropriate permit limitations.

In cement kilns, main stack emissions of total hydrocarbons are dominated by organics that are volatilized from the raw materials prior to entering the high temperature regions of the kiln (Schreiber and Strubberg 1994). The chlorination of these hydrocarbons is a potential source of D/F precursors, such as monochlorobenzene (Dellinger and others 1993). Bench-scale, as well as full-scale, tests by the industry have confirmed that hydrocarbons from raw materials play a significant role in governing the production of D/Fs (Sidhu and Dellinger 1997; Schreiber undated). In addition, D/Fs may actually be present in the raw materials and may volatilize once the raw materials reach sufficient temperatures, although the significance of these contributions to total D/F stack emissions is still under debate (EPA 1999d). Considering this information, EPA OSW recommends that D/F testing be performed at the upper end of the operating range for total hydrocarbons, as measured in both the main and bypass stacks, not to exceed applicable regulatory limits.

Although the operating conditions necessary for achieving high total hydrocarbon emissions may vary by facility, maximum total hydrocarbon levels are likely to be achieved by some combination of high production rate, high gas temperatures at the raw material feed end of the kiln, and low oxygen at the raw material feed end of the kiln. Dellinger observed an inverse relationship between total hydrocarbons and stack oxygen concentrations (Dellinger and others 1993), and Schreiber and Strubberg observed that raw-material-generated hydrocarbons decrease as kiln oxygen increases (Schreiber and Strubberg 1994). The organic content of the raw material can also significantly influence hydrocarbon levels. However, raw material characteristics are largely dictated by quarry location, and are not easily controlled for the purpose of testing. If total hydrocarbon levels increase substantially after the risk burn because of changes in raw materials, then re-testing may be necessary.

In the context of D/F and other organic testing, total hydrocarbon levels are recommended for use as a control parameter indicating levels of organics within raw materials that may be chlorinated from the hazardous waste fuel. In this case, total hydrocarbons are not being used strictly as an indicator of waste fuel combustion efficiency. EPA OSW recommends that site-specific risk assessments quantify risks from hazardous waste combustor emissions, regardless of source. Therefore, it may be appropriate for cement kilns that only monitor carbon monoxide, or that only monitor carbon monoxide or total hydrocarbons in a bypass stack, to install temporary total hydrocarbon monitors in the main and bypass stacks prior to and

during the D/F tests to ensure that total hydrocarbon emissions are being maximized. The need for permanent total hydrocarbon monitoring can be assessed by the permit writer after the risk assessment is completed and potential risks are evaluated.

Feed characteristics that can potentially influence D/F emissions are discussed in Section 4.2.3. The relevance to cement kilns is discussed here. Contradictory information exists regarding the significance of waste fuel chlorine. It has been proposed that the highly alkaline environment in a cement kiln scavenges available chlorine, making it unavailable for chlorination of organics. Data presented by Lanier from testing conducted at a full-scale facility showed 97% acid gas capture by the alkali material, and no effect on D/F emissions due to variations in chlorine feed rate (Lanier and others 1996). However, equilibrium calculations show lower chlorine capture at high temperatures and conversion of HCl to Cl_2, suggesting that even a highly basic chemical species such as calcium hydroxide would not always be expected to effectively control chlorinated hydrocarbon formation (including D/Fs) at temperatures above 400 °F (Dellinger and others 1993). In addition, D/F emissions were reduced during full-scale testing at another facility where Na_2CO_3 was injected at the fuel end to react with chlorine, suggesting that fuel-based chlorine *can* affect D/F emissions in cement kilns (Schreiber and others 1995). Considering the uncertainty on this issue, a recommendation to maintain normal levels of chlorine during the risk burn is reasonable.

Metal catalysts in the waste, as discussed in Section 4.2.3.2, are not expected to be relevant to D/F testing at cement kilns. Spiking wastes with copper was not observed to affect D/F emission rates during full-scale testing of a cement kiln (Lanier and others 1996). Also, other metals that have been identified as D/F catalysts (iron and aluminum) are major ingredients in cement kiln raw materials.

D/F precursors, as discussed in Section 4.2.3.3, are expected to be dominated by precursors in the cement kiln raw materials, rather than precursors in the waste. However, if a facility burns wastes with significant quantities of D/F precursors, these wastes are recommended for use during D/F testing, rather than wastes without the precursors.

Naturally occurring D/F inhibitors, such as sulfur, are discussed in Section 4.2.3.4. Sulfur is expected to be present in the coal used for co-firing a cement kiln. During the D/F testing, EPA OSW recommends that coal not be fed at higher-than-normal rates, and low sulfur coal is preferred if a facility uses several coal

suppliers. Section 4.2.3.4 suggests that, if S/Cl molar feed ratios approach 0.3 or greater, waste and fossil fuel tracking conditions in the permit may be necessary after the risk burn to protect human health and the environment by ensuring that a minimum S/Cl ratio is maintained on an ongoing basis. In cement kilns, where the alkali raw materials provide some control of acid gases, the S/Cl molar ratio in the stack may be more relevant than the ratio in the feed. Other potential D/F inhibitors, such as calcium, may already be present in the raw materials.

In some cases, sulfur or other D/F inhibitors are intentionally added to a cement kiln to achieve D/F control. Schreiber has documented D/F emissions reductions after sulfur was added to the raw materials to increase the stack concentrations of SO_x from less than 20 ppm to above 300 ppm (Schreiber and others 1995). Schreiber also documented D/F emissions reductions when Na_2CO_3 was injected at the fuel feed end to react with chlorine in the system (Schreiber 1995). If sulfur or other D/F inhibitors are intentionally added to the system to achieve D/F control, then EPA OSW suggests that the recommendations in Section 4.2.5 for specific D/F control technologies should be followed.

There are currently no hazardous waste burning cement kilns utilizing carbon injection for D/F control. A special consideration for cement kilns is that injected carbon may interfere with the common practice of recycling cement kiln dust back into the production process. For a cement kiln to effectively utilize carbon injection, the carbon injection system may have to be installed after the APCD, along with a second APCD to collect the carbon. In addition, the use of carbon may increase total D/F synthesis when D/Fs in the cement kiln dust are accounted for, as explained in Section 4.2.5.

4.6 D/F EMISSIONS FROM AGGREGATE KILNS

Lightweight aggregate kiln design and operating practices are described in detail in a technical support document to the hazardous waste combustor MACT rule (EPA 1999f). Lightweight aggregate kilns typically burn only high-Btu, liquid fuel, and do not burn wastes at locations other than the hot end. Depending on the feed and system design, the temperature at the hot end of the kiln varies from 2,050 to 2,300 °F, and combustion gas exit temperatures vary from 300 to 1,200 °F (EPA 1999f). All hazardous waste burning lightweight aggregate kilns utilize fabric filters for particulate matter control (EPA 1999f).

D/F emissions data are available for only a few hazardous waste burning lightweight aggregate kilns. Test condition averages range from 0.04 to 2.9 ng TEQ/dscm (EPA 1999d). The data suggest that D/F emissions from lightweight aggregate kilns are influenced by more than APCD operating temperature, since all available D/F emissions data were generated at similar fabric filter inlet temperatures of around 400 °F. As explained in Section 4.2.1.3, D/F emissions from lightweight aggregate kilns appear to be primarily affected by the inlet temperature to extensive runs of un-insulated ductwork downstream of the kiln, where flue gas cools slowly through the 400 to 750 °F temperature range.

Table 4-2 summarizes potential control parameters associated with D/F and other organic emissions from lightweight aggregate kilns. Dry particulate hold-up temperatures to extensive runs of ductwork and fabric filters are the primary control parameters related to D/F formation (see Section 4.2.1.3). Collection of D/F emissions data should generally occur during a test condition that achieves maximum ductwork inlet temperatures and APCD inlet temperatures (for example, the SRE test condition, which is performed at a maximum APCD inlet temperature).

Parameters related to combustion quality are discussed in Section 4.2.2. Demonstration of combustion parameters at lightweight aggregate kilns should generally be considered on a case-by-case basis. Lightweight aggregate kilns do not operate at combustion temperatures as high as those in cement kilns (see Section 4.5). However, the potential for poor combustion situations may be minimized, because aggregate kilns typically only burn high-Btu, liquid wastes in the flame zone. Historical operating data should generally be reviewed to determine whether a facility frequently experiences operating transients, as discussed in Section 4.2.2.3.1. If so, then the transient operations should generally be represented during the D/F testing. Permit limitations on the combustion parameters listed in Section 4.2.2.2 (or other parameters as appropriate) may be necessary to protect human health and the environment. However, if a facility maintains steady-state operations with very few fluctuations, demonstration of absolute minimum or maximum values for the Section 4.2.2.2 combustion parameters may be less critical.

As discussed in Section 4.5 for cement kilns, the raw materials which are fed to the cold end of aggregate kilns may contribute to elevated organic precursor concentrations which can affect D/F emissions. Therefore, D/F testing should generally be performed at the upper end of the operating range for total hydrocarbons. Since most aggregate kilns only monitor carbon monoxide, it may be appropriate to install

temporary total hydrocarbon monitors for the testing.

Feed composition is discussed in Section 4.2.3. Recommendations regarding feed characteristics that can potentially influence D/F emissions are similar to those discussed in Section 4.5 for cement kilns.

CHAPTER 5

ORGANIC EMISSIONS OTHER THAN DIOXINS AND FURANS

EPA OSW has recommended that human health and ecological risk assessments evaluate potential risks associated with organic emissions other than D/Fs, in addition to the risks from D/Fs (EPA 1998a and 1999b). The EPA OSW risk assessment guidance (EPA 1998a and 1999b) recommends that the final risk assessment clearly distinguish between the portion of stack emissions evaluated for risk, the portion considered to be non-toxic, and the portion that remains unknown. Therefore, the objective for the risk burn should be to characterize organic stack emissions as completely as possible. As stated in Chapter 2, it is recommended that the largest possible percentage of organic emissions be identified and quantified initially to minimize the need for re-testing, even though some compounds may eventually be eliminated from quantitative risk evaluation as part of the COPC selection process recommended in the EPA OSW risk assessment guidance (EPA 1998a).

This chapter addresses identification and quantification of organic emissions other than dioxins and furans. Stack determinations are discussed in Section 5.1. Key control parameters that EPA OSW recommends be demonstrated during the testing are identified in Section 5.2. All parameters may not be relevant for all systems, and the information in Section 5.2 should be considered in conjunction with the industry-specific information provided for incinerators and boilers in Section 5.3, and for cement kilns and lightweight aggregate kilns in Section 5.4, as well as facility-specific information.

5.1 STACK DETERMINATIONS FOR ORGANICS

EPA has conducted research to identify the types and quantities of organics emitted from hazardous waste combustion facilities (EPA 1998e; Ryan and others, 1996 and 1997; Midwest Research Institute and A.T.

Kearney 1997; Lemieux and others 1999). These research efforts indicate frequent detection of volatile and semivolatile organics including chloro-, bromo-, and mixed bromochloro-alkanes, alkenes, alkynes, aromatics, and polyaromatics, D/Fs, PAHs, PCBs, phthalates, nitrogenated and sulfonated organics, and short-chain alkanes (such as methane and propane). EPA reports frequent detection of chlorinated and brominated alkanes and alkenes (such as chlorinated ethenes), and suggests that chlorinated ethenes can serve as potential indicators of D/F formation (EPA 1998e). EPA supports ongoing research to improve the identification and quantification of organic emissions. However, uncertainty remains regarding the full suite of organic emissions from hazardous waste combustion facilities and the potential risks associated with those emissions.

Because organic emissions cannot be reliably predicted based on the feed, design, or operating practices at a particular facility, this guidance recommends that comprehensive organic emissions testing be performed to develop emissions data for site-specific risk assessments to accomplish the following three objectives:

- Identification and quantification of specific toxic organic compounds (such as PAHs and PCBs) to assess their contribution to the total potential risk posed by the facility;
- Identification and quantification of as many other constituents as possible, regardless of toxicity, to reduce uncertainty for the risk assessment;
- Construction of an organics mass balance which estimates the completeness of the organic emissions characterization, to evaluate remaining uncertainty associated with the risk assessment.

The first objective can typically be achieved by sampling and analysis for specific compounds listed on volatile, semivolatile, and other target analyte lists. The second objective involves determinations for constituents that are not typically included on target analyte lists. Examples include tentatively identified compounds, as well as simple hydrocarbons. The third objective involves a measurement of Total Organic Emissions. Each of these objectives is discussed in more detail.

5.1.1 Target Analyte Lists

The first recommended objective of organics testing is to identify and quantify specific toxic organic compounds to assess their contribution to the total potential risk posed by the facility. Recommended target analyte lists for organics are provided in Appendix B of this document. Standard EPA methods (EPA 1996b) can be used to identify and quantify many organics that are potentially toxic, persistent, and bioaccumulative. For volatile and semivolatile organic compounds, SW-846 Methods 8260 and 8270 gas chromatography/mass spectrometry (GC/MS) procedures are preferred (EPA 1996b). The EPA methods, as written, are intended as guidance and are recommended as starting points for the development of standard operating procedures that will actually be used. Guidance on appropriate method modifications is provided in SW-846 (refer to Chapter 2 of SW-846 [EPA 1996b] and the applicable methods.) However, the facility should be able to demonstrate and document that the modified methods meet the DQOs for the particular application. Other methods not found in SW-846 may also be used if the user can demonstrate and document that the methods will generate data that meet the appropriate DQOs.

Stack determinations for PCBs are also recommended, 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 emitted as by-products of the combustion process. It is possible that PCBs are formed by the same reactions that produce D/Fs, discussed previously in Section 4.1. 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. An apparent trend was indeed found showing increased PCB emissions with increased D/F emissions. 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.

Alcock (Alcock and others 1999) and EPA (EPA 1997b) have established that waste combustion units contribute significantly to total emission inventories of PCBs. In addition, PCBs can be important from a risk standpoint. 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% of the TEQ for a cement kiln facility. For

other sources, the PCB contribution was more minimal.

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

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

The 12 dioxin-like PCBs are important because the rings can rotate into the same plane, similar to that of a D/F molecule. Studies have shown that these dioxin-like congeners can react with the aryl hydrocarbon receptor. This is the same reaction that is believed to initiate the adverse effects of D/Fs. The World Health Organization has derived interim toxicity equivalency factors (TEFs) for these coplanar PCBs (Van den Berg and others 1998). The TEFs are applied to congener-specific concentrations to evaluate dioxin-like toxicity. Risks from the dioxin-like congeners (evaluated using the slope factor for dioxins) 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). With proper planning, the PCB determination can be made using portions of the D/F sampling train extracts. More detail regarding sampling and analysis for PCBs is provided in Appendix B.

Finally, it may be appropriate for a facility to sample and analyze for additional constituents based on the types of wastes burned. For example, in addition to constituents on the volatile, semivolatile, and other target analyte lists, it may be appropriate for a facility to sample and analyze for compounds such as pesticides, nitroaromatics, and cyanides. It is recommended that stack determinations be considered for any highly toxic, persistent, or bioaccumulative constituent burned in significant quantities. Section 5.2.2 lists examples of historical waste feed information that can be reviewed to determine the significance of a particular constituent. Although the determination is somewhat subjective, a constituent may be appropriate to address as part of the stack sampling and analysis if it is prominent on several of the suggested rankings. Additional information on testing for facility-specific compounds is provided in Appendix B.

5.1.2 Tentatively Identified Compounds

The second recommended objective of organics testing is to identify and quantify as many non-target constituents as possible, regardless of toxicity. By identifying a larger portion of the unknown peaks in a chromatogram, a more complete organics mass balance can be achieved; and uncertainty in the risk assessment can be reduced.

In support of this second objective, a MS library search to identify non-target compounds is recommended, followed by review of the results by an experienced mass spectroscopist. Constituents identified based on the library search are referred to as tentatively identified compounds (TICs), since there is no reference standard analyzed at the same time as the unknown. The nearest internal standard is used for quantitation, and a relative response factor of one (1) is assumed. The resulting concentration is considered to be a semi-quantitative estimate, due to lack of a compound-specific response factor. Determinations for tentatively identified compounds are discussed further in Appendix B.

The EPA OSW risk assessment guidance (EPA 1998a) recommends that the semi-quantitative results for tentatively identified compounds be added into the "identified" portion of the stack emissions to ensure that appropriate credit is given to defensible efforts at identifying the maximum number of organic compounds. EPA OSW recommends that tentatively identified compounds that could significantly contribute to risk be considered for confirmation and quantification through the use of known standards.

5.1.3 Simple Hydrocarbons

Many organics lack EPA toxicity values, or they may not be toxic at all. These compounds are not typically included on standard target analyte lists. However, an important advantage of identifying, and quantifying as many organics as possible is the reduction of uncertainty for the risk assessment. Methane and other aliphatics can comprise a significant percentage of total stack organics, and specific determinations for methane, propane, and other short-chain aliphatics can potentially alleviate concerns about the percentage of the total organic mass that might be toxic.

One simple way to quantify non-toxic volatile hydrocarbons without expanding the sampling effort is to utilize information already available as part of the Total Organic Emissions determination (discussed in Section 5.1.4). The Total Organic Emissions determination involves measurement of volatiles by field gas chromatography, and an initial calibration is performed using methane, ethane, propane, butane, pentane, hexane and heptane. If sample 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 prefer 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 organic stack emissions. Analysis for simple hydrocarbons is discussed further in Appendix B.

5.1.4 Total Organic Emissions

Unfortunately, only a limited number of organic compounds can be accurately identified and quantified using standard stack gas sampling and analysis methods. A portion of the emissions profile remains unaccounted for. The third recommended objective of organics testing is construction of an organics mass balance to qualify the completeness of the organic emissions characterization. This information is used to evaluate remaining uncertainty associated with the risk assessment. This third objective involves a measurement of Total Organic Emissions.

The Total Organic Emissions determination (EPA 1996d) measures organic fractions for three boiling point ranges: 1) a volatile field gas chromatography (FGC) fraction (boiling points less than 100 °C); 2) the semivolatile, total chromatographable organics (TCO) fraction (boiling points between 100 and 300 °C); and 3) the non-volatile, gravimetric (GRAV) fraction (boiling points greater than 300 °C). The sum of the concentrations for the three fractions represents total organic mass. The procedure is discussed further in Appendix B.

EPA OSW recommends the procedure described in Appendix B as the best currently available way to cost effectively determine total recoverable organic mass and characterize uncertainty in the risk assessment. Permit writers should generally consider updated or expanded techniques if and when they become

available.

EPA OSW has recommended that the final result from the Total Organic Emissions determination be used to compute a total organic emissions (TOE) factor, defined as total organic emissions divided by the sum of the identified organics (EPA 1998a). The TOE factor is typically presented in the uncertainty section of the risk assessment report to clearly qualify how much of the stack emissions have been evaluated for risk. Permitting authorities can evaluate the TOE factor and assess to what extent actual risks may be greater than estimated risks (EPA 1998a). TOE factors ranging from 2 to 40 have been computed (EPA 1998a). Lower TOE factors can be achieved by more complete characterization of stack emissions (i.e., more "identified" compounds in the denominator), and facilities should consider this in determining appropriate stack measurements for the risk burn (Sections 5.1.1 through 5.1.3).

The importance of the Total Organic Emissions determination for site-specific risk assessments cannot be over-emphasized. Studies (EPA 1976; Pellizzari and others 1980) have shown that analyses based strictly on target analyte lists may account for less than 20% of the total organic material in an emission sample. Without a Total Organic Emissions determination, a final risk assessment report cannot explain how much of the total stack emissions have been evaluated for risk, significantly complicating the risk management decision.

5.2 CONTROL PARAMETERS TO BE CONSIDERED FOR RISK BURNS

This section identifies key control parameters that are expected to affect organic emissions, and that EPA OSW recommends be considered in establishing the risk burn test conditions. Depending on site-specific considerations, these control parameters may need to be limited in the RCRA permit after the risk burn to protect human health and the environment by ensuring that organic emissions remain within the measured levels on an ongoing basis.

Most of the control parameters listed in this section pertain to combustion conditions that have already been discussed in Section 4.2.2. Information from Section 4.2.2 is referenced, as appropriate, instead of repeating the information here.

Several of the control parameters identified in this section may currently be limited in association with the DRE standard, or will soon be limited pursuant to the requirements of the hazardous waste combustor MACT rule. To the extent that risks from non-D/F organics are already adequately controlled by regulatory limits on key control parameters, then fewer risk-based limits may be needed in the RCRA permit. However, if regulatory controls are not applicable or sufficiently comprehensive, then additional risk-based limits may be necessary to protect human health and the environment. A greater number of risk-based permit limitations may be necessary when the risk burn and RCRA or MACT performance tests reflect different operating modes.

Recommended control parameters that are expected to affect organic emissions are categorized according to combustion conditions (Section 5.2.1) and feed composition (Section 5.2.2). All parameters may not be relevant for all systems, and the information in Section 5.2 should be considered in conjunction with the industry-specific information provided for incinerators and boilers in Section 5.3, and for cement kilns and lightweight aggregate kilns in Section 5.4, as well as facility-specific information. The discussions and recommendations in this section are based on the underlying assumption that all hazardous waste combustors are required by RCRA or MACT regulation to operate under combustion conditions that meet or exceed 99.99 percent DRE.

5.2.1 Combustion Conditions

Recommendation *– EPA OSW recommends that, whenever possible, facilities perform testing for non-D/F organics during the DRE test conditions and that the challenging combustion scenarios discussed in Section 4.2.2.3 be represented during the testing (if applicable to a particular system). The challenging combustion situations described in Section 4.2.2.3 include: 1) transient conditions; 2) operation with containerized or batch waste feeds; and 3) high carbon monoxide situations.*

Combustion parameters identified in Section 4.2.2.2 should automatically be addressed when organics testing is performed during the DRE test conditions, since these parameters are typically demonstrated and limited as part of the DRE determination. The combustion

parameters listed in Section 4.2.2.2 include: 1) minimum primary and secondary combustion chamber exit temperatures; 2) maximum combustion gas velocity; 3) maximum waste feed rate at each feed location; 4) limitations on waste feed composition and batch feeds; and 5) maximum flue gas carbon monoxide and/or total hydrocarbon concentrations.

The recommendation for organics sampling during the DRE test is a general guideline. Some facilities and permit writers may be faced with situations where this general guideline is not appropriate. For example, DRE testing may already have been conducted in advance of the risk burn, or the use of surrogate waste for the DRE test might conflict with the objective to use actual wastes during the non-D/F organic testing. These and other situations call for decisions regarding the specific combustion conditions to be demonstrated. Therefore, this guidance recommends that the challenging combustion scenarios described in Section 4.2.2.3 (if applicable) be preferentially targeted for organics testing. As appropriate, it is recommended that permit limits for the Section 4.2.2.2 combustion parameters be established based on organics testing conducted under these challenging combustion scenarios. In addition, a facility-specific review of trial burn and historical operating data should generally be performed to determine whether the challenging combustion scenarios correlate with other operating or feed parameters. If so, it is recommended that the correlating parameters be demonstrated during the testing and limited in the permit as necessary to protect human health and the environment in addition to, or possibly in lieu of, the combustion parameters listed in Section 4.2.2.2. Caution should be exercised to ensure that targets during the organics testing for the Section 4.2.2.2 combustion parameters are not substantially different from those demonstrated during the DRE test.

Finally, it is important to recognize that some combustion units operate under extremely steady-state conditions, at temperatures and residence times that should routinely ensure good combustion. Challenging combustion situations, such as those described in Section 4.2.2.3, do not occur. Combustion conditions may not fluctuate at all, and carbon monoxide may be near zero. Ideally, logistics will favor combining the organics testing with the DRE test. If so, then the combustion parameters listed in Section 4.2.2.2 should automatically be addressed, since

they are typically demonstrated and limited as part of the DRE determination. However, if combined testing is not possible, then consideration may be given to testing under normal combustion conditions, as appropriate (see Section 3.3.2.2). Historical operating data for the appropriate combustion parameters should generally be reviewed to verify that the facility maintains steady-state operations with very few fluctuations. Demonstration of absolute maximum or minimum values for the combustion parameters listed in Section 4.2.2.2 during organics testing may be less critical for steady-state operations. In lieu of specific permit limits for the parameters listed in Section 4.2.2.2, periodic reporting to confirm continued absence of transients may be appropriate. When organics testing cannot be performed in conjunction with the DRE test, caution should be exercised to ensure that targets during the organics testing for the combustion parameters listed in Section 4.2.2.2 are not substantially different from the levels demonstrated during the DRE test.

For most incineration and boiler systems, the generation of organic products of incomplete combustion is typically associated with poor combustion situations (organic emissions from cement kilns and lightweight aggregate kilns are typically dominated by organics that are volatilized from the raw materials, but this is discussed later in Section 5.4). Berger has documented the effects of inefficient burner operation and oxygen control (Berger and others 1996). These conditions led to incomplete combustion and subsequent increases in fly ash and carbon monoxide and total hydrocarbon concentrations. Linak has documented PCC exit total hydrocarbon levels in excess of 10,000 ppm during very intense transient puffs arising from batch feed operations at a pilot-scale unit, and has performed chemical analysis to show that the puffs can contain numerous hazardous compounds, even though adequate DREs (>99.99%) may be achieved (Linak and others 1987). Historically, levels of oxygen, carbon monoxide, and total hydrocarbons have been used as surrogate indicators of good combustion to minimize PIC emissions.

Examples of operating conditions that may lead to increased PIC formation include:

- Insufficient temperatures in either the PCC or SCC, leading to incomplete combustion.
- Excess flue gas velocity or flow leading to shorter residence times in the combustion unit and incomplete combustion;
- Batch-fed containers with high oxygen demand that can lead to transient, low oxygen

conditions and incomplete combustion;

- Feeding of low-Btu solids or aqueous liquids that can reduce combustion temperatures.

These situations are typically addressed during performance testing under DRE conditions. To the extent possible, DRE tests are conducted at minimum combustion temperatures in the PCC and SCC, maximum flue gas velocity or flow, and maximum feed rate of each waste type (EPA 1989 and 1992b). Therefore, a successful DRE test should generally result in the maximum organic PIC emissions for incinerators and boilers. In addition, the challenging combustion scenarios discussed in Section 4.2.2.3 should generally be represented during the testing if they are applicable to a particular system. The challenging combustion situations described in Section 4.2.2.3 include: 1) transient conditions; 2) operation with containerized or batch feeds; and 3) high carbon monoxide situations.

The combustion parameters which should generally be emphasized for organic emission testing are the same as those identified in Section 4.2.2.2. These parameters include:

- Minimum PCC and SCC combustion temperatures;
- Maximum combustion gas velocity as an indicator of residence time;
- Maximum waste feed rate for each feed location;
- Limitations on waste feed composition and batch/containerized feeds;
- Maximum flue gas carbon monoxide and/or total hydrocarbon concentrations.

These parameters are usually demonstrated in conjunction with the DRE test condition. However, there may be situations where it may not be possible to perform non-D/F organic emissions testing during the DRE test. For example, the use of surrogate waste for the DRE test might conflict with the objective to use actual wastes during the non-D/F organic testing. In these situations, EPA OSW recommends that the challenging combustion scenarios described in Section 4.2.2.3 be preferentially targeted for organics testing (if applicable) because of increased potential for localized oxygen deficiencies and carbon monoxide/total hydrocarbon spikes. As necessary to protect human health and the environment, permit limits for the Section 4.2.2.2 combustion parameters should be established based on organics testing conducted under

these challenging combustion scenarios. In addition, a facility-specific review of trial burn and historical operating data should generally be performed to determine whether the challenging combustion scenarios correlate with other operating or feed parameters. If so, it is recommended that the correlating parameters be demonstrated during the testing and limited in the permit as necessary to protect human health and the environment in addition to, or possibly in lieu of, the combustion parameters listed in Section 4.2.2.2.

At some facilities, the challenging combustion scenarios identified in Section 4.2.2.3 may not occur. For steady-state systems, demonstration of absolute minimum or maximum values for the Section 4.2.2.2 combustion parameters during organics testing may be less critical. Although demonstration of these control parameters can ideally be accomplished by combining the organics testing with the DRE demonstration (which is preferred whenever possible), consideration may be given for some steady-state systems to performing the organics testing under normal conditions. As discussed in Section 3.3.2.2, testing at normal conditions may be appropriate where the facility can establish a monitoring plan and permit conditions can be developed as necessary to protect human health and the environment to ensure that the test conditions are representative of long-term operations. A permit writer generally should consider the extent to which normal conditions represent potential emissions and risks over the permitted operating range in determining whether testing at normal conditions is appropriate. If organic emissions data are collected under normal conditions, caution should be exercised with respect to operating parameters where the average value is significantly different than operating extremes.

5.2.2 Feed Composition

Recommendation *– EPA OSW recommends that, whenever possible, actual wastes (rather than surrogate wastes synthesized from pure compounds) be burned during the non-D/F organics testing, and that representative, but challenging, feeds be selected for the test. High quantity, routine and recurring waste streams are generally preferred, with special emphasis on wastes that may cause combustion transients (Section 4.2.2.3.1) and wastes containing highly toxic, persistent and bioaccumulative constituents.*

Waste selection for non-D/F organic testing can be very important, because the types of organic PICs may

relate directly to the chemical composition of the waste. EPA OSW recommends that actual wastes, and not surrogate wastes synthesized from pure compounds, be used whenever possible. The goal for the risk burn is to choose representative, but challenging, feeds: actual wastes which may cause elevated or more highly toxic emissions are preferred for the test.

When choosing actual wastes, EPA OSW recommends that the focus be on high quantity, routine, and recurring waste streams, with special emphasis on wastes that may cause combustion transients (Section 4.2.2.3.1) and wastes containing highly toxic, persistent, or bioaccumulative constituents. Examples of historical information that can assist in a review of actual wastes include the following:

- A listing of the top percentage (e.g., top 75 percent) waste receipts by quantity for a given period with descriptions of:
  - source or process generating the waste;
  - annual weight treated;
  - hazardous waste code(s);
  - physical description;
  - chemical description;
  - feed mechanism and feed location to the combustion unit.
- A ranking by weight of the top percentage of chemical constituents treated over a given period.
- A ranking which identifies wastes containing constituents with the highest toxicity, persistence, and bioaccumulation potential.
- A summary of minimum, maximum, and average values for the wastes fed via each feed mechanism into the combustion unit over a given period for:
  - heating value;
  - percentage total chlorine;
  - percent ash;
  - percent water;
  - percent solids;
  - viscosity (as appropriate).
- If historical operating data indicates that the facility experiences routine transients, a summary of the waste streams or waste characteristics which appear to correspond to the transient operations.

EPA OSW recommends that candidate wastes for organic emissions testing be identified considering the ability of the waste to achieve the desired combustion conditions (i.e., tax the combustion unit), the ability of the waste to represent toxic, persistent, and bioaccumulative compounds, and predicted availability of sufficient quantities of the waste streams to complete the relevant portions of the risk burn. Efforts generally should be made to schedule the testing for a time period when the target wastes will be available. However, it may be appropriate to review and evaluate waste selection a few weeks prior to the test based on actual waste stockpiles or scheduled waste receipts.

If a facility burns a large number of small waste streams, or if large quantities of uniform wastes are not available, then the inventory of actual wastes might be insufficient for completing the non-D/F organics emissions testing. A combination of real waste and synthetic waste (or spiked actual wastes) should generally be used in this situation. To the extent possible, simulated wastes should represent the high quantity, routine actual waste streams at a facility, while also achieving the goals outlined in this section. For example, simulated wastes should generally be physically and chemically configured to challenge the combustion unit. Key characteristics from Section 4.2.2.3.1 include physical form, viscosity, moisture, heating value, chlorine, volatility and oxygen demand. It may also be appropriate to spike the simulated wastes to be chemically similar to actual wastes in terms of highly toxic, persistent, or bioaccumulative constituents. In certain circumstances (e.g., to represent a significant waste stream that is not yet being generated, or to represent mixed hazardous/radioactive wastes which present special sampling and analytical challenges), it may be appropriate to use 100 percent surrogate wastes. In the case of batch or containerized wastes, it will generally be more important to focus on maximizing the amount of volatile material within each container, as discussed in Section 4.2.2.3.2, than to use a real waste with less oxygen demand.

Finally, the facility should generally provide protocols for monitoring and tracking waste stream information on an ongoing basis. The protocols should generally identify methods and procedures for comparing future waste characteristics to the wastes burned during the organic emissions testing. This information may be used to define the permitted variation in waste stream composition after the test, or to determine the need for retesting. Parameters of interest are generally expected to closely mirror those reviewed to plan the test in the first place.

5.3 ORGANIC EMISSIONS FROM INCINERATORS AND BOILERS

Hazardous waste incineration and boiler systems are described briefly in Sections 4.3 and 4.4. Non-D/F organic emissions from incinerators and boilers are likely to be dependent on both combustion conditions and feed composition. In summary, all of the considerations discussed in Section 5.2 are also appropriate to consider with respect to incinerators and boilers. Key control parameters are summarized in Table 4-1.

As discussed in Section 4.4, demonstrating key control parameters related to combustion quality may be problematic for some boilers. For boilers, conflicting parameters of maximum waste feed rate and minimum combustion temperature are very prevalent, especially for those boilers with varying production loads for steam generation. Minimum combustion temperature will occur at minimum loads (and therefore at lower fuel feed rates). Maximum waste feed rate will normally occur at maximum production load (maximum steam generation) at a temperature higher than the minimum. Thus, two test conditions may be appropriate in some cases to demonstrate all of the key control parameters related to combustion.

5.4 ORGANIC EMISSIONS FROM CEMENT KILNS AND LIGHTWEIGHT AGGREGATE KILNS

Cement kiln and lightweight aggregate kiln systems are described briefly in Sections 4.5 and 4.6. As discussed in Section 4.5, parameters related to combustion quality are generally less relevant for cement kilns and lightweight aggregate kilns than for incinerators and boilers. However, naturally occurring organics are driven out of the raw materials at the cold end of the kiln.

Control parameters associated with organic emissions from cement kilns are identified in Table 4-2. Conditions relative to combustion quality are generally limited to situations where batch or containerized wastes are fed. Batch wastes injected at mid- or feed-end locations may not experience the same elevated temperatures and long residence times as liquid wastes introduced at the hot end. The remaining recommendations in Section 5.2.1 regarding combustion conditions are not typically relevant to cement kilns.

Since organic emissions from cement kilns are likely to be dominated by organics volatilized from the raw

materials, the recommended focus during the risk burn is to maximize total hydrocarbon emissions in the main and bypass stacks, not to exceed applicable regulatory limits. Although the operating conditions necessary for achieving high total hydrocarbon emissions may vary by facility, maximum total hydrocarbon levels are likely to be achieved by some combination of high production rate, high gas temperatures at the raw material feed end of the kiln, and low oxygen at the raw material feed end of the kiln. These conditions are most likely to be achieved during a high temperature or SRE test. The recommendation to maximize total hydrocarbon emissions is discussed further in Section 4.5.

Control parameters associated with organic emissions from lightweight aggregate kilns are identified in Table 4-2. For lightweight aggregate kilns, EPA OSW recommends that demonstration of combustion parameters be considered on a case-by-case basis. Lightweight aggregate kilns do not operate at combustion temperatures as high as those in cement kilns. However, the potential for poor combustion situations may be minimized, because aggregate kilns typically only burn high-Btu, liquid wastes in the flame zone. Historical operating data should generally be reviewed to determine whether a facility frequently experiences operating transients, as discussed in Section 4.2.2.3.1. If so, it is recommended that the transient operations be represented during the organic emissions testing and permit limitations on the combustion parameters listed in Section 4.2.2.2 (or other parameters as appropriate) may be necessary to protect human health and the environment. However, if a facility maintains steady-state operations with very few fluctuations, demonstration of absolute minimum or maximum values for the Section 4.2.2.2 combustion parameters may be less critical. As discussed for cement kilns, raw materials may contribute to elevated organic emissions at lightweight aggregate kilns, and it is recommended that organics testing be performed at the upper end of the operating range for total hydrocarbons.

The recommendations in Section 5.2.2 regarding feed composition are generally appropriate for cement kilns and lightweight aggregate kilns. Although organic emissions may be influenced more by the raw materials than the waste feeds, it is reasonable to expect that representative, actual wastes should be burned for the risk burn. Selection of liquid wastes burned at the hot end of a cement kiln or aggregate kiln is expected to be less complex than for incinerators and boilers, because wastes are blended to meet fuel specifications. However, the waste characterization information discussed in Section 5.2.2 generally should be provided for the as-blended fuel to the extent possible, as well as for wastes fed at locations other

than the hot end of the kiln. For blended fuel, it may not be possible to perform a characterization by top percentage of waste receipts. In this case, EPA OSW recommends that an alternate ranking scheme be developed to reflect the chemical and physical characteristics of the blended fuel.

CHAPTER 6

METAL EMISSIONS

EPA OSW has recommended that metal emissions be evaluated in site-specific risk assessments because they can pose potential human and ecological risks (EPA 1998a and 1999b). Since most facilities are either controlling metals emissions or will soon control metals emissions pursuant to the requirements of the hazardous waste combustor MACT rule, the primary consideration for the risk burn is whether additional control beyond applicable regulatory standards may be warranted at a particular site (see also Sections 1.3.2 and 1.3.3). This chapter reviews emissions and operating data that may need to be gathered during the risk burn to assist in this determination.

Metal emissions from hazardous waste combustors are highly dependent on metal volatility, metal feed rates, and air pollution control efficiency. Section 6.1 provides information on metals volatility. Section 6.2 reviews specific feed and APCD control parameters that can influence metal emissions, with emphasis on the control parameters identified in the hazardous waste combustor MACT rule. Section 6.3 discusses additional risk-based emissions and feed rate limitations which may need to be considered on a site-specific basis. Finally, Section 6.4 discusses metals speciation. Although recommended speciation assumptions for combustion risk assessments are provided in the EPA OSW risk assessment guidance (EPA 1998a), additional emissions data may need to be collected during the risk burn if a facility wishes to utilize site-specific information.

6.1 METAL VOLATILITY GROUPINGS

Metals can be grouped as volatile, semivolatile, or low-volatile. The distinctions between the three volatility groupings are not absolute, since metals behavior can vary for different combustion systems. However, volatility is a fundamental indicator of metals behavior and control in hazardous waste combustion systems, and the volatility groupings establish a general framework regarding metals behavior.

This section reviews the general characteristics of each volatility group and graphically depicts the relative volatility of the eighteen potentially toxic metals identified in Section 2.3. The discussion in this section is intended to be a general discussion encompassing all of the metals that may be addressed in a risk assessment. For six metals specifically regulated under the MACT rule, volatility groupings are defined by regulation, and the MACT rule volatility designations are reviewed later in Section 6.2.

Volatile metals are defined by EPA as metals that have high vapor pressures (and are typically in vapor form) in the combustion chamber as well as in the cooler downstream APCD components of the combustion system (EPA 1997e). Emissions of volatile metals are highly dependent on feed rate and the use of air pollution control techniques involving adsorption or absorption (e.g., carbon technologies and wet scrubbers). Volatile metals are not controlled by air pollution control technologies designed for removal of particulate matter, such as fabric filters or electrostatic precipitators. (EPA 1996a, 1997e, 1999d, and 1999e).

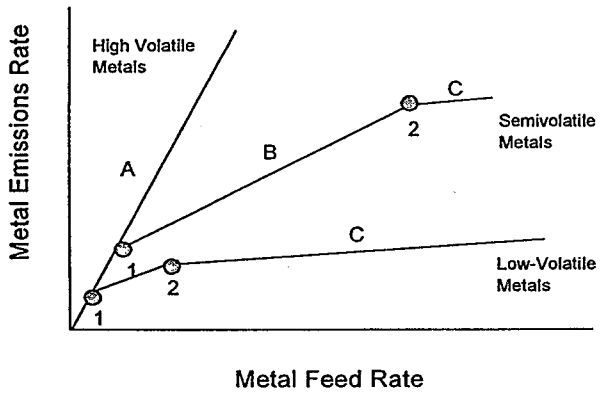
The theoretical relationship between metal feed rate and emissions for volatile metals, assuming that all other variables are held constant, is depicted in Figure 6-1 (EPA 1997e). Volatile metals are dominated by the regime designated as "Region A" on Figure 6-1, where the metal completely vaporizes in the combustion chamber and remains in a vapor form throughout the entire system, including the cooler APCD components. Conversely, Region A is relatively small or non-existent for semivolatile and low-volatile metals, due to their very low vapor pressures at APCD temperatures.

Semivolatile metals typically have higher vapor pressures at combustion temperatures and lower vapor pressures at APCD temperatures (EPA 1997e), leading to vaporization in the combustion chamber, followed by condensation onto particulates (often of less than a 1-micron diameter) before entering the APCD (EPA 1996a, 1997e and 1999d). Emissions of semivolatile metals are a function of both feed rate and APCD removal efficiency for fine, submicron particulate matter (EPA 1996a, 1997e and 1999d).

Figure 6-1 depicts the theoretical relationship between metal feed rate and emissions for semivolatile metals, assuming that all other variables are held constant (EPA 1997e). Semivolatile metals are dominated by the regime designated as "Region B" on Figure 6-1. As the feed rate of a metal increases, the

FIGURE 6-1

METAL VOLATILITY REGIMES



A - Metal in vapor phase
B - Metal condensed on fine particulate
C - Metal entrained as larger particulate

1 - Saturated vapor at APCD temperature
2 - Saturated vapor at combustion temperature

Reproduced from EPA (1997e)

metal vapor at the APCD temperature becomes saturated (Point 1). In Region B, the metal begins to condense at the APCD temperatures, primarily onto fine particulate matter. The slope of the line in Region B is determined by the APCD removal efficiency for fine particulate matter.

Low-volatile metals vaporize to a lesser extent at combustion temperatures and partition to a greater extent to bottom ash, other residue, cement kiln clinker, or entrained particulate matter in the flue gas (EPA 1996a, 1997e and 1999d). Low-volatile metal emissions are more strongly related to the operation of the APCD than to feed rate. Evaluations conducted by Springsteen (Springsteen and others 1997) and EPA

(EPA 1997e) indicate that there is a stronger relationship between emissions and feed rate for volatile and semivolatile metals than for low-volatile metals. For low-volatile metals, SREs tend to increase strongly with increasing feed rate (i.e., emissions increases are not generally proportional to feed rate increases).

The theoretical relationship between metal feed rate and emissions for low-volatile metals, assuming that all other variables are held constant, is depicted in Figure 6-1 (EPA 1997e). Low-volatile metals are dominated by the regime designated as "Region C" on Figure 6-1 because of their low vapor pressures, even at high combustion temperatures. As the feed rate of a metal increases, the metal vapor at the combustion temperature becomes saturated (Point 2). Additional metals fed beyond this rate remain as solids in the combustion chamber. Metal emissions continue to increase somewhat with increased feed rate in Region C, due to increased concentrations of metals in the entrained fly ash. However, emissions do not increase as rapidly as in Region B because no more metals vaporize, and metals entrained as larger particulate are captured in the APCD more efficiently than metals condensed onto submicron particulate matter.

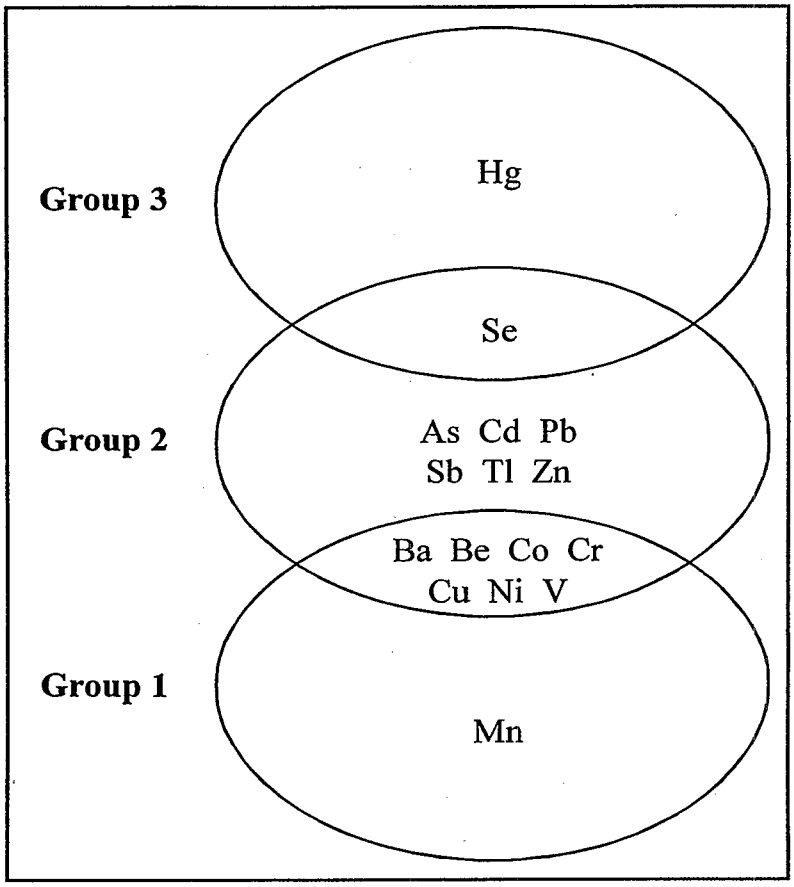
Figure 6-2, reproduced from *Trace Elements - Emissions from Coal Combustion and Gasification* (Clark and Sloss 1992), graphically depicts the relative volatility for sixteen of the potentially toxic metals discussed in Section 2.3. Group 1 represents the low-volatile metals, Group 2 represents the semivolatile metals, and Group 3 represents the volatile metals. The overlapping circles indicate that partitioning behavior can vary for different combustion systems with different operating conditions.

Aluminum and silver were not categorized by Clark and Sloss. However, based on vapor pressure data for aluminum and on information found in a report sponsored by the Portland cement kiln industry (Dellinger and others 1993), aluminum would be expected to exhibit low-volatile behavior as an oxide. As a chloride, aluminum could be semivolatile to volatile. Silver would likely be classified as a low-volatile metal, based on the species expected to be formed within combustion environments.

It is important to note that distinctions between volatile, semivolatile, and low-volatile metals can vary among studies, test conditions, and type of facility (Springsteen and others 1997; Clark and Sloss 1992). Moreover, metal emissions are affected by design differences in combustion units (such as differences

FIGURE 6-2

METAL VOLATILITY GROUPS



Reproduced from Clark and Sloss (1992)

among kilns, liquid injection, and controlled air designs), combustion stoichiometry and flue gas flow rates (higher gas velocities can lead to higher particle/metal entrainment), operating temperatures (metal volatility typically increases with increasing temperature), the physical form and species of the metal, the presence of mineral species which may preferentially bind with metals (these may be contained in the raw materials in cement kilns and lightweight aggregate kilns), the presence of chlorine (which generally increases metal volatility), and APCD removal efficiency (Energy and Environmental Research Corporation [EER] 1991; Cesmebasi and others 1991; Springsteen and others 1997; Linak and Wendt 1998). The figure reproduced from Clark and Sloss may not fully represent the behavior of certain metals in certain systems. For example, Springsteen found that the metals antimony and arsenic exhibit low-volatile behavior in cement kilns (probably due to their affinity for the cement matrix) (Springsteen and others 1997).

Control parameters for volatile, semivolatile, and low-volatile metals and their expected behavior in incinerators, boilers, cement kilns, and lightweight aggregate kilns are discussed further in the following section.

6.2 MACT CONTROL PARAMETERS FOR METALS

The metals emission standards which apply to hazardous waste combustors vary considerably, depending on the type of combustion device and the time frame being considered. For hazardous waste burning boilers and industrial furnaces, metals emissions have been regulated since 1991 under the BIF rule (40 CFR Part 266 Subpart H). The BIF standards are risk-based standards, but only consider exposures via the inhalation exposure pathway, as explained previously in Section 1.3.1. BIF control parameters are discussed in *Technical Implementation Document for EPA's Boiler and Industrial Furnace Regulations* (EPA 1992b). Similar provisions have been applied at some hazardous waste incineration facilities through individual permit decisions, pursuant to the omnibus authority of Section 3005(c)(3) of RCRA, as codified at 40 CFR 270.32(b)(2). More recently, technology-based MACT metals emission limits have been promulgated for hazardous waste burning incinerators, cement kilns, and lightweight aggregate kilns (EPA 1999c). Facilities have three years from the MACT rule promulgation date (September 30, 1999) to comply with the revised standards. Upon documentation of compliance with MACT, the BIF metal

emissions standards are superseded (however, any RCRA permit requirements or conditions related to the combustor remain in effect until that permit is either modified to remove the conditions or the permit is terminated or expires). Technology-based standards for hazardous waste burning boilers are anticipated in a future MACT rulemaking.

This section reviews the key control parameters influencing metal emissions, with emphasis on the control parameters identified in the hazardous waste combustor MACT rule. The MACT control parameters for metals are similar to BIF control parameters. However, the MACT parameters have been reviewed more recently against an extensive metals emissions database.

The purpose of reviewing MACT control parameters is not to suggest that MACT emissions standards should necessarily be imposed within the context of risk-based permitting, or to imply that any facility will be required to achieve early compliance with MACT emissions standards. Rather, the purpose of reviewing the MACT control parameters in this guidance is to identify the feed and operating conditions that influence metals emissions, as well as to highlight the controls which will be implemented at most hazardous waste combustors in accordance with the requirements of the MACT rule. To the extent that risks from metals are already adequately controlled by regulatory limits on key control parameters, then fewer site-specific risk-based limits may be needed in the RCRA permit. However, if regulatory controls are not applicable or sufficiently comprehensive, then additional site-specific risk-based limits may be necessary to ensure protection of human health and the environment. A greater number of risk-based permit limitations may be necessary when the risk burn and RCRA or MACT performance tests reflect different operating modes.

6.2.1 Volatile Metals (Mercury)

The MACT rule regulates mercury as a volatile metal. EPA considers mercury to be a high priority hazardous air pollutant with the potential to cause significant human health and environmental effects (EPA 1996a, 1997a and 1999c). Mercury is the most volatile regulated metal, is the most difficult metal to control, and has been the subject of many detailed studies, including the *Mercury Study Report to Congress* (EPA 1997a).

At temperatures found in hazardous waste combustion devices, nearly all mercury volatilizes to form gaseous mercury that includes both elemental (reduced) and divalent (oxidized) forms (EPA 1999d). Partitioning between elemental and divalent mercury is critical, because it directly affects the ability to control mercury in the APCD system (EPA 1999d). In general, the divalent form of mercury is more likely to be removed in the APCD.

Mercury speciation is dependent on both the fuel and physical characteristics of the combustor, and may vary for an individual unit as feed and operating conditions change. Mercury speciation in the flue gas depends on factors such as waste composition (in particular, chlorine and sulfur levels), the flue gas temperature profile, and the type of air pollution control (EPA 1999d). If chlorine is not present or if 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 the use of an adsorption technology, such as carbon injection.

In the presence of chlorine, formation of divalent mercuric chloride 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.

Mercury emissions are primarily controlled by limiting feed rate and through the use of air pollution control techniques involving adsorption or absorption (e.g., carbon technologies and wet scrubbers). MACT control parameters related to mercury emissions from hazardous waste combustion facilities include the following (EPA 1999e):

- Mercury emissions increase with increasing mercury feed rate. The MACT rule (EPA 1999c) requires that limits be established for total maximum mercury feed rate to the unit (including hazardous waste, raw materials, and fossil fuels). A separate limit for pumpable feed streams is not necessary, since mercury is highly volatile in any form.

- Chlorine feed rate may affect mercury emissions when wet scrubbers are used as APCDs. In the case of mercury, the presence of chlorine is expected to decrease emissions through conversion to the soluble divalent species. However, because only *de minimis* levels of chlorine are necessary for mercury conversion to the soluble salt, minimum chlorine limits are not recommended. A maximum chlorine limit is typically established for most metals

(because increased levels of chlorine can increase metal volatility). However, a maximum chlorine limit is not necessary for mercury, since mercury is already volatile.

- Combustion chamber temperature is not believed to be a critical operating parameter. At typical mercury feed rates and combustion temperatures, all mercury vaporizes in the combustion chamber.

- Wet scrubbers have been demonstrated to be effective at controlling water soluble forms of mercury. The MACT rule (EPA 1999c) requires that limits be established for operating parameters associated with wet scrubbers (such as minimum pressure drop across the scrubber, minimum liquid feed pressure, and minimum liquid-to-flue-gas ratio). Gaspar and others have observed that rapid quenching of hot flue gases from municipal waste incinerators reduces mercury removal in wet scrubbers (Gaspar and others 1997). They believe that rapid quenching does not allow sufficient residence time for elemental mercury (which is favored at typical incineration temperatures) to shift to soluble mercuric chloride (which is favored at temperatures below approximately 600 °C in the presence of chlorine). This concern is reiterated in a technical support document to the MACT rule (EPA 1999d).

- Carbon injection and carbon bed technologies may also be used for mercury control. When carbon technologies are used, the MACT rule (EPA 1999c) requires that limits be established for operating parameters associated with those technologies as described in a technical support document to the MACT rule (EPA 1999e).

MACT control parameters for mercury are summarized in Table 6-1. If a facility bases compliance on an assumption of zero SRE, then only mercury feed rate is limited.

In hazardous waste incinerators and boilers, mercury emissions are currently controlled by limiting waste feed rates and, in some cases, by using wet scrubbers designed for acid gas removal. EPA has estimated that the addition of carbon injection or carbon bed technologies could increase mercury removal in incineration systems up to 90 to 99 percent (EPA 1996a).

Cement kilns and lightweight aggregate kilns currently control mercury emissions by limiting mercury feed rate. Raw materials and coal (as an auxiliary fuel) can add to the mercury emissions. Once mercury is in a cement kiln or lightweight aggregate kiln system, it is generally regarded as "uncontrolled," even though mercury SREs have been documented in some cases (EPA 1999d). Currently, cement kilns and lightweight aggregate kilns do not employ adsorptive or absorptive control technologies (e.g., carbon technologies or wet scrubbers), and mercury is typically not contained in clinker or cement kiln dust unless the cement kiln

dust has an elevated carbon content, which is unlikely (EPA 1999d). The mercury SREs which have been reported for cement kilns and lightweight aggregate kilns may be due to measurement uncertainties associated with the very low levels of mercury in the stack gas or feed streams (EPA 1999d).

6.2.2 Semivolatile Metals

MACT regulates lead and cadmium as semivolatile metals. Emissions of semivolatile metals are a function of both feed rate and APCD removal efficiency for fine, submicron particulate matter (Springsteen and others 1997; EPA 1996a, 1997e and 1999d). Wet scrubbers are generally considered more effective at controlling larger particulates, whereas fabric filters, ESPs and ionizing wet scrubber (IWS) devices are considered most effective in removing smaller particulates (Clarke and Sloss 1992; EER 1991; EPA 1999d). MACT control parameters for semivolatile metal emissions from hazardous waste combustion facilities include the following (EPA 1999e):

- Semivolatile metal emission rates increase as the metal feed rates increase. The MACT rule (EPA 1999c) requires that limits be established for total maximum semivolatile feed rate to the unit (including hazardous waste, raw materials, and fossil fuels). A separate limit for pumpable feed streams is not necessary, because partitioning between the combustion flue gas and bottom ash or product does not appear to be affected by physical state.

- Chlorine increases metal volatility. The MACT rule (EPA 1999c) requires that a limit be established for maximum chlorine feed rate to the unit. The limit is based on total chlorine from all sources, including organic and inorganic chlorine sources.

- Higher combustor gas flow rates can increase particulate and metals entrainment. The MACT rule (EPA 1999c) requires that a limit be established on maximum gas flow rate or kiln production rate.

- Maximum combustion chamber temperature has traditionally been established under the BIF rule to control metal volatility. However, maximum combustion chamber temperature is less important than other operating parameters when considering metal emissions from most hazardous waste combustion facilities. For semivolatile metals, typical combustion temperatures are generally high enough to volatilize most of the metals in the combustion chamber, and evaluation of emissions data does not provide any support for a relationship between combustion chamber temperature and semivolatile metals emissions levels (EPA 1999e).

- APCD type and operating parameters are recognized as critical to the control of

semivolatile metals, and the MACT rule (EPA 1999c) requires that limits be established on APCD parameters. In addition, the operating temperature of the APCD may also be important. For metals which volatilize in the combustion chamber and are carried out with the flue gas, the APCD temperature affects the degree of condensation and control (lower temperatures result in a higher degree of condensation and control). The MACT rule (EPA 1999c) requires that a limit be established on maximum inlet temperature to the dry APCD to control semivolatile metals emissions.

- Cement kilns and lightweight aggregate kilns that recycle collected particulate matter should receive special consideration to ensure that emissions reach steady-state prior to testing, as described in two earlier EPA documents (EPA 1992b and 1999c).

MACT control parameters for semivolatile metals are summarized in Table 6-1. If a facility bases compliance on an assumption of zero SRE, then only total semivolatile feed rate is limited.

In hazardous waste incinerators and boilers, semivolatile metals emissions are most effectively controlled by limiting waste feed rates and utilizing APCD systems that control fine particulate matter (i.e., fabric filters, ESPs, and IWS devices). Units equipped with wet scrubbers are typically less efficient at controlling semivolatile metals. A few incinerators and boilers are not equipped with any air pollution control systems, and therefore rely strictly on feed rate control.

Hazardous waste burning cement kilns and lightweight aggregate kilns currently control semivolatile metal emissions by limiting waste feed rates and utilizing fabric filters or ESPs. It is also speculated that certain raw material constituents preferentially bind with semivolatile metals, providing additional control. Semivolatile metals behavior varies to some extent in cement kilns, depending on the particular system configuration. For kilns with in-line raw mills, semivolatile metals emissions are generally lower when the in-line raw mill is operating, due to additional scavenging of vapors in the low temperature raw mill. For short, dry cement kilns equipped with alkali bypass stacks, the majority of semivolatile metals concentrate in the bypass APCD. Semivolatile metals concentrate preferentially in the bypass due to an internal recycle where metals vaporize at kiln temperatures and condense in the preheater towers (EPA 1999d).

6.2.3 Low-Volatile Metals

MACT regulates arsenic, beryllium and total chromium as low-volatile metals. Emissions of low-volatile metals are a function of both feed rate and APCD efficiency for particulate matter (EPA 1997e and 1999d). MACT control parameters associated with the low-volatile metals are consistent with those for the semivolatile metals described in Section 6.2.2, with the following exceptions (EPA 1999e):

- The MACT rule (EPA 1999c) requires that a separate limit be established for low-volatile metals in pumpable feed streams, since these may partition at a higher rate to the combustion flue gas. However, if a facility wants to base their total feed rate limit only on the feed rate of the pumpable waste feed streams during the test, then separate feed rate limits for total and pumpable feed streams are not needed.

- Low-volatile metals are less apt to vaporize completely at typical combustion temperatures. Thus, a limit on maximum combustion temperature could theoretically be more important for low-volatile metals than for semivolatile metals. However, the amount of additional vaporization at slightly higher temperatures could be negligible compared to the amount of metals contained in entrained flue gas particulate matter, especially for kilns and pulverized coal boilers. Thus, maximum combustion chamber temperature is most likely less important than APCD operating parameters. In addition, analysis of emissions data does not indicate a strong relationship between combustion chamber temperature and low-volatile metal emissions levels (EPA 1999e).

MACT control parameters for low-volatile metals are summarized in Table 6-1. If a facility bases compliance on an assumption of zero SRE, then only total low-volatile metal feed rate is limited.

Similar to the semivolatile metals, operation of the APCD is critical to removal of low-volatile metals. In cement kilns, a significant fraction of the low-volatile metals partitions to the clinker product. Low-volatile metals do not tend to become concentrated in cement kiln bypass gases or build up an internal recycle to the same extent as semivolatile metals. There is also no strongly expected influence of in-line raw mill operational status on low-volatile metal emissions from cement kilns (EPA 1999d).

TABLE 6-1

MACT CONTROL PARAMETERS ASSOCIATED WITH METALS EMISSIONS

	Control Parameter	Limits From	Averaging Period	How Limit Is Established	Other Considerations
VOLATILE METAL CONTROL PARAMETERS (MERCURY)					
Feed Rate	Maximum total mercury feed rate in all feed streams [1]	Comprehensive performance test	12 hour	Average of the test run averages	
Wet Scrubbers High Energy: - venturi - hydrosonic - collision - free jet Low Energy: - spray tower - packed bed - tray tower	Maximum flue gas flow rate or kiln production rate	Comprehensive performance test	1 hour	Average of the maximum hourly rolling averages for each run	
	High energy scrubbers: minimum pressure drop across scrubber	Comprehensive performance test	1 hour	Average of the test run averages	
	Low energy scrubbers: minimum pressure drop across scrubber	Manufacturer specifications	1 hour	N/A	
	Low energy scrubbers: minimum liquid feed pressure	Manufacturer specifications	1 hour	N/A	
	Minimum liquid pH	Comprehensive performance test	1 hour	Average of the test run averages	
	Minimum liquid scrubber flow rate and maximum flue gas flow rate or minimum liquid/gas ratio	Comprehensive performance test	1 hour	Average of the test run averages	
	Ionizing wet scrubbers: minimum power input	Comprehensive performance test	1 hour	Average of the test run averages	

TABLE 6-1

MACT CONTROL PARAMETERS ASSOCIATED WITH METALS EMISSIONS (Continued)

	Control Parameter	Limits From	Averaging Period	How Limit Is Established	Other Considerations
VOLATILE METAL CONTROL PARAMETERS (MERCURY)					
Activated Carbon Injection	Maximum flue gas flow rate or kiln production rate	Comprehensive performance test	1 hour	Average of the maximum hourly rolling averages for each run	
	Minimum carbon feed rate	Comprehensive performance test	1 hour	Average of the test run averages	
	Minimum carrier fluid flow rate or nozzle pressure drop	Manufacturer specifications	1 hour	N/A	
	Identification of carbon brand and type or adsorption properties	Comprehensive performance test	N/A	Same properties based on manufacturer specifications	
	Good particulate matter control	See control parameters listed for wet scrubbers, fabric filters, ESPs, and IWS devices under semivolatile metals			
Activated Carbon Bed	Maximum flue gas flow rate or kiln production rate	Comprehensive performance test	1 hour	Average of the maximum hourly rolling averages for each run	
	Determination of maximum age of each carbon segment	Comprehensive performance test	N/A	Maximum age of each segment during testing	Age limits may be based on manufacturer specifications for the initial performance test

TABLE 6-1

MACT CONTROL PARAMETERS ASSOCIATED WITH METALS EMISSIONS (Continued)

	Control Parameter	Limits From	Averaging Period	How Limit Is Established	Other Considerations
VOLATILE METAL CONTROL PARAMETERS (MERCURY)					
Activated Carbon Bed (continued)	Identification of carbon brand and type or adsorption properties	Comprehensive performance test	N/A	Same properties based on manufacturer specifications	
	Maximum gas temperature at the inlet or exit of the bed	Comprehensive performance test	1 hour	Average of the test run averages	
	Good particulate matter control	Same as for activated carbon injection			
SEMIVOLATILE METAL CONTROL PARAMETERS (Pb, Cd)					
Feed Rate	Maximum total semivolatile metal feed rates from all feed streams [1]	Comprehensive performance test	12 hour	Average of the test run averages	
Chlorine	Maximum total chlorine feed rate from all feed streams [1]	Comprehensive performance test	12 hour	Average of the test run averages	
Gas Flow Rate	Maximum flue gas flow rate or kiln production rate	Comprehensive performance test	1 hour	Average of the maximum hourly rolling averages for each run	
Inlet Temperature to Dry Particulate Matter Control Device	Maximum temperature	Comprehensive performance test	1 hour	Average of the test run averages	

TABLE 6-1

MACT CONTROL PARAMETERS ASSOCIATED WITH METALS EMISSIONS (Continued)

	Control Parameter	Limits From	Averaging Period	How Limit Is Established	Other Considerations
SEMIVOLATILE METAL CONTROL PARAMETERS (Pb, Cd)					
Wet Scrubber: High Energy and Ionizing Scrubbers	Maximum flue gas flow rate or kiln production rate	Comprehensive performance test	1 hour	Average of the maximum hourly rolling averages for each run	
	For high energy wet scrubbers only, minimum pressure drop across scrubber	Comprehensive performance test	1 hour	Average of the test run averages	
	For high energy wet scrubbers only, minimum scrubber liquid flow rate and maximum flue gas flow rate, or minimum liquid/gas ratio	Comprehensive performance test	1 hour	Average of the test run averages	
All Wet Scrubbers	Minimum blowdown rate and minimum scrubber tank volume or level, or	Comprehensive performance test	1 hour	Average of the test run averages	
	Maximum solids content of water	Comprehensive performance test	12 hour for continuous monitor	Average of the test run averages	
			1 hour for manual sampling	Average of manual sampling run averages	

TABLE 6-1

MACT CONTROL PARAMETERS ASSOCIATED WITH METALS EMISSIONS (Continued)

	Control Parameter	Limits From	Averaging Period	How Limit Is Established	Other Considerations
SEMIVOLATILE METAL CONTROL PARAMETERS (Pb, Cd)					
Fabric Filter	Maximum flue gas flow rate or kiln production rate	Comprehensive performance test	1 hour	Average of the maximum hourly rolling averages for each run	
	Minimum pressure drop and maximum pressure drop across each cell	Manufacturer specifications	1 hour	N/A	
Electrostatic Precipitator and Ionizing Wet Scrubber	Maximum flue gas flow rate or kiln production rate	Comprehensive performance test	1 hour	Average of the maximum hourly rolling averages for each run	
	Minimum power input (kVA) based on secondary voltage and current to each field	Comprehensive performance test	1 hour	Average of the test run averages	
LOW-VOLATILE METAL CONTROL PARAMETERS (As, Be, Cr)					
Feed Rate	Maximum total low-volatile metal feed rates from all feed streams [1]	Comprehensive performance test	12 hour	Average of the test run averages	
	Maximum total low-volatile metal feed rates from all pumpable feed streams [1]	Comprehensive performance test	12 hour	Average of the test run averages	See Section 6.2.2
Chlorine	Same as semivolatile metals				

TABLE 6-1

MACT CONTROL PARAMETERS ASSOCIATED WITH METALS EMISSIONS (Continued)

	Control Parameter	Limits From	Averaging Period	How Limit Is Established	Other Considerations
LOW-VOLATILE METAL CONTROL PARAMETERS (As, Be, Cr)					
Gas Flow Rate	Same as semivolatile metals				
Inlet Temperature to Dry Particulate Matter Control Device	Same as semivolatile metals				
Wet Scrubber: High Energy and Ionizing Scrubbers	Same as semivolatile metals				
All Wet Scrubbers	Same as semivolatile metals				
Fabric Filter	Same as semivolatile metals				
Electrostatic Precipitator and Ionizing Wet Scrubber	Same as semivolatile metals				

Notes:
As = arsenic
Be = beryllium
Cd = cadmium
Cr = total chromium
ESP = electrostatic precipitator
IWS = ionizing wet scrubber
kVA = kilovolt-amperes
Pb = lead
MACT = maximum achievable control technology
N/A = not applicable

[1] = This limit applies to all feed streams except natural gas, process air, and feed streams from vapor recovery systems, provided that expected levels of constituents in those feed streams are accounted for in documenting compliance with feed rate limits. See the MACT rule preamble (EPA 1999c) for further information.

6.3 RISK-BASED LIMITATIONS

The MACT control parameters discussed in Section 6.2, or similar parameters under the BIF rule, either apply or will apply to most hazardous waste combustors. However, risk-based limitations beyond these regulatory requirements may be necessary to protect human health and the environment for some facilities. This section addresses potential site-specific risk-based controls beyond BIF or MACT, with emphasis on metal feed rate and emissions restrictions. Since there is generally a strong relationship between metals emissions and feed rates, feed rate reduction is expected to be the primary means of achieving a more stringent risk-based metal emissions level if necessary.

Several topics are addressed in this section. Site-specific risk-based emissions and feed rate limitations for regulated metals (i.e., metals specifically controlled under either BIF or MACT) are discussed in Section 6.3.1. Restrictions for other potentially toxic metals which are not specifically enumerated in the BIF or MACT regulations, but which may be COPCs for site-specific risk assessments, are discussed in Section 6.3.2. Special considerations related to acute risks are discussed in Section 6.3.3. Finally, the use of extrapolation and metals surrogates for establishing site-specific risk-based feed rate limits is discussed in Sections 6.3.4 and 6.3.5, respectively.

Although the metal control parameters discussed in Section 6.2 were presented in terms of metal volatility groups, this guidance does not recommend that risk-based permit limits be established for metal volatility groups (rather than individual metals). The divisions between volatility groups are not absolute. More importantly, EPA OSW has recommended that individual metals be modeled separately for risk assessments using the fate and transport parameters and toxicity information specific to each metal (EPA 1998a and 1999b). The use of volatility groupings for risk-based permitting should generally be limited to the metal extrapolation and surrogate applications discussed later in Sections 6.3.4 and 6.3.5.

6.3.1 Regulated Metals

As noted at the beginning of Section 6.2, the metals emissions standards that apply to hazardous waste combustors vary considerably, depending on the type of combustion device and the time frame being

considered. In assessing the need for risk-based controls, a permit writer will need to consider which regulatory standards apply to a particular facility for which metals, and whether the applicable standards are expected to change over time. Boilers, cement kilns and lightweight aggregate kilns are currently subject to standards for ten BIF metals (antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium). Nickel and selenium have also been regulated at some facilities through omnibus authority of RCRA (EPA 1992a). For cement kilns and lightweight aggregate kilns, the BIF standards for mercury, lead, cadmium, arsenic, beryllium, and chromium will be superseded by MACT technology-based metals standards, and a MACT technology-based particulate standard will serve as surrogate control for antimony, cobalt, manganese, nickel and selenium. The three remaining BIF metals (barium, silver and thallium) are not hazardous air pollutants under the Clean Air Act, and so do not have MACT limits. For hazardous waste incinerators, MACT standards for mercury, lead, cadmium, arsenic, beryllium, chromium and particulate matter will apply. MACT standards for hazardous waste burning boilers have not yet been developed, and thus will not apply until a future rulemaking has been completed.

The particular regulatory standards which apply at a given facility will inform decisions regarding the need for supplemental risk-based permit conditions, as well as the type of supplemental risk-based permit conditions which may be appropriate. For example, it may be necessary to supplement the BIF standards to protect human health and the environment because the BIF standards may not sufficiently protect against risks via indirect exposure routes, or because the BIF standards may not reflect current toxicological information. Lower emissions and feed rate limits for mercury may be necessary to assure protection of human health and the environment because of its propensity to bioaccumulate, and for nickel, because of potential carcinogenic risks through the direct inhalation exposure route (EPA 1998a and 1999b). The MACT standards are viewed as more stringent than the RCRA 40 CFR Part 266 Subpart H standards for BIFs (EPA 1999c). However, risk-based controls to supplement the MACT standards may be appropriate on a site-specific basis. Lower emissions and feed rate limits for certain metals may be appropriate at some sites to assure protection of human health and the environment. In addition, fewer metals are directly regulated under MACT (for some metals, a particulate matter standard serves as a surrogate control measure), and risk-based controls for the non-regulated metals and for the indirectly controlled metals may need to be considered, as discussed in Section 6.3.2. Finally, the MACT rule provides an option for alternative standards at cement kilns and lightweight aggregate kilns when the MACT metal emissions

standards cannot be achieved because of metals in the raw materials. The alternative standards represent another scenario where MACT may need to be supplemented with site-specific risk-based limits to ensure that a facility does not pose an unacceptable risk (EPA 1999c).

A preliminary risk assessment can provide information to determine whether operation within regulatory emissions limits (either BIF or MACT) may present a significant risk to human health and the environment. As discussed in Section 3.2, EPA OSW recommends that the preliminary risk assessment be performed prior to the risk burn to better define the risk burn data needs. If a regulatory limit applies for a particular metal and is sufficiently protective, additional risk-based limits should generally not be needed. However, if the regulatory limit for a particular metal is not sufficiently protective, a lower, site-specific risk-based emissions limit for that metal may need to be established in the RCRA permit to assure protection of human health and the environment.

In addition to providing information on whether operation within a regulatory emissions limit may present a significant risk to human health and the environment, the preliminary risk assessment can also indicate the extent of emissions reduction necessary to assure protection of human health and the environment. After a protective emissions limit has been defined, a correspondingly lower metal feed rate limit can be determined. A variety of methodologies can be used to establish a risk-based feed rate limit from a risk-based emissions limit. Several approaches are outlined below, and a combination of methodologies may be appropriate in some cases:

- Zero SRE: A facility may choose to establish a risk-based feed rate limit from the risk-based emissions limit for a particular metal by assuming zero SRE (i.e., the feed rate limit is the same as the risk-based emissions rate limit).

- Existing SRE: A facility may have data from an existing SRE test performed for BIF or MACT documenting that the lower, risk-based emissions limit is already being achieved. In this case, the risk-based metal feed rate limit is the same as the feed rate during the SRE test where the risk-based emissions limit was demonstrated.

- New SRE: With careful planning, a future SRE test may serve as the vehicle for determining risk-based feed rate limits. For example, a facility may be due for BIF re-certification testing, or may be about to perform the initial MACT performance test. If the facility has performed a preliminary risk assessment which indicates the need for risk-based controls, the facility may be able to reduce (or eliminate) metals spiking, as well as perform sampling for

additional non-regulated metals, to meet the objectives of both the performance test and the risk burn. In this case, the risk-based metal feed rate limit is established as the feed rate during the SRE test where the risk-based emissions limit is demonstrated.

- Normal Test: Where appropriate (see Section 3.3.2.2), a separate test conducted at normal metal feed rates may be considered for establishing risk-based metal feed rate limits. When metals emissions data collected during a normal test are utilized for the site-specific risk assessment, a dual testing and permitting scheme such as the following is recommended:

  - An SRE test is performed to demonstrate that maximum emissions meet applicable BIF or MACT limits, and to establish maximum hourly or 12-hour feed rate limits

  - A normal test is performed to generate emissions data for evaluation in the site-specific risk assessment, and to establish long-term average feed rate limits

- Extrapolated Feed Rate: The use of extrapolation to establish risk-based feed rate limits is discussed further in Section 6.3.4. Opportunities for using extrapolation to establish risk-based feed rate limits may be somewhat limited, since only upward extrapolation is recommended (whereas risk-based permitting involves *lowering* feed rates). However, some situations may be amenable to extrapolation. For example, a facility may have collected data for the entire suite of metals during a previous SRE test (even though only a few metals were spiked). Upward extrapolation for the unspiked metals could be considered.

- Surrogate SRE: The use of surrogates to establish risk-based feed rate limits is discussed further in Section 6.3.5. If existing metals emissions data are available, but data on a certain metal were not collected, or if the data for a particular metal are not useful (i.e., an SRE cannot be determined because of non-detects for the feed inputs), use of data for a surrogate metal based on volatility groupings may be considered.

The approach selected to establish risk-based metal feed rate limits from risk-based emissions limits will affect the scope of the risk burn. For example, if a facility chooses the "Zero SRE" approach for all metals where risk-based limits are needed, then metal emissions measurements may not be needed during the risk burn. However, if a facility chooses the "Normal Test" approach, the risk burn may involve extra test conditions.

Under any of these options, EPA OSW recommends that an averaging period for the risk-based feed rate limit be specified. A facility may choose to comply using the same feed rate averaging periods as specified by BIF or MACT (1 hour or 12 hours) to minimize need for extra monitoring. On the other hand, if these averaging periods do not allow sufficient operating flexibility, a facility may choose to comply using a

longer-term averaging period. Long-term metal feed rate averaging periods should generally be adequate for controlling long-term, chronic risks, as discussed in Section 3.3.2.2.

6.3.2 Other Toxic Metals

In addition to the original ten BIF metals, other metals that EPA OSW has recommended be considered as COPCs for site-specific risk assessments include aluminum, cobalt, copper, manganese, nickel, selenium, vanadium, and zinc (EPA 1998a and 1999b). Summaries of specific human health and ecological concerns for these metals are found in Section 2.3 of this document.

For these eight metals (if a facility is subject to BIF) and for twelve metals (if a facility is subject to MACT), specific regulatory restrictions on metal emissions or feed rates do not apply (although MACT does establish a particulate matter standard as a surrogate control measure for antimony, cobalt, manganese, nickel, and selenium). EPA OSW recommends that the need for risk-based restrictions on these metals be determined on a site-specific basis, considering the potential risks associated with the metals. A preliminary risk assessment can provide an indication as to whether specific feed rate controls on these metals may be necessary. As discussed in Section 3.2, EPA OSW recommends that the preliminary risk assessment be performed prior to the risk burn to better define the risk burn data needs.

To perform a preliminary risk assessment, initial emissions estimates for the non-BIF or non-MACT metals are needed. Actual emissions data may not be available, since some of these metals have never been subject to specific regulatory emission or feed rate standards. In the absence of actual emissions data, a facility might consider performing the preliminary risk assessment based on the assumption that the non-regulated metals are fed at normal feed rates (considering the composition of the wastes burned at the facility) and are completely emitted (i.e., zero SRE). If a preliminary risk assessment indicates that risks may be significant (for nickel, for example, which may be evaluated in the risk assessment as a carcinogen per the EPA OSW risk assessment guidance [EPA 1998a]), emissions sampling during the risk burn may be appropriate.

The need for risk-based controls on the non-BIF/non-MACT metals will generally depend on whether emissions of these metals are predicted to present a significant risk to human health and the environment. If

potential risks associated with the metals are insignificant, a permit writer may simply choose to document the risk assessment feed and emissions assumptions in the administrative record instead of imposing specific feed rate limits in the permit. As risks from non-BIF/non-MACT metals approach significant levels, feed rate monitoring and tracking may be necessary for protection of human health and the environment by ensuring that potentially significant changes in feed rates which could warrant re-evaluation in the risk assessment are identified. Alternatively, risk-based emissions limits and long-term average feed rate limits may be established in the permit.

As discussed in Section 6.3.1 for BIF/MACT metals, a variety of methodologies can be used to establish risk-based feed rate limits from risk-based emissions limits. The same options listed in Section 6.3.1 may be appropriate for the non-BIF/non-MACT metals. It is generally anticipated that feed rates of these metals will not need to be limited on a short-term (i.e., 1 or 12 hour) basis, but that long-term average feed rate limits will be sufficient. In addition, testing for these metals will not typically involve spiking.

6.3.3 Acute Risks

Sections 6.3.1 and 6.3.2 discuss establishing site-specific risk-based emissions limits and corresponding feed rate limits, with options involving testing at normal conditions and performing feed rate monitoring using long-term averaging periods. Testing at normal conditions and applying long-term averaging periods may be appropriate for the purpose of controlling long-term, chronic risk from metals. However, the EPA OSW risk assessment guidance (EPA 1998a) also recommends an evaluation of acute risk associated with short-term (maximum 1 hour) exposure through the inhalation pathway. The acute evaluation is based on an estimate of maximum potential 1-hour metal emissions rates. The normal test option mentioned in Sections 6.3.1 and 6.3.2 would not be appropriate for generating maximum emissions estimates for an acute evaluation, and other options may need to be considered. Also, if acute risks at maximum emissions rates appear to be a concern for a particular metal, then a maximum 1-hour feed rate limit may need to be established in the permit (in addition to the longer-term feed rate limit which may be established per Sections 6.3.1 and 6.3.2 to control chronic risks).

6.3.4 Extrapolation

As discussed in Section 6.3.1, one option for establishing risk-based feed rate limits from risk-based emissions limits involves the use of extrapolation (subject to approval). Extrapolation involves using test data collected at one metals feed rate to project an emissions level at a different metals feed rate. "Upward" extrapolation refers to projecting the emissions associated with a higher metals feed rate, whereas "downward" extrapolation refers to projecting the emissions associated with a lower metals feed rate. Extrapolation is of interest because: 1) it potentially eliminates the need to re-test at different metals feed rates to show compliance with more stringent risk-based emission limits; and 2) it can help to minimize the need for metals spiking.

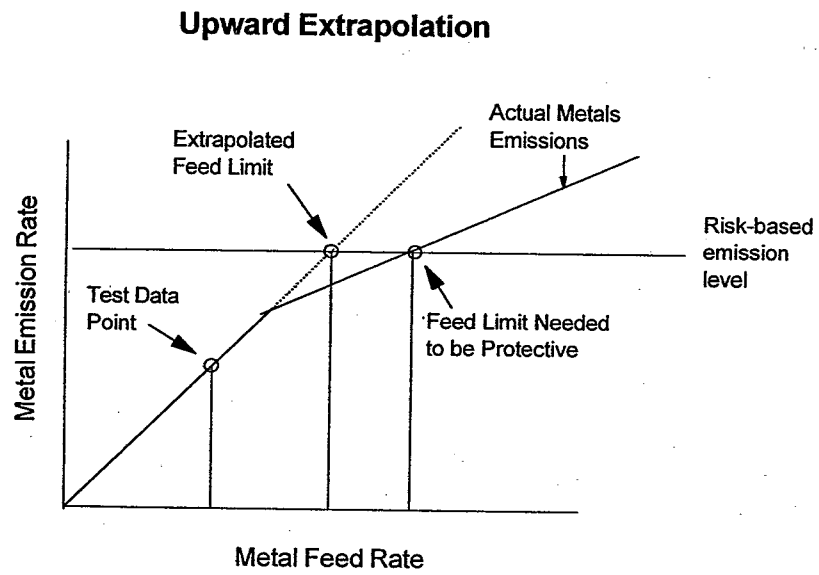
Trends in facility-specific data (EPA 1997e) support the following observations, as illustrated in Figure 6-1:

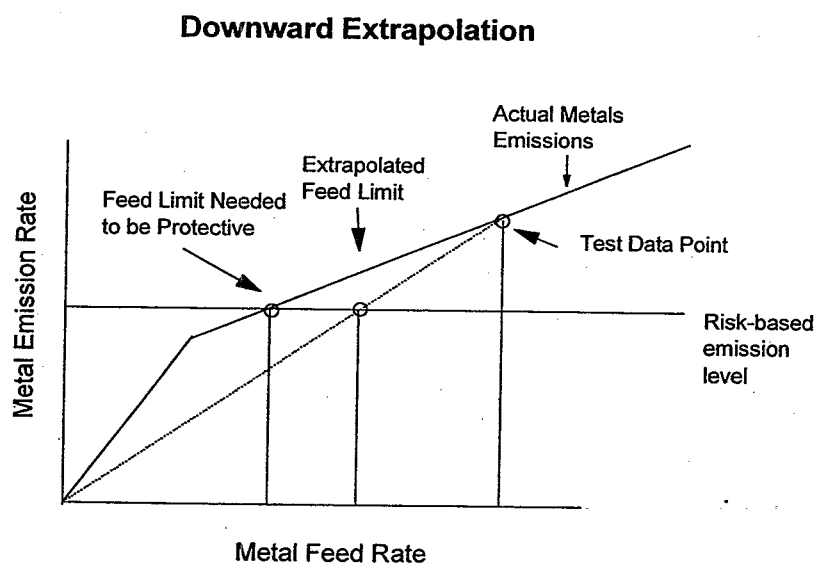
- Emissions tend to increase as feed rate increases;
- The relationship between emissions and feed rate for volatile and semivolatile metals tends to be stronger than that for low-volatile metals (i.e., there is a more proportional relationship between emissions and feed rates for volatile and semivolatile metals);
- The relationship between emissions rate and feed rate for low-volatile metals tends to be more flat (not a strong function of feed rate). SRE strongly tends to increase with increasing feed rate for low-volatile metals.

Given these trends, EPA has determined that upward extrapolation from the origin (i.e., from a metal feed rate and emissions rate of zero) is conservative for all metal types and volatilities, as illustrated in Figure 6-3 (EPA 1997e). Upward extrapolation is conservative because the predicted emissions rates at higher feed rates are likely to be equal to or greater than actual emissions rates. SRE tends to stay the same or increase with increasing feed rate. However, as also illustrated in Figure 6-3, downward extrapolation may not always be conservative. Downward extrapolation may result in predicted emissions that are less than actual emissions. Thus, downward extrapolation is generally not recommended. Downward extrapolation for low-volatile metals can be particularly problematic, because there is not a strong linear relationship between emissions and feed (see Figure 6-1).

FIGURE 6-3

METALS EXTRAPOLATION





Since only upward extrapolation is recommended as being conservative, the opportunities for using extrapolation to establish risk-based feed rate limits may be somewhat limited. Risk-based permitting generally involves *lowering* emissions and feed rates (i.e., downward extrapolation). However, some risk-based permitting situations may be amenable to upward extrapolation. For example, a facility may have collected emissions data for unspiked metals during a previous SRE test. Upward extrapolation for the unspiked metals could be considered. In reviewing a proposal to use extrapolation for establishing risk-based feed rate limits, the permitting authority should generally consider information similar to the guidelines specified in the hazardous waste combustor MACT rule and supporting documents (EPA 1999c and 1999e):

- **Is there sufficient confidence in the test data being used for the extrapolation?** Upward extrapolation to establish a risk-based metal feed rate limit is likely to involve the use of test data where spiking was not performed. However, there may be a high degree of uncertainty associated with this type of data. At low concentrations, the error bounds on the sampling and analysis procedures tend to be more significant. Errors associated with sampling and analysis for heterogeneous feed streams can be particularly high. In addition, it may not be possible to calculate an SRE at all if a metal is not detected in one or more of the feed streams. In determining whether there is sufficient confidence in the test data being used for the extrapolation, it is recommended that the permit writer consider the incidence and potential impact of non-detect data points, as well as the reproducibility between test runs.

- **Are the requested feed rates warranted?** A permit writer should generally not approve extrapolation to feed rates that are significantly higher than the historical range of feed rates, unless a facility documents that future operations will necessitate higher metals feed rate limits.

A variety of metal extrapolation procedures have been proposed over the years (EPA 1992b, 1997d, 1997e, 1999c and 1999e; Springsteen and others 1997). It is recommended that available feed and emissions data be plotted graphically before a decision is made regarding the suitability of extrapolation and a specific extrapolation method. A graphical representation can assist in identifying non-linear behavior, high data variability, and potential outliers. It may also be useful to plot metals within the same volatility group on the same graph. A combined plot can support a determination of whether metals in the same volatility group behave similarly (as would theoretically be expected), and a wider range of feed rates for a particular volatility group may be represented when the data for several metals are grouped together.

The permit writer should generally ensure that a proposed extrapolation procedure will be appropriately conservative, considering the extent and quality of the metals feed rate and emissions data. Depending on a review of the actual data, a conservative extrapolation procedure might include:

- Extrapolation from the lowest observed SRE that is not an outlier. The lowest SRE can either be determined for an individual metal, or it might be selected based on the collective data for metals within a given volatility group. Provided that the grouped data confirm that the metals behave similarly, a wider range of feed rates may be represented when the data for several metals are grouped together.

- Extrapolation from the "Lower Confidence Limit" of the test condition average SRE for a particular metal, calculated based on the test condition average and the within-test-condition standard deviation at a particular confidence limit bound (such as 95 percent).

- For cases where data for a particular metal are more extensive (for example, if repeated tests have been conducted over the years), extrapolation from a statistically-based analysis of the entire database.

A permit writer may choose to disapprove extrapolation if there is not a high degree of confidence that average emissions at the extrapolated feed rate will be at or below the risk-based emissions rate. Alternatively, a permit writer may choose to condition the extrapolation on performance of follow-up testing to confirm that the risk-based emissions levels are being achieved, or to limit the extent of extrapolation, or to limit the proximity of the extrapolation to the risk-based emissions limit.

Section 6.2.3 explains that the MACT rule requires that separate feed rate limits be established for low-volatile metals in total feed streams and for low-volatile metals in pumpable feed streams, since metals in the pumpable feed streams may partition at a higher rate to the combustion flue gas. When extrapolation is performed to establish a total risk-based feed rate limit for a low-volatile metal, the permit writer should also generally consider whether a separate feed rate limit is appropriate for pumpable feed streams and, if so, how to establish that limit. One option is to maintain the pumpable and total feed rate ratio the same for the extrapolated feed rates as in the original data used for the extrapolation. Another, very conservative, option is to base the total extrapolated feed rate limit only on extrapolation from the feed rate of the pumpable feed stream. In this later case, separate feed rate limits for total and pumpable streams should not be needed.

6.3.5 Surrogate SREs

As discussed in Section 6.3., another option for establishing risk-based feed rate limits from risk-based emissions limits involves the use of SREs for surrogate metals. The use of an SRE for a surrogate metal may be appropriate in several situations. For example, if existing metals emissions data are available, but data were not collected for a particular metal, or if the data for a particular metal are not useful (i.e., an SRE cannot be determined because of non-detects for feed inputs), the use of a surrogate SRE may be appropriate. In addition, use of surrogate SREs may be considered to limit the need for spiking during a risk burn if certain metals are not normally present in the feed streams at reliable levels.

In reviewing a proposal to use surrogate SREs for establishing risk-based feed rate limits from risk-based emissions limits, EPA OSW recommends that the permitting authority consider whether one metal is an appropriate surrogate for another. In general, metals within a volatility grouping can be used interchangeably for each other, and metals of a "higher" volatility grouping can be used as surrogates for metals in a lower grouping. Figure 6-2 depicts the relative volatility for sixteen of the potentially toxic metals discussed in Section 2.3. Springsteen and others provide further analysis based specifically on trends in hazardous waste combustor data (Springsteen and others 1997). Springsteen categorizes mercury and selenium as "volatile" metals in hazardous waste combustor systems. This categorization compares favorably with the Group 3 metals in Figure 6-2, reproduced from Clark and Sloss (Clark and Sloss 1992). These metals tend to vaporize completely at combustion temperatures. Mercury may remain volatile in the APCD, while selenium is more likely to condense. Because of its behavior in the APCD, selenium is often treated as a semivolatile metal (although it is the most volatile metal in that category, as indicated by Figure 6-2). Selenium may not completely fit within either category.

Springsteen and others categorize cadmium, lead and thallium as "semivolatile" (Springsteen and others 1997). This categorization compares favorably with the Group 2 metals identified in Figure 6-2, reproduced from Clark and Sloss (Clark and Sloss 1992).

Springsteen and others categorize barium, beryllium, chromium and nickel as "low-volatile" (Springsteen and others 1997). Figure 6-2 also places these metals in the Group 1 low-volatile metal category. However, in

Figure 6-2, these metals fall in the area of the circle that overlaps with the Group 2 semivolatile metal category, indicating that partitioning behavior may vary for different combustion systems with different operating conditions. Facility-specific data should generally be reviewed to determine whether any of these metals exhibit semivolatile metal behavior (as evidenced by more enrichment of these metals in air pollution control residues than in bottom ash or clinker residues). Or, in the absence of site-specific information, these metals could be treated conservatively as semivolatile metals.

Finally, Springsteen and others explain that three metals exhibit low-volatile behavior in cement kilns but may behave more like semivolatiles in incineration systems (Springsteen and others 1997). These metals include arsenic, antimony, and silver. Springsteen includes special recommendations for arsenic, antimony, and silver, since their behavior can be dependent on combustion system type (Springsteen and others 1997). In cement and lightweight aggregate kilns, these metals are included within the low-volatile grouping, and all low-volatile metals can be used interchangeably as surrogates for each other. In incinerators and boilers, arsenic, antimony, and silver can conservatively be used as surrogates for low-volatile metals, but low-volatile metals generally should not be used as surrogates for arsenic, antimony, and silver. In addition, arsenic, antimony, and silver generally should not be used as surrogates for each other for incinerators and boilers.

EPA OSW recommends that the general guidelines regarding specific metals and volatility groupings always be reviewed in conjunction with facility-specific data. Volatile metals will not be present in significant concentrations in either fly ash or bottom ash. Semivolatile metals are more likely to be enriched in air pollution control residues such as fly ash (or cement kiln dust), and low-volatile metals are more likely to be enriched in the bottom ash (or clinker).

It is important to recognize that use of a surrogate SRE will often involve extrapolation, and the concepts presented in Section 6.3.4 apply. That is, "upward" extrapolation is usually conservative, but "downward" extrapolation may not be. Therefore, an SRE determined at a higher feed rate for one metal should generally not be used to calculate a lower feed rate for a surrogate metal. In addition, the permit writer should feel comfortable that use of a surrogate SRE will be appropriately conservative, considering the extent and quality of the metals feed rate and emissions data. A conservative approach may involve:

- Use of the lowest observed SRE that is not an outlier. The lowest SRE can either be determined for an individual metal, or it might be selected based on the collective data for metals within a given volatility group. Where the grouped data confirms that the metals behave similarly, a wider range of feed rates may be represented when the data for several metals are grouped together.

- Use of the "Lower Confidence Limit" of the test condition average SRE for a particular metal, calculated based on the test condition average and the within-test-condition standard deviation at a particular confidence limit bound (such as 95 percent).

- For cases where data are more extensive (for example, if repeated tests have been conducted over the years), it may be appropriate to perform a statistically-based analysis of the entire database to determine a conservative SRE.

6.4 METAL SPECIATION

The mobility, bioavailability and toxicity of a metal varies, depending on the specific chemical compound. However, the ability to measure individual metal compounds and to assess the risks associated with those compounds is currently limited. EPA OSW's human health and ecological risk assessment guidance documents (EPA 1998a and 1999b) generally address metals in the elemental form, with the exception of mercury, chromium, and nickel. For mercury, chromium and nickel, the guidance (EPA 1998a and 1999b) provides recommended assumptions regarding valence state or chemical form. Based on the conservative nature of these assumptions, a facility may want to perform speciation sampling during the risk burn or present other information to replace the recommended assumptions with site-specific data.

6.4.1 Mercury

As discussed in Section 6.2.1, mercury can be present in the divalent (oxidized) form or the elemental (reduced) form. The form of mercury significantly influences its fate and transport in the environment. The divalent form is water soluble and more likely to adsorb to particles. Stack emissions can thus be removed from the atmosphere by precipitation, which can lead to partitioning into methyl mercury in nearby surface waters. This partitioning will tend to drive indirect ecological risks and food chain risks to humans. Elemental mercury, on the other hand, is less prone to rapid atmospheric removal and deposition near the source. The EPA OSW risk assessment guidance (EPA 1998a and 1999b) assumes that the vast majority

(99 percent) of elemental mercury is diffused to the free atmosphere to become part of the global mercury cycle (rather than being deposited near the source).

The recommended mercury emissions speciation assumptions provided in the EPA OSW risk assessment guidance (EPA 1998a and 1999b) are: 60 percent divalent vapor phase, 20 percent divalent particle-bound phase, and 20 percent elemental vapor phase. The rationale for these assumptions is discussed in greater detail in the EPA OSW risk assessment guidance (EPA 1998a). A facility may wish 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 (EPA 1999g).

Standard EPA sampling methods for mercury speciation are not currently available. However, methodologies which have been evaluated for their ability to provide mercury speciation information are discussed in Appendix B of this document. If mercury speciation sampling is performed, care should be taken to avoid operating the unit in a manner which could result in a high bias for the elemental form of mercury. Higher percentages of elemental mercury tend to decrease risks, because the EPA OSW risk assessment guidance (EPA 1998a and 1999b) assumes that only 1% of elemental mercury deposits near the source. As discussed in Section 6.2.1 of this document, elemental mercury can comprise a significant fraction of the total mercury if chlorine levels are low or if sulfur levels are high. In addition, rapid quenching may increase the percentage of elemental mercury because the elemental mercury (which is favored at typical combustion temperatures) may not have sufficient residence time to shift to the divalent form (which is favored at temperatures below approximately 600 °C in the presence of chlorine).

6.4.2 Chromium

Chromium exists in multiple valance states. The hexavalent form is most toxic and has been shown to be a human carcinogen via the direct inhalation exposure route (EPA 1998a). The hexavalent form typically occurs as either chromate or dichromate. Trivalent chromium has not been shown to be carcinogenic in either human or laboratory animals (EPA 1998a). EPA OSW has not recommended that other chromium valence states be considered in risk assessments (EPA 1998a).

Available information suggests that substantial quantities of chromium are not likely to be emitted in the hexavalent form from combustion units. Laboratory work by Linak and others indicates that the fraction of hexavalent chromium emitted may be very small, typically ranging from less than one percent to approximately two percent of the total chromium measured (Linak and others 1996; Linak and Wendt 1998). The hexavalent fraction in the exhaust was found to be enhanced somewhat by high levels of chlorine, but was reduced to below analytical detection limits by the addition of small quantities of sulfur. Additional information indicating low percentages of hexavalent chromium from combustion units is provided by EPA (EPA 1990) and Bailiff and Kelly (Bailiff and Kelly 1990). However, in limited situations and under certain conditions, a high percentage of hexavalent chromium has been found in combustor emissions (EPA 1991).

The recommended chromium emissions speciation assumption provided in the EPA OSW risk assessment guidance (EPA 1998a) is a worst-case assumption (i.e., that 100 percent of the chromium emissions are in the hexavalent form). The basis for this assumption is that there is not sufficient evidence to reliably estimate the partitioning of chromium between the two valence states. The recommended assumption is very conservative. Therefore, a facility may wish to sample for hexavalent chromium during the risk burn to replace the recommended assumption with site-specific data. SW-846 (EPA 1996b) provides an in-stack emissions method (Method 0061) for differentiating between trivalent and hexavalent chromium.

6.4.3 Nickel

Nickel can achieve several oxidation states (up to four), with the most common being +2. The most prevalent forms of nickel are sulfides, oxides, chlorides, and silicates. Some forms of nickel (including nickel carbonyl, nickel subsulfide, and nickel refinery dust) are considered to be carcinogenic. Previously under the BIF regulations, EPA did not treat nickel as a carcinogen because of the presumption that nickel can only be emitted from combustion units as nickel oxide (which, by itself, is not considered to be a carcinogen).

The recommended assumption provided in the EPA OSW risk assessment guidance (EPA 1998a) is that nickel be evaluated as an inhalation carcinogen using the carcinogenic slope factor for nickel refinery dust. This recommendation represents a change from the regulatory approach under the BIF rule. The basis for the revised approach is that nickel oxide is a major component of nickel refinery dust, and the component in nickel refinery dust which causes it to be carcinogenic has not been established. For exposure pathways

other than direct inhalation, EPA OSW has recommended that nickel be evaluated as a noncarcinogen using the oral reference dose for soluble nickel salts (EPA 1998a). A similar approach was utilized in the risk assessment conducted in support of the MACT rule (RTI 1999).

Standard EPA sampling methods for nickel speciation do not exist at this time. Therefore, it is not possible for a facility to generate site-specific stack emissions data to replace the recommended assumptions provided in the EPA OSW risk assessment guidance (EPA 1998a). However, the risk assessment guidance discusses an approach where a facility may present data at potential points of inhalation exposure indicating the absence of carcinogenic nickel refinery dust components or the presence of noncarcinogenic species such as soluble salts.

CHAPTER 7

HYDROGEN CHLORIDE/ CHLORINE EMISSIONS AND PARTICLE-SIZE DISTRIBUTION

EPA OSW has recommended that hydrogen chloride and chlorine be evaluated for potential risks in site-specific risk assessments (EPA 1998a). Potential risks from HCl and Cl_2 are limited to the inhalation pathway. Since most facilities are either controlling or will control HCl and Cl_2 emissions under the hazardous waste combustor MACT rule, the primary consideration for the risk burn is whether additional control beyond applicable regulatory standards may be warranted at a particular site (see also Sections 1.3.2 and 1.3.3). This chapter (Section 7.1) identifies risk burn data needs and control parameters related to HCl and Cl_2. Since HCl and Cl_2 have been discussed at length in other documents (EPA 1992b, 1999d and 1999e), they are only mentioned briefly here.

This chapter (Section 7.2) also identifies risk burn data needs related to particle-size distribution. Information on particle-size distribution is needed for the air dispersion and deposition modeling that supports risk assessments (EPA 1998a and 1999b).

7.1 HYDROGEN CHLORIDE AND CHLORINE

The HCl and Cl_2 emissions standards which apply to hazardous waste combustors vary, depending on the type of combustion device and the time frame being considered. Technology-based limits for HCl have applied to hazardous waste incinerators since 1981 (40 CFR Part 264.343). The technology-based standards limit HCl emissions to the larger of 4 pounds per hour or 99% removal. The 40 CFR Part 264.343 provisions do not include an emission limit for Cl_2. For hazardous waste burning boilers and industrial furnaces, HCl and Cl_2 emissions have been regulated since 1991 under the BIF rule (40 CFR Part 266, Subpart H). The BIF standards are risk-based standards which consider exposure via the inhalation pathway

based on RACs specified in the regulations. However, updated toxicological information (instead of the RACs specified in 40 CFR Subpart H) may be available and may need to be considered for site-specific risk assessments at BIF facilities. Similar provisions to those prescribed by 40 CFR Subpart H have been applied at some hazardous waste incineration facilities through individual permit decisions pursuant to the omnibus authority of Section 3005(c)(3) of RCRA and 40 CFR 270.32(b)(2). More recently, technology-based MACT emission limits have been promulgated for hazardous waste burning incinerators, cement kilns, and lightweight aggregate kilns (EPA 1999c). The MACT standards establish limits on parts per million volume (ppmv) of HCl and Cl_2 emissions, expressed as HCl equivalents (calculated as ppmv HCl + 2*ppmv Cl_2). Facilities have three years from the MACT rule promulgation date (September 30, 1999) to comply with the revised standards. Upon documentation of compliance with MACT, the RCRA incinerator and BIF emission standards are superseded (however, any RCRA permit requirements or conditions related to the combustor remain in effect until that permit is either modified to remove the conditions or the permit is terminated or expires). Technology-based standards for hazardous waste burning boilers are anticipated in a future MACT rulemaking.

The particular regulatory standards which apply at a given facility will inform decisions regarding the need for supplemental risk-based controls on HCl and Cl_2 emissions, as well as the type of supplemental risk-based permit conditions which may be appropriate. For example, it may be necessary to supplement the 40 CFR Part 264.343 incinerator standards to protect human health and the environment, because Cl_2 emissions are not limited at all by 40 CFR Part 264.343, and because the HCl removal efficiency standard does not equate to a specific emission limitation. It may be necessary to supplement the BIF standards when updated toxicological information (instead of the RACs specified in 40 CFR Subpart H) is available. Risk-based controls to supplement the MACT standards, including lower emissions and feed rate limits, may be appropriate to assure protection of human health and the environment on a site-specific basis.

A preliminary risk assessment can provide information to determine whether operation within a regulatory emissions limit for HCl and Cl_2 (for example, BIF or MACT) may present a significant risk to human health and the environment. Both pollutants are noncarcinogens and pose risks only through the inhalation pathway. As discussed in Section 3.2, EPA OSW recommends that the preliminary risk assessment be performed prior to the risk burn to better define risk burn data needs. If a regulatory limit applies and is sufficiently

protective, additional site-specific risk-based limits should generally not be needed. However, if the regulatory limit is not sufficiently protective, a lower site-specific risk-based emissions limit for HCl or Cl_2 may need to be established in the RCRA permit to assure protection of human health and the environment.

When it is appropriate to establish a lower, site-specific risk-based emission limit for HCl or Cl_2 in the RCRA permit to supplement applicable regulatory standards, then EPA OSW recommends that stack emission measurements for both HCl and Cl_2 be performed to verify the feed and operating conditions necessary for achieving compliance with the more stringent emission limits. HCl and Cl_2 emission levels cannot be predicted from feed rate information or from extrapolation of stack test data because of the difficulty in predicting the partitioning between HCl and Cl_2 at various operating conditions (additional information on HCl and Cl_2 partitioning is provided in a technical support document for the hazardous waste combustor MACT rule, EPA 1999d). The use of existing test data may be appropriate in some cases, particularly if the data already demonstrates compliance with the more stringent risk-based limits. Otherwise, sampling during the risk burn may be appropriate.

EPA OSW recommends that the risk burn for HCl and Cl_2 generally be conducted while demonstrating control parameters for chlorine feed rate and scrubber performance as identified in Table 7-1. Table 7-1 summarizes the MACT control parameters related to HCl and Cl_2 emissions. As suggested by the information in Table 7-1, HCl and Cl_2 emissions from hazardous waste combustors are primarily dependent on chlorine feed rates and air pollution control efficiency for acid gases (wet or dry scrubbing). For cement kilns, some dry scrubbing may occur within the process because of the highly alkaline limestone used in the manufacture of cement. Additional information regarding the control parameters and their influence on HCl and Cl_2 emissions is available in other documents (EPA 1992b, 1999d, 1999e) and is not discussed at length here. The MACT control parameters encompass the key control parameters influencing HCl and Cl_2 emissions, and are similar to BIF control parameters. However, the MACT parameters have been reviewed more recently against an extensive emissions database.

The purpose of summarizing the MACT control parameters in Table 7-1 is not to suggest that MACT emission standards should necessarily be imposed within the context of risk-based permitting, or to imply that any facility will be required to achieve early compliance with MACT emissions standards. Rather, the

purpose of reviewing the MACT control parameters in this guidance is to identify the feed and operating conditions that influence HCl and Cl_2 emissions, as well as to highlight the controls which will be implemented at most hazardous waste combustors in accordance with the requirements of the MACT rule. To the extent that risks from HCl and Cl_2 emissions are already adequately controlled by regulatory limits on key control parameters, then fewer site-specific risk-based limits may be needed in the RCRA permit. However, if regulatory controls are not applicable or sufficiently comprehensive, then additional site-specific risk-based limits may be warranted to ensure protection of human health and the environment.

Risk-based limits for chlorine feed rates, scrubber parameters, and maximum HCl and Cl_2 emission rates may be established in the RCRA permit based on the risk burn and risk assessment as necessary for protection of human health and the environment. Alternatively, the permit writer may determine that limits imposed pursuant to MACT or other regulatory provisions are sufficient. Fewer permit limitations based on the risk burn may be necessary when the risk burn can be performed in conjunction with a RCRA trial burn or MACT performance test. A greater number of risk-based permit limitations may be necessary when the risk burn and RCRA or MACT performance tests reflect different operating modes.

TABLE 7-1

MACT CONTROL PARAMETERS ASSOCIATED WITH HYDROGEN CHLORIDE AND CHLORINE EMISSIONS

	Control Parameter	Limits From	Averaging Period	How Limit Is Established	Other Considerations
Chlorine Feed Rate	Maximum total chlorine (organic and inorganic) feed rate in all feed streams [1]	Comprehensive performance test	12 hour	Average of the test run averages	
Wet Scrubbers High Energy: - venturi - hydrosonic - collision - free jet Low Energy: - spray tower - packed bed - tray tower	Maximum flue gas flow rate or kiln production rate	Comprehensive performance test	1 hour	Average of the maximum hourly rolling averages for each run	
	High energy scrubbers: minimum pressure drop across scrubber	Comprehensive performance test	1 hour	Average of the test run averages	
	Low energy scrubbers: minimum pressure drop across scrubber	Manufacturer specifications	1 hour	N/A	
	Low energy scrubbers: minimum liquid feed pressure	Manufacturer specifications	1 hour	N/A	
	Minimum liquid pH	Comprehensive performance test	1 hour	Average of the test run averages	
	Minimum liquid scrubber flow rate and maximum flue gas flow rate or minimum liquid/gas ratio	Comprehensive performance test	1 hour	Average of the test run averages	

TABLE 7-1

MACT CONTROL PARAMETERS ASSOCIATED WITH HYDROGEN CHLORIDE AND CHLORINE EMISSIONS (continued)

	Control Parameter	Limits From	Averaging Period	How Limit Is Established	Other Considerations
Dry Scrubber	Maximum flue gas flow rate or kiln production rate	Comprehensive performance test	1 hour	Average of the maximum hourly rolling averages for each run	
	Minimum sorbent feed rate	Comprehensive performance test	1 hour	Average of the test run averages	
	Minimum carrier fluid flow rate or nozzle pressure drop	Manufacturer specifications	1 hour	N/A	
	Identification of sorbent brand and type or adsorption properties	Comprehensive performance test	N/A	Same properties based on manufacturer specifications	

Notes:

ESP = electrostatic precipitator
IWS = ionizing wet scrubber
MACT = maximum achievable control technology
N/A = not applicable

= This limit applies to all feed streams except natural gas, process air, and feed streams from vapor recovery systems, provided that expected levels of constituents in those feed streams are accounted for in documenting compliance with feed rate limits. See the MACT rule preamble (EPA 1999c) for further information.

7.2 PARTICLE-SIZE DISTRIBUTION

Information on particle-size distribution and particle density are recommended for the air dispersion and deposition modeling that supports risk assessments (EPA 1998a and 1999b). Particle size and particle density directly affect particle terminal velocity. Large particles fall more rapidly than small particles and are more easily removed from the atmosphere by precipitation. Smaller particles have lower terminal velocities, and very small particles remain suspended in the air flow (EPA 1998a). For site-specific risk assessments, EPA OSW has recommended that most metals and a few organics with very low volatility be assumed to occur only in the particle phase (EPA 1998a). EPA OSW has recommended that mercury and more volatile organics be assumed to partition between the particle and vapor phases. Very volatile organics are modeled only in the vapor phase (EPA 1998a).

Because particle dispersion and deposition are directly related to particle size, predicted ambient impacts and associated risks are also highly dependent on particle-size distribution. A particle-size distribution that is more heavily weighted towards larger particles will result in higher deposition near the source, and reduced air concentration and deposition further away from the source. A particle-size distribution that is more heavily weighted towards smaller particles will decrease deposition near the source, and increase air concentrations and deposition away from the source. In general (but not necessarily in every case), higher deposition near the source is expected to result in higher risks. However, the relationship between deposition and risk will vary, depending on the size of the site and the location of potential receptors relative to maximum deposition. In an air model sensitivity analysis (The Air Group 1997), the particle-size distribution element was found to be a "moderately" sensitive parameter on a scale of "none" to "severe" sensitivity. Moderate sensitivity meant that site-specific data could result in variations in the model outputs of up to 50 percent from default assumptions.

In many cases, the APCD equipment is the primary determinant of particle size and total particle mass emitted from hazardous waste combustion facilities. Advances in air pollution control technology have led to improvements in particulate removal efficiency. Removal efficiencies typically decrease as particle size decreases (i.e., smaller particles are more difficult to remove). According to the proposed MACT rule (EPA 1996a), cyclone separators have typical removal efficiencies of less than 20 percent for particles less than 1

micron in diameter, and about 5 percent for particles less than 0.5 microns in diameter. Fabric filters are extremely efficient and have reported removal efficiencies of 99 to 99.99 percent for particles as low as 0.1 micron in diameter. ESPs are less efficient at capturing particles in the 0.1 to 1.0 micron range and have reported removal efficiencies of 90 to 95 percent (EPA 1999f). Based on these observations, a well-operated APCD greatly decreases the potential mass and mean particle size emitted from combustion facilities.

Some hazardous waste combustion facilities are not equipped with APCD devices. For these facilities, particle-size distribution is driven strictly by combustor design, feed composition, combustion quality, and flue gas cooling profile. In a comparison of particle-size distributions for two different types of combustion equipment, Linak found significantly different distributions (Linak and others 1999) . A laboratory scale refractory-lined combustor, which was shown to simulate the combustion conditions of a large utility residual oil fired boiler with respect to particulate emissions, produced very fine particulate with a mean diameter around 0.1 micron. Conversely, a pilot scale fire-tube package boiler produced a small fraction (approximately 0.2 percent) of mass with particle diameters less than 0.1 micron, and a very large fraction (approximately 99.8 percent) of the mass with particle diameters between 0.5 and 100 microns. The larger particles were shown to be porous, carbonaceous cenospheres resulting from poor carbon burnout.

7.2.1 Model Inputs

Particle-size inputs to the air dispersion and deposition model 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). Because so many variables influence particle-size distribution, a representative distribution is very difficult to predict. Therefore, the EPA OSW risk assessment guidance (EPA 1998a) has recommended that existing facilities perform site-specific measurements to determine particle density and particle-size distribution. Particle density and particle-size distribution measurements are discussed in Appendix B.

Detailed procedures for calculating mean particle diameters and mass and surface area distributions from stack measurements are discussed in the EPA OSW risk assessment guidance (EPA 1998a). When measured mass is below the detection limit, it may be appropriate to use a mean particle-size diameter of 1.0 microns in

the model to represent all particle mass (EPA 1998a). The use of a 1.0 micron particle-size results in the particles behaving similar to a vapor in the air model.

7.2.2 Test Conditions for Measuring Particle-Size Distribution

EPA OSW recommends that particle-size data generally be collected under normal operating conditions where ash spiking is not performed. Ash spiking will bias the particle-size distribution and is not likely to be representative of ongoing emissions in terms of particle size.

In lieu of sampling during normal operating conditions, a facility may prefer to measure particle-size distribution during the worst-case test conditions (when these tests do not involve ash spiking). In this case, EPA OSW recommends that the particle-size distribution measurement generally be performed during both the high temperature and low temperature operating extremes. Finer particles are likely to result from higher combustion temperatures, good combustion conditions, and rapid flue gas cooling profiles. Larger particles may be associated with poorer combustion situations or slower flue gas cooling profiles (such as through a heat exchanger or waste heat boiler). Testing during both the high temperature and low temperature operating extremes will allow potential variations in particle-size distribution to be determined and subsequently reflected in the air modeling.

Finally, soot blowing practices at a boiler may affect particle-size distribution. Normal soot blowing practices should generally be determined from the facility's operating record and reflected during one run of the particle-size determination. To the extent possible, EPA OSW recommends that the timing of the soot blowing and particle-size testing be coordinated so that soot blowing is not over-represented or under-represented in the sample, as compared to the number of hours per day that soot blowing normally occurs.

7.2.3 Alternatives When Site-Specific Measurements Are Not Available

In some cases, a site-specific particle-size distribution measurement will not be available. For example, a proposed new facility that needs to develop a particle-size distribution estimate may decide to use a representative distribution from a similar device as recommended by the EPA OSW risk assessment guidance

(EPA 1998a). Stack measurements from a similar unit equipped with similar APCD are preferred whenever possible. However, in the event that stack data from a similar unit are not available, a facility may explore several options. These include: 1) using literature estimates for similarly equipped facilities, 2) using APCD vendor estimates, or 3) performing multiple air and risk modeling runs to bound the range of potential impacts. Each of these options is discussed further below.

7.2.3.1 Literature Estimates

If a particle-size distribution stack measurement is not available for the actual facility (or for a similar facility), the use of a literature estimate may be considered. The literature estimate should generally match the actual facility as closely as possible with respect to the types of fuels and wastes burned and APCD equipment.

For sources equipped with ESPs or fabric filters, the EPA OSW risk assessment guidance (EPA 1998a) recommends a nine-category particle-size assumption to be used for site-specific risk assessment modeling if a more representative site-specific estimate cannot be obtained. The recommended assumptions are reproduced here as Table 7-2. The assumed particle-size diameters range from less than 0.7 to greater than 15.0 microns, with a mass distribution approximately 48% < 2.5 microns and approximately 82% < 10 microns. The risk assessment guidance also recommends a value for particle density of 1 gram per cubic centimeter (g/cm^3).

For cement kilns equipped with ESPs or fabric filters, a technical support document to the hazardous waste combustor MACT rule (EPA 1999g) uses a particle-size mass distribution estimate of 50% < 2.5 microns and 85% < 10 microns. This distribution compares favorably with the distribution provided in Table 7-2 for sources equipped with ESPs or fabric filters. The estimate is based on the distributions for Portland cement kilns provided in AP-42 (EPA 1995b) of 45 to 64% < 2.5 microns and 85% < 10 microns, as well as distribution data for three hazardous waste burning cement kilns ranging from 50 to 75% < 2.5 microns and 70 to 90% < 10 microns (EPA 1999g).

Particles from cement kilns may have a higher particle density than the density of 1 gm/cm^3 provided in the

TABLE 7-2

GENERALIZED PARTICLE-SIZE DISTRIBUTION TO BE USED AS A DEFAULT IN DEPOSITION MODELING IF SITE-SPECIFIC DATA ARE UNAVAILABLE

Mean Particle Diameter[a] (μm)	Particle Radius (μm)	Surface Area/Volume (μm)	Fraction of Total Mass[b]	Proportion of Available Surface Area	Fraction of Total Surface Area
>15.0	7.50	0.400	0.128	0.0512	0.0149
12.5	6.25	0.480	0.105	0.0504	0.0146
8.1	4.05	0.741	0.104	0.0771	0.0224
5.5	2.75	1.091	0.073	0.0796	0.0231
3.6	1.80	1.667	0.103	0.1717	0.0499
2.0	1.00	3.000	0.105	0.3150	0.0915
1.1	0.55	5.455	0.082	0.4473	0.1290
0.7	0.40	7.500	0.076	0.5700	0.1656
<0.7	0.40	7.500	0.224	1.6800	0.4880

Notes:
[a]Geometric mean diameter.
[b]The terms mass and weight are used interchangeably when using stack test data.

EPA OSW risk assessment guidance (EPA 1998a). A higher density, for example 2 gm/cm^3, may result in up to 50 percent greater dry deposition near the source (The Air Group 1997). The use of a particle density of 2 gm/cm^3 is based on information from the cement kiln industry. Material Safety Data Sheets for cement kiln dust (http://www.lafargecorp.com) list, among the physical and chemical properties, a specific gravity of 2.6 to 2.8 gm/cm^3. This value is for bulk cement kiln dust stored and shipped from a silo as a product. In actuality, the density of stack dust emissions from a cement kiln will depend on the chemical composition and size distribution, which is also a function of the APCD design and operation. Therefore, site-specific measurements of particle density are preferred.

Some hazardous waste burning incinerators and boilers are equipped with wet scrubbing devices to control acid gas emissions. In a technical support document to the hazardous waste combustor MACT rule (EPA 1999g), EPA estimates mass particle-size distributions for incinerators equipped with wet APCD devices as follows:

- Liquid injection units: 95% < 2.5 microns and 100% < 10 microns
- Solids units: 70% < 2.5 microns and 90% < 10 microns

These estimates are based on data from two hazardous waste burning incinerators, one equipped with an IWS and one equipped with a wet ESP, as well as limited data from municipal and medical waste incinerators. The liquid injection estimate compares favorably with the estimate available in AP-42 (EPA 1995b) for residual oil burning utility boilers equipped with wet scrubbers (97% < 2.5 microns and 100% < 10 microns).

Some liquid injection incinerators and boilers burning low ash, low halogen wastes may not be equipped with any APCD at all. A particle-size distribution is identified in AP-42 (EPA 1995b) for an uncontrolled utility boiler firing residual oil. This mass distribution is 52% < 2.5 microns and 71 % < 10 microns.

Finally, AP-42 (EPA 1995b) identifies several particle-size distribution estimates for coal-fired boilers. These distributions may be appropriate for hazardous waste burning boilers if coal is routinely co-fired as an auxiliary fuel. Selected distributions are summarized here as follows:

	% Mass < 2.5 microns	% Mass < 10 microns
Bituminous and Sub-bituminous Coal		
Dry bottom boiler w/ ESP	29	67
Dry bottom boiler w/ fabric filter	53	92
Dry bottom boiler w/ scrubber	51	71
Spreader stoker w/ ESP	61	90
Spreader stoker w/ fabric filter	26	60
Anthracite Coal		
Dry bottom boiler w/ fabric filter	32	67

It is important to emphasize that EPA OSW only recommends the use of literature estimates, such as those summarized in this section, if site-specific data is unavailable. As documented by Linak (Linak and others 1999), particle-size distributions can vary significantly from unit to unit, and a site-specific determination is

always preferred.

7.2.3.2 APCD Vendor Estimates

In some cases, a facility may be able to obtain particle-size distribution data from the APCD vendor if site-specific data are not available. For example, vendor data for sources equipped with HEPA filters may be sufficient for estimating mass distributions within the three particle-size categories (>10 microns, 2-10 microns, and <2 microns) because 100% of the particle mass would be expected to be below 2 microns in diameter downstream of a HEPA filter.

7.2.3.3 Multiple Modeling Runs to Bound Potential Impacts

Another option when site-specific particle-size distribution data are not available is to perform multiple air and risk modeling runs, using a range of assumed size distributions, to bound the range of potential impacts. For this option, EPA OSW recommends that three different size distributions be modeled to determine the highest impacts for site-specific receptors considering all exposure pathways:

- 100% mass at 1 micron in diameter;
- 100% mass at 5 to 7.5 microns in diameter;
- 100% mass at 12 to 15 microns in diameter.

This approach may be very resource-intensive, but should assure that predicted impacts are conservatively bounded by the risk assessment in the absence of site-specific particle-size data.

CHAPTER 8

DATA ANALYSIS

Once the risk burn has been completed and emissions data are available, the data can be analyzed and the risk assessment can be performed. This chapter (Section 8.1) discusses consolidation of the emissions data from each risk burn test condition prior to evaluation in the risk assessment. This chapter (Section 8.2) also identifies various emissions scenarios that may be evaluated in the risk assessment. Since a risk burn can involve multiple test conditions, EPA OSW recommends that the permit writer and facility give early consideration to how the data from more than one test condition will be combined for subsequent evaluation. In addition, EPA OSW recommends that the permit writer and facility consider whether the risk burn data will be evaluated in conjunction with emissions estimates that may be based on information other than the risk burn (for example, emissions corresponding to an applicable regulatory standard).

8.1 DATA REDUCTION AND COPC SELECTION

A large amount of data will be generated during the risk burn, and these data will need to be reduced prior to evaluation in the risk assessment. Consolidation of data for each risk burn test condition, including treatment of non-detects, is discussed in Section 8.1.1. Section 8.1.2 explains how constituents which are not detected in any test run are addressed in the COPC selection process.

8.1.1 Data Reporting and Treatment of Non-Detects

Consolidation of risk burn emissions data prior to evaluation in a risk assessment is a multi-step process. First, analytical results for the various fractions of a stack gas sampling train are summed to determine a train total. A train total is reported for each constituent and each test run. Eventually, the reported results for three test runs are consolidated to arrive at a test condition total. At several points in the process, questions arise regarding how to treat non-detects. The EPA OSW risk assessment guidance (EPA 1998a)

provides a recommended procedure, and portions of that procedure are repeated here for the convenience of the reader.

Detection limits are defined a number of ways, and terms are not always consistently applied. For the purpose of combustion risk assessments, the EPA OSW risk assessment guidance (EPA 1998a) recommends that the following be reported when constituents are not detected in a stack gas emissions sample:

> ***Reliable detection limits (RDLs):*** RDLs should generally be reported when constituents are analyzed with non-isotope dilution methods, such as the methods for volatile and semivolatile organics, and are not detected. The RDL is a total of 8 standard deviations above the Method Detection Limit (MDL) developmental test data, where the MDL is determined from analysis of at least seven replicate samples of a given matrix in accordance with 40 CFR Part 136, Appendix B. The reported RDL should be adjusted, as appropriate, to account for sample-specific volumetric treatments (e.g., splits and dilutions) that differ from those utilized in the Part 136 MDL determination.
>
> ***Estimated detection limits (EDLs):*** EDLs should generally be reported when constituents are analyzed with isotope dilution methods, such as the method for D/Fs, and are not detected. EDLs are defined by the individual SW-846 (EPA 1996b) test method, such as Method 8290 for D/Fs, and represent an estimate 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.

EPA OSW recommends that a facility inform the laboratory of these reporting conventions prior to development of the risk burn QAPP and analysis of the risk burn samples. In particular, MDLs are specific to each laboratory, and some laboratories may not have pre-determined MDLs for all compounds that are quantifiable by a particular method. MDLs determined per 40 CFR Part 136 may need to be explicitly requested for all chemicals to be analyzed and subsequently reported in the risk burn report.

EPA OSW also recommends that a facility provide clear direction to the laboratory regarding how to report a total sampling train mass for each constituent and each run if a constituent is not detected in certain of the analytical determinations. For most of the stack gas sampling trains, separate analyses are performed on various train fractions (for example, a resin fraction and a condensate fraction). The MDLs (and therefore the RDLs) are matrix-specific (i.e., separate MDLs are determined for the resin fraction and the condensate fraction). For data reporting to support site-specific risk assessments at combustion facilities, the following reporting convention is recommended when the results from each sampling train fraction have to be summed

to arrive at a total train mass:

- If results for all fractions are non-detect, then the full RDLs (or EDLs) should be summed and the result reported with a "less than" sign;
- If a constituent 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 full RDLs or EDLs for the non-detects). For D/Fs, Method 0023A specifically 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.

Blank results can also affect whether or not a constituent is considered to be detected. Blanks are not addressed here, but are discussed in detail in Appendix B.

For D/F analysis by Method 8290, there is also the issue of how to report ***estimated maximum possible concentrations (EMPCs)***. An EMPC is characterized by a response with a signal to noise ratio of at least 2.5 for both quantitation ions that meets all the relevant identification criteria except ion abundance ratio. For an EMPC, the ion abundance ratio and quantitative ion signal may be affected by co-eluting interferences. Therefore, an EMPC is a worst-case estimate of the concentration. The EPA OSW risk assessment guidance (EPA 1998a) recommends that EMPCs be treated as full detections in the risk assessment, and encourages application of techniques to minimize EMPCs.

8.1.2 COPC Selection and Treatment of Non-Detects

As discussed in Section 8.1.1, EPA OSW recommends that non-detects be fully carried through the risk burn data reporting process. However, this does not necessarily mean that all non-detected constituents will be evaluated in the risk assessment. Once the data is reported, decisions are needed as to whether the non-detected constituents will be retained as COPCs for the risk assessment. The EPA OSW risk assessment guidance (EPA 1998a) recommends a logical process for making these decisions, and portions of that process are repeated here for the convenience of the reader.

EPA OSW has recommended that constituents that are not detected in the stack emissions during any test run be re-evaluated for inclusion in the risk assessment using the final COPC selection process and flowchart

found in the EPA OSW risk assessment guidance (EPA 1998a). A compound may be excluded from the COPC list if: 1) it is not present in the waste being burned, and 2) it does not have a high potential to be emitted as a PIC, and 3) it has no potential of being emitted and is not of concern due to other site-specific factors (such as background concentrations and community or regulatory concern) (EPA 1998a). Based on this COPC selection process, some constituents that are not detected during any of the test runs and which meet the specified criteria will be eliminated from further consideration in the risk assessment.

In the COPC selection process, EPA OSW recommends that care be taken not to eliminate non-detected constituents that may be limited quantitatively in the final permit, because compliance with an emission rate limit of zero cannot be determined. Quantitative emission limits for certain toxic and bioaccumulative constituents may be established in the final permit to ensure that emissions of those constituents do not exceed the levels which were evaluated in the risk assessment and found not to posé a significant risk to human health and the environment. Constituents which may be candidates for risk-based emission limits in the final permit include D/Fs, specific metals, HCl and Cl_2, and significant waste constituents (for example, chemical warfare agents). Although emission limits for individual organics other than D/Fs may not be routinely established, the permit writer may limit other organic contaminants that are found to be risk drivers, as appropriate.

At the conclusion of the COPC selection process, the constituents retained as COPCs will include: 1) constituents detected in at least one run of the risk burn, 2) constituents which are not detected during the risk burn, but which cannot be excluded as COPCs because they have the potential to be emitted or are otherwise of concern, and 3) constituents which may be limited by quantitative emission rates in the final RCRA permit. For constituents which are not detected but are retained as COPCs, EPA OSW has recommended that the full RDL or EDL generally be used in calculating an emission rate for each run and each test condition for subsequent evaluation in the risk assessment (EPA 1998a).

The final step in the risk burn data consolidation process is calculation of a test condition emission rate from the three test runs. For each test condition, EPA OSW has recommended that the emission rate for each constituent be calculated as the 95th percentile of the arithmetic test mean, or the maximum value from the three test runs, whichever is lower (EPA 1998a). The EPA OSW risk assessment guidance (EPA 1998a and

1999b) recommends that emissions data from the risk burn be evaluated in a site-specific risk assessment to provide reasonable maximum exposure (RME) estimates of potential risks to human and ecological receptors. Results from probabilistic risk assessments show that setting as few as two factors at RME levels or high end (e.g., near the 90th percentile) while the remaining variables are set at less conservative, typical or "central tendency" values (e.g., near the 50th percentile) results in a product of all input variables at an RME level (e.g., 99th percentile value) (EPA 1998a). The EPA OSW risk assessment guidance identifies risk burn emissions data as one of the variables that is recommended to be set at the RME level.

8.2 EMISSION SCENARIOS TO BE EVALUATED FOR RISK

Once the risk burn data have been consolidated for each test condition and COPCs have been selected as discussed in Section 8.1, the risk assessment can be performed When a risk burn involves multiple test conditions, the permit writer and facility will need to decide whether the data from each test condition should be evaluated separately, or whether the data will be combined in some manner. In addition, decisions will be needed regarding evaluation of emissions beyond those measured during the risk burn. For example, a facility may prefer to evaluate risks associated with emissions at a regulatory standard or with an emissions estimate (i.e., zero SRE) in the risk assessment. This section identifies various emissions combinations that may be evaluated for risk.

Consolidation of data from multiple test conditions can encompass a range of options, depending on how the test conditions are structured and how the data will be presented for the risk management decision. EPA OSW recommends that these options be considered carefully prior to establishing test conditions and subsequent data collection. As discussed in Chapter 3, EPA OSW recommends that the emissions scenarios to be evaluated in the risk assessment be clearly identified in the risk burn plan, and that the test plan also indicate whether the risk assessment will consider emissions estimates based on information other than the risk burn.

Possible emissions scenarios to be evaluated for risk include: 1) calculation of risk ranges corresponding to specific test conditions (e.g., DRE and SRE); 2) consolidation of the highest emissions data from multiple test conditions for calculation of a single high-end risk value; 3) combining test data with emission rate

estimates; 4) combining test data with regulatory standards; 5) combining test data with emission rate estimates for abated and unabated fugitive emissions and emission rate estimates for expected chemicals that could not be incorporated into the test (i.e., due to lack of validated stack sampling methods, lack of available waste quantities for the test, or an inability to represent waste diversity during the test); or 6) any combination. Unless complete emissions determinations (for D/Fs, other organics, metals, and HCl/Cl_2) are conducted during every test condition, then consolidation of data from multiple conditions will need to be considered. Examples of possible emission scenarios to be evaluated for risk are provided below and in Appendix A.

Calculation of Risk Ranges Corresponding to Specific Test Conditions

A facility may choose to collect risk burn emissions data in conjunction with both the DRE and SRE tests. The DRE and SRE tests typically bound the operating extremes of the combustion unit by representing the lowest and highest combustion temperatures, as well as worst-case feed and APCD conditions. If complete risk burn emissions data (D/Fs, other organics, metals, HCl/Cl_2, and particle size information) are collected during both test conditions, then the facility may prefer to evaluate the emissions data set from each test condition separately in a site-specific risk assessment to calculate risks corresponding to each end of the operating envelope.

Consolidation of Multiple Tests for Calculation of a Single High-End Risk Value

It is more likely that the facility described above would not sample for metals during the DRE test, perhaps to limit metals spiking. In this case, complete data for all COPCs would not be available for both test conditions, and the risk burn data would need to be consolidated to complete the site-specific risk assessment. One option might involve combining the metals emissions from the SRE test with the *higher* of the D/F and organic emissions from either the SRE or DRE tests to calculate a single RME risk estimate.

Combining Test Data with Emissions Estimates

For either of the above approaches, the facility may have preferred to estimate maximum mercury emissions

by assuming zero SRE at a maximum mercury feed rate instead of spiking mercury during the SRE test. This maximum mercury emissions estimate could be combined with the measured emissions data for calculation of either a risk range or a single risk estimate.

Combining Test Data with Regulatory Standards

Finally, the facility described thus far may be planning for future compliance with the hazardous waste combustor MACT standards. The facility may have determined that physical modifications to the combustion system are not needed, but plans to reduce the feed rate of certain metals to meet the MACT standards. The facility may decide to evaluate an extra scenario in the site-specific risk assessment to reflect post-MACT operation. In this scenario, the MACT emission rate limits for D/Fs, metals, and HCl/Cl_2 might be evaluated in the risk assessment, together with emissions data for the non-MACT metals collected during the SRE test condition and the non-D/F organic emissions data from the DRE test condition of the risk burn.

Obviously, if a facility collects emissions data under additional test conditions, then the data management and analysis options become more complex. As explained in Chapter 3, EPA OSW recommends early communication and coordination between the permit writer and facility.

Finally, EPA OSW recommends that recent EPA direction in characterizing and communicating risk (EPA 1995c) to the public be considered. The *Guidance for Risk Characterization* (EPA 1995c) recommends that risk assessments include risks based on data reflecting both RME and central tendency (average) conditions. As appropriate, site-specific risk assessments may be completed based on both RME and average emissions data. This could assist in the risk communication process by allowing the facility and EPA to discuss a broader risk range with the public and to consider effects of variations in operating conditions on potential risks. However, RME conditions are generally expected to form the basis of permit conditions.

CHAPTER 9

RISK-BASED PERMIT CONDITIONS

After the site-specific risk assessment is performed and results are available, a final decision can be made regarding inclusion of risk-based conditions in the RCRA permit. The final RCRA permit represents an important and integral conclusion to the risk-based permitting process. The final permit identifies the operational conditions that are necessary to protect human health and the environment, and how that will be assured on an ongoing basis. This chapter concludes the ongoing dialogue provided throughout this document regarding potential risk-based permit terms.

Risk-based permit terms may be appropriate when emissions are projected to present a significant risk to human health and the environment. The EPA OSW risk assessment guidance (EPA 1998a) recommends several options when a risk assessment indicates potentially significant risks, and these options are repeated here for the convenience of the reader:

- Collecting additional site-specific information that is more representative of the exposure setting and performing additional iterations of the risk assessment based on the new information;
- Establishing permit terms (for example, waste feed limitations, process operating conditions, or environmental monitoring) to limit operations and performing additional iterations of the risk assessment to demonstrate that the resulting emissions are protective of human health and the environment;
- Denying the permit, if the initial risk assessment or subsequent iterations indicate potentially unacceptable risks.

However, even if the risk assessment indicates that projected risks will not be significant, risk-based permit terms may still be necessary to protect human health and the environment by ensuring that emissions remain below the levels which were measured during the risk burn and found to be protective. The risk burn and risk

assessment are typically based on assumptions that include:

- Waste composition, physical form, and feed rates, with key considerations outlined in Chapters 4-7;
- Operating conditions and parameters, including those related to combustion conditions (temperature, turbulence, and residence time) and APCD operation (pressure drops, flow rates, liquid-to-gas ratios, inlet temperatures, and power) as identified in Chapters 4-7;
- Emission rates associated with specific feed and operating conditions.

Within the bounds of the conditions demonstrated during the risk burn, emissions are characterized and evaluated in the risk assessment to determine whether they may present a significant risk to human health and the environment. Outside of those bounds (unless additional information is available), emissions and risks are generally unknown. Therefore. in order to protect human health and the environment, it may be necessary to limit operations to prevent higher emissions than those represented by the risk burn and risk assessment.

Site-specific factors will inform a decision regarding the need for, as well as the extent of, any risk-based RCRA permit limits to assure that ongoing emissions do not present a significant risk to human health and the environment. Key factors generally include, but are not necessarily limited to: 1) the emissions scenarios evaluated in risk assessment; 2) the feed and operating scenarios demonstrated during the risk burn; 3) whether key feed and control parameters are already limited by another permit or regulatory mechanism; 4) facility-specific operating practices; and 5) the potential for emissions to pose significant risks to human health and the environment.

As discussed in Chapter 3, few (if any) risk-based permit limitations may be necessary when the risk burn can be combined with a RCRA or MACT performance test, and when emissions and key control parameters are already sufficiently addressed by regulatory limits. A greater number of permit limitations may be necessary when the risk burn and performance tests reflect different operating modes, or when emissions and key control parameters are not limited by another mechanism. EPA OSW recommends that expectations regarding risk-based permit terms be clearly articulated in the risk burn plan, as discussed in Section 3.5.

The potential for emissions to pose significant risks to human health and the environment is an important

consideration in determining appropriate permit terms. If the potential risks associated with all foreseeable operating modes and operating extremes are insignificant, it may be appropriate for the permit writer to conclude that risk-based permit conditions are not necessary to protect human health and the environment, and to simply document the basis for the risk assessment emissions assumptions in the administrative record. In some cases, it may be appropriate for the permit writer to incorporate general monitoring and reporting provisions into the final permit to protect human health and the environment by ensuring that significant changes that could affect emissions (including types of wastes treated or major changes to operating parameters) are reported to EPA or the appropriate state agency. When potential risks are more significant, a permit writer may conclude that specific permit limits are necessary to protect human health and the environment. As identified in Chapter 3, risk-based permit terms may take the form of emission limits and specifications for periodic stack testing, restrictions on feed or operating control parameters and associated monitoring provisions, or some combination.

In summary, the emission rates (and related feed and operating conditions) that are demonstrated during the risk burn and evaluated in the risk assessment should clearly correspond to potential permit terms and conditions. The permit terms can ensure protection of human health and the environment by prohibiting operations outside of the operating boundaries represented by a risk burn and risk assessment that demonstrates emissions will not pose a significant risk. When a permit decision involves the use of a site-specific risk assessment, final RCRA permit terms will ultimately depend on the operating practices, emission levels, and risk results specific to each facility, and the permit writer should work closely with the facility to determine appropriate conditions for the risk burn and a corresponding permit approach. Illustrations are provided in Appendix A.

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APPENDIX A

RISK BURN CONDITIONS AND PERMIT LIMITS FOR EXAMPLE FACILITIES

A.1 Risk Burn Conditions and Permit Limits for a Liquid Injection Incinerator (13 pages)

A.2 Risk Burn Conditions and Permit Limits for a Rotary Kiln Incinerator Burning Containerized Wastes (16 pages)

APPENDIX A.1

RISK BURN CONDITIONS AND PERMIT LIMITS FOR A LIQUID INJECTION INCINERATOR

Note: This illustrative example does not represent the only approach to structuring a trial burn/risk burn/MACT performance test. Other regulatory and permitting options exist. Test plans and final permit conditions should always be developed on a site-specific basis after close interaction between the regulator and facility.

Appendix A.1 describes the risk burn and resulting permit limits for an example liquid injection incineration facility (Facility Z). Facility Z burns organic liquid and aqueous wastes in a liquid injection combustion chamber, followed by a heat recovery boiler and an air pollution control system consisting of a fabric filter and venturi scrubber. Facility Z typically operates the combustion chamber within a 1,750 $\pm$ 50 °F temperature window, with exit gas temperatures from the heat recovery boiler in the range of 350 to 550 °F. Gas exit temperatures from the heat recovery boiler generally increase and decrease with combustion temperature. A review of historical operating data indicates that Facility Z consistently maintains steady-state operations, with very low carbon monoxide and few waste feed cutoffs.

Facility Z needs to complete performance testing and a risk burn for a Resource Conservation and Recovery Act (RCRA) permit renewal. In addition, Facility Z anticipates complying with the hazardous waste combustor Maximum Achievable Control Technology (MACT) standards in the future, and has already added an activated carbon injection system to control dioxins. By carefully structuring the test plan, Facility Z can satisfy the current RCRA permitting needs, as well as generate data that may be submitted at a later date as "data in lieu of the initial performance test" for MACT.

Facility Z begins writing the test plan with the following test conditions (summarized in Table A.1-1):

Destruction and Removal Efficiency Test Condition

A destruction and removal efficiency (DRE) demonstration will be conducted at a minimum combustion temperature of 1,600 °F. This combustion temperature corresponds to a fabric filter inlet temperature of

350°F. Other control parameters to be demonstrated during the DRE test include: 1) maximum combustion gas velocity, as an indicator of minimum gas residence time; 2) maximum waste feed rate to each feed location; and 3) worst-case operating conditions for air pollution control parameters (to the extent possible). Continuous carbon monoxide and total hydrocarbon monitoring is also planned for this test. Operating parameters to ensure good operation of the waste firing system will be based on manufacturer's specifications.

System Removal Efficiency Test Conditions

In anticipation of future MACT compliance, Facility Z adds test conditions to demonstrate system removal efficiencies (SREs) for semivolatile and low-volatile metals (arsenic, beryllium, cadmium, chromium, and lead). Stack determinations for particulate matter (PM) and hydrogen chloride (HCl) and chlorine (Cl_2) are also planned for the SRE tests.

The SRE demonstrations will be conducted at a maximum combustion temperature of 1,850 °F in order to achieve a maximum inlet fabric filter temperature of 550 °F. Maximum semivolatile and low-volatile metal feed rates will be achieved by spiking one metal from each of the two volatility groups. Since all of the feed mechanisms at Facility Z are for liquid feeds, there is no distinction between total metal feed rates and pumpable metal feed rates. Other control parameters to be demonstrated during the SRE test conditions include: 1) maximum combustion gas velocity; 2) maximum chlorine feed rate; 3) maximum ash feed rate; and 4) worst-case operating conditions for air pollution control parameters.

Two SRE test conditions are necessary to resolve conflicting parameters. Demonstration of the maximum combustion gas velocity control parameter conflicts with demonstration of minimum pressure differential for the venturi scrubber. The two SRE test conditions are designated as SRE 1 and SRE 2 in Table A.1-1. During the SRE 1 test condition, maximum combustion gas velocity will be demonstrated. During the SRE 2 test condition, minimum pressure differential for the venturi scrubber will be demonstrated, and all other control parameters will be maintained as close as possible to the SRE 1 conditions. Demonstration of the maximum combustion gas velocity control parameter also conflicts with demonstration of minimum pressure differential for the fabric filter. However, Facility Z observes that the MACT rule allows minimum and

maximum fabric filter pressure differential to be established based on manufacturer's specifications, and the permit writer agrees with this approach.

For mercury, Facility Z wishes to avoid spiking and will not demonstrate a maximum mercury feed rate during the SRE test. Facility Z plans to conservatively assume that 100% of the mercury fed to the unit is emitted (even though some mercury control will be achieved from the carbon injection system).

Risk Burn Determinations and Addition of a Normal Test Condition

To complete a site-specific risk assessment, Facility Z recognizes that stack emissions determinations are needed for: dioxins/furans (D/Fs); organics other than D/Fs; the eighteen toxic metals listed in Section 2.3; particle-size distribution; and HCl/Cl_2. Facility Z incorporates these determinations into the test plan as follows:

D/Fs

The primary operating parameters related to D/F formation for Facility Z are boiler exit temperature and fabric filter inlet temperature (both operating parameters are represented by the same measurement location for the Facility Z system configuration), as well as control parameters for the carbon injection system. D/Fs are expected to be maximized at the maximum fabric filter inlet temperature of 550 °F, and will therefore be measured in conjunction with the SRE tests.

D/F testing will also be performed during the DRE test because of the permit writer's concern that the high combustion temperatures demonstrated during the SRE test might not adequately represent D/F precursors which could be formed during lower temperature combustion situations. In general, the formation of D/F precursors due to poor combustion should not be a significant concern for this system (because of the historical data indicating steady-state operation). Also, the 350°F fabric filter inlet temperature planned for the DRE test is outside of the critical D/F temperature range (400.- 750 °F). However, the facility agrees that D/F sampling during DRE conditions will better represent the complete operating envelope, and will put Facility Z in a better position to potentially use the data for

future MACT compliance (control parameters for minimum combustion temperatures, maximum waste feed rates, and maximum gas flow rates are required to be demonstrated during D/F testing pursuant to MACT). Therefore, Facility Z adds a D/F determination to the DRE test

Non-D/F Organics

The feed and operating conditions that influence organic products of incomplete combustion (PICs) are already represented during the DRE test. Therefore, the facility plans to measure PICs and total organics in conjunction with the DRE performance demonstration. In addition, Facility Z arranges for the sampling contractor to operate a temporary total hydrocarbon continuous emissions monitor during the DRE/PIC testing.

Metals

The SRE tests already involve stack determinations for the five toxic metals identified in the MACT rule. However, Facility Z is concerned that the metals spiking during the SRE tests may result in emissions that exceed risk target values. Therefore, Facility Z proposes a separate test condition for the purpose of generating metals emissions data for the risk assessment. A normal test is proposed (as summarized in Table A.1-1) since Facility Z is capable of defining and maintaining normal operating conditions for metals.

The normal test for metals will be conducted at normal metal feed rates, at a combustion temperature of approximately 1,750 °F and a fabric filter inlet temperature of 450 °F. Emissions testing will be performed for eighteen metals.

Particle-Size Distribution

For Facility Z, the fabric filter will be the primary determinant of particle-size distribution. Therefore, significant variation in particle-size distribution between the different test conditions is not expected. A particle-size determination is added to the normal test, since this test does not include

ash spiking.

HCl and Cl_2

Determinations for HCl and Cl_2 are already included in the SRE tests, and this data can also be used for the risk assessment.

TABLE A.1-1

FACILITY Z TEST CONDITIONS

	TEST CONDITIONS AND EMISSIONS DETERMINATIONS			
	DRE	SRE 1	SRE 2	NORMAL
	POHCs, PICs, D/Fs, TOE, Total Hydrocarbons, Carbon Monoxide	Metals, D/Fs, PM, HCl/Cl_2, Carbon Monoxide		Metals, Particle Size
Combustion temperature	1,600 °F	1,850 °F		1,750 °F
Fabric filter inlet temperature	350 °F	550 °F		450 °F
Organic liquid feed rate	Maximum	Maximum		Normal
Aqueous liquid feed rate	Maximum	Minimum		Normal
Combustion gas velocity	Maximum *	Maximum *		Normal
Ash feed rate	Above average	Maximum		Normal
Chlorine feed rate	Maximum	Maximum		Normal
Spiked metal feed rates	N/A	Maximum		Normal
Other metal feed rates	N/A	Normal		Normal
Fabric filter differential pressure	Within manufacturer's specifications	Within manufacturer's specifications		Normal
Venturi differential pressure	Minimum * (or as close as possible)	Minimum *		Normal
Venturi liquid-to-gas ratio	Minimum	Minimum		Normal
Venturi scrubber liquid exit pH	Minimum	Minimum		Normal
Scrubber blowdown rate	Minimum	Minimum		Normal
Carbon feed rate	Minimum	Minimum		Normal

Notes:

* = conflicting parameters

D/Fs = Dioxins/furans
DRE = Destruction and removal efficiency
N/A = Not applicable
PICs = Products of incomplete combustion
PM = Particulate matter
POHCs = Principal organic hazardous constituents
SRE = System removal efficiency
TOE = Total organic emissions

Site-Specific Risk Assessment

Facility Z performs the tests according to the approved test plan. As expected, D/F emissions are highest during the SRE test conditions. Emissions data are consolidated from all of the test conditions for evaluation in a single multi-pathway human health and ecological site-specific risk assessment as follows:

- D/F emissions from the SRE test conditions are evaluated, together with . . .
- Organic PIC emissions from the DRE test condition, and . . .
- Metals emissions (18 metals) from the normal test condition, and . . .
- HCl and Cl_2 emissions from the SRE test conditions.

Total chronic risks from these consolidated emissions are determined to be below target levels.

An acute risk evaluation is also performed to assess inhalation risks associated with maximum potential one-hour emissions. Maximum one-hour emissions for the acute evaluation are estimated for D/Fs , other organics, and HCl/Cl_2 based on the test data listed above, with an upward adjustment to reflect upsets. However, for metals, the test data are not representative of maximum potential one-hour emissions. For the metals represented by the spiked metals (arsenic, beryllium, cadmium, chromium, and lead), the facility uses an approved extrapolation procedure to estimate maximum one-hour emission rates based on maximum anticipated one-hour feed rates and the SREs demonstrated during the testing. The extrapolated emissions estimates are then adjusted further to reflect upsets. For the remaining metals, the facility estimates maximum emissions based on maximum anticipated one-hour feed rates and an assumption of zero SRE. Further upward adjustment for these metals is not necessary, since the "zero SRE" assumption already represents the most conservative estimate. Acute risks associated with these maximum emissions estimates are determined to be below target levels.

Finally, Facility Z performs a "post-MACT scenario" chronic risk evaluation. This evaluation is based on emissions estimates for D/Fs, mercury, semivolatile metals, low-volatile metals, and HCl/Cl_2, where the emissions are determined assuming that Facility Z emits at the allowable MACT standard for these

pollutants. These emission estimates are combined with the organic PIC emissions measured during the DRE test, as well as the metals emissions for the non-MACT metals measured during the normal test. Total chronic risks from these consolidated emissions are determined to be below target levels, with the exception of mercury.

Final Permitted Emission Rates

As summarized in Table A.1-2, maximum emission rate limits are established in the RCRA permit for D/Fs, metals, and HCl/Cl_2 based on the levels needed to achieve target risk levels. The limits are established for the purpose of periodic verification testing to ensure that emissions remain below those evaluated in the risk assessment. If emissions increases occur above the permitted levels, then the permit calls for the risk assessment to be repeated. Since none of the non-D/F organics were found to be risk drivers, emission limits for individual non-D/F organic compounds are not established in the permit.

The "post-MACT scenario" risk evaluation showed that the MACT standards for D/Fs, arsenic, beryllium, cadmium, chromium, lead, and HCl/Cl_2 will be sufficiently protective. Therefore, the RCRA permit includes "sunset" provisions on the emission limits for these pollutants in the RCRA permit. In this instance, the sunset provisions are structured so that the RCRA emission limits will no longer apply once the facility has documented compliance with MACT, and once the regulatory agency has completed a finding of compliance. For mercury, the MACT standard will not be sufficiently protective if one assumes that the source continuously emits at the standard. Therefore, the risk-based emission limits for mercury will remain in the RCRA permit. Emission limits for the non-MACT metals (aluminum, antimony, barium, cobalt, copper, manganese, nickel, selenium, silver, thallium, vanadium, and zinc) will also remain in the RCRA permit.

Final Permit Limits for Control Parameters

Table A.1-2 provides the final permit limits on relevant control parameters for Facility Z. Total hydrocarbon levels were negligible during the DRE test condition. Therefore, the permit writer determines that there is no need to specify continued total hydrocarbon monitoring as a condition of the RCRA permit.

For arsenic, beryllium, cadmium, chromium, lead, mercury, and nickel, acceptable risks were projected for at

least one of the risk scenarios evaluated. However, since the projected risks came close to approaching target risk levels, the permit writer determines that closer monitoring and control for these metals is warranted. Therefore, quarterly average metals feed rate limits are established in the RCRA permit to ensure that these metals are not fed at higher rates than those demonstrated. With the exception of mercury, the metals feed rate limits are established in the RCRA permit based on feed rates demonstrated during the testing. For mercury, a risk-based feed rate limit is conservatively calculated from the risk-based emissions limit by assuming zero SRE (i.e., 100% of the mercury fed to the unit is emitted).

For the non-mercury metals, quarterly average feed rate limits are established based on two different test scenarios. For arsenic, beryllium, cadmium, chromium and lead, the quarterly average feed rate limits are established based on the SRE test (since the higher feed rates demonstrated during the SRE test were demonstrated to achieve compliance with the MACT standards, and since the MACT standards were shown to be sufficiently protective in the risk assessment). The RCRA permit is written with sunset provisions for the feed rate limits on these five metals. For nickel, quarterly average feed rate limits are established based on the normal test. The risk-based feed rate limits for nickel will remain in the RCRA permit after MACT. Since risks from the remaining eleven metals were very far from target levels, and since target risk levels could not possibly be exceeded based on the wastes burned at Facility Z, the permit writer decides to simply document the risk assessment feed and emissions assumptions for the remaining metals in the administrative record instead of imposing specific feed rate limits in the permit.

Short-term metal feed rate limits are not necessary for the RCRA permit, because acute risks were determined to be negligible (considering the range of inputs for metals at Facility Z). Although the SRE tests were performed for the purpose of establishing short-term metal feed rate limits for arsenic, beryllium, cadmium, chromium, and lead, these limits will apply in the future pursuant to MACT and are not a RCRA concern.

The RCRA permit is written with sunset provisions for all control parameters except for the quarterly average feed rate limits for mercury and nickel.

TABLE A.1-2

FINAL RCRA PERMIT LIMITS FOR FACILITY Z

Parameter	Value	Basis		Sunset
		Test	Established As:	
Summary of Performance Standards and Emission Limits				
DRE	99.99% for POHCs	N/A	Regulatory Limit	Yes
Maximum PM Emissions	0.08 gr/dscf	N/A	Regulatory Limit	Yes
HCl	Larger of 99% removal or 4 lbs/hr	N/A	Regulatory Limit	Yes
Maximum HCl and Cl_2 emissions	Inhalation risk-based limits	N/A	Target levels from risk assessment	Yes
Maximum D/F emissions	Multi-pathway risk-based limit	N/A	Target level from risk assessment	Yes
Maximum emissions (arsenic, beryllium, cadmium, chromium, lead)	Multi-pathway risk-based limits	N/A	Target levels from risk assessment	Yes
Maximum emissions (aluminum, antimony, barium, cobalt, copper, manganese, mercury, nickel, selenium, silver, thallium, vanadium, zinc)	Multi-pathway risk-based limits	N/A	Target levels from risk assessment	No
Group A Control Parameters - Interlocked with AWFCO				
Minimum combustion temperature	1,600 °F, HRA	DRE	Avg. of the test run averages	Yes
Maximum combustion gas velocity	cfm, HRA	SRE 1/ DRE	Avg. of the test run averages [1]	Yes
Maximum organic liquid feed rate	lbs/hr, HRA	DRE	Avg. of the test run averages [1]	Yes
Maximum aqueous feed rate	lbs/hr, HRA	DRE	Avg. of the test run averages [1]	Yes
Maximum fabric filter inlet temperature	550 °F, HRA	SRE	Avg. of the test run averages	Yes

TABLE A.1-2

FINAL RCRA PERMIT LIMITS FOR FACILITY Z (continued)

Parameter	Value	Basis		Sunset
		Test	Established As:	
Minimum and maximum fabric filter pressure differential	inches water column, HRA	N/A	Manufacturer's specifications	Yes
Minimum venturi scrubber differential pressure	inches water column, HRA	SRE 2	Avg. of the test run averages	Yes
Minimum venturi liquid-to-gas ratio	gal/cfm, HRA	SRE	Avg. of the test run averages	Yes
Minimum venturi scrubber liquid exit pH	pH, HRA	SRE	Avg. of the test run averages	Yes
Minimum carbon injection feed rate	lbs/hr, HRA	DRE/ SRE	Avg. of the test run averages	Yes
Maximum stack carbon monoxide concentration	100 ppm at 7% oxygen, dry basis, HRA	N/A	Limit based on established guidance	Yes
Maximum combustion chamber pressure	inches water column, vacuum, instantaneous limit	N/A	As necessary to maintain negative pressure	Yes
Group B Control Parameters				
Restrictions on "more difficult-to-burn POHCs"	Allowable Appendix VIII constituents	DRE	More difficult-to-burn constituents than those which achieved 99.99% DRE are prohibited	Yes
Maximum chlorine feed rate	lbs/hr, HRA [2]	SRE	Avg. of the test run averages	Yes
Maximum ash feed rate	lbs/hr, HRA [3]	SRE	Avg. of the test run averages [3]	Yes
Maximum feed rates (arsenic, beryllium, cadmium, chromium, and lead)	lbs/hr, quarterly average [2]	SRE	Avg. of the test run averages	Yes

TABLE A.1-2

FINAL RCRA PERMIT LIMITS FOR FACILITY Z (continued)

Parameter	Value	Basis		Sunset
		Test	Established As:	
Maximum nickel feed rate	lbs/hr, quarterly average	Normal	Avg. of the test run averages	No
Maximum mercury feed rate	lbs/hr, quarterly average[4]	N/A	Feed rate calculated from the risk-based emission limit assuming zero SRE[4]	No
Minimum scrubber blowdown	gpm, HRA	SRE	Avg. of the test run averages	Yes
Carbon adsorption properties	Manufacturer's brand	N/A	Same as test	Yes
Group C Control Parameters				
Maximum heat input	million Btu/hr	N/A	Design basis	Yes
Burner/atomizer: - Maximum viscosity - Maximum turndown - Maximum solids - Minimum atomizing pressure differential	 - centipoise - gpm range - percent solids - psig (interlocked with AWFCO)	N/A	Manufacturer's recommendations	Yes
Minimum venturi scrubber nozzle pressure	psig (interlocked with AWFCO)	N/A	Manufacturer's recommendations	Yes
Minimum carbon carrier fluid nozzle pressure drop	psig (interlocked with AWFCO)	N/A	Manufacturer's recommendations	Yes

Notes:

AWFCO = Automatic waste feed cutoff system
Avg. = Average
Btu/hr = British thermal units per hour
cfm = Cubic feet per minute
D/F = Dioxin/furan
DRE = Destruction and removal efficiency
gal/cfm = Gallons per cubic feet per minute
gpm = Gallons per minute
gr/dscf = Grains per dry standard cubic foot
HRA = Hourly rolling average
lbs/hr = Pounds per hour
N/A = Not applicable
PM = Particulate matter
ppm = Parts per million
psig = Pounds per square inch, gauge
POHC = Principle organic hazardous constituent
SRE = System removal efficiency

TABLE A.1-2

FINAL RCRA PERMIT LIMITS FOR FACILITY Z (continued)

1 Under MACT, the limit will be based on the average of the maximum hourly rolling averages for each run.

2 Under MACT, the averaging period will be 12 hours.

3 Under MACT, the averaging period will be 12 hours and the limit will be based on the average of the maximum hourly rolling averages for each run.

4 Under MACT, the averaging period will be 12 hours and the limit will be based on the maximum theoretical emission concentration assuming that all mercury from all feed streams is emitted.

APPENDIX A.2

RISK BURN CONDITIONS AND PERMIT LIMITS FOR A ROTARY KILN INCINERATOR BURNING CONTAINERIZED WASTES

Note: This illustrative example does not represent the only approach to structuring a trial burn/risk burn/MACT performance test. Other regulatory and permitting options exist. Test plans and final permit conditions should always be developed on a site-specific basis after close interaction between the regulator and facility.

Appendix A.2 describes the risk burn and resulting permit limits for an example rotary kiln incineration facility (Facility Y). Facility Y burns a variety of waste streams including organic liquids, aqueous wastes, organic sludges, bulk solids, and containerized wastes in a rotary kiln combustion chamber. The rotary kiln is followed by a secondary combustion chamber, where organic liquids and aqueous wastes are fired. The downstream air pollution control system consists of a spray dryer and fabric filter. Facility Y is a commercial facility, and the waste streams received at the facility can be highly variable. A review of historical operating data indicates that Facility Y routinely experiences transient operations, with carbon monoxide spikes that often correlate with charges of containerized wastes to the unit.

Facility Y needs to complete performance testing and a risk burn for a Resource Conservation and Recovery Act (RCRA) permit renewal. In addition, Facility Y anticipates complying with the hazardous waste combustor Maximum Achievable Control Technology (MACT) standards in the future. By carefully structuring the test plan, Facility Y can satisfy the current RCRA permitting needs, as well as generate data that may be submitted at a later date as "data in lieu of the initial performance test" for MACT (this facility does not need to physically modify the combustion system to comply with MACT).

Facility Y begins writing the test plan with the following test conditions (summarized in Table A.2-1):

Destruction and Removal Efficiency Test Conditions

Destruction and removal efficiency (DRE) demonstrations will be conducted at minimum primary combustion chamber (PCC) and secondary combustion chamber (SCC) combustion temperatures of

1,400 °F and 1,800 °F, respectively. Other control parameters to be demonstrated during the DRE tests include: 1) maximum combustion gas velocity, as an indicator of minimum gas residence time; 2) maximum waste feed rate to each feed location; and 3) worst-case operating conditions for air pollution control parameters (to the extent possible). Continuous carbon monoxide and total hydrocarbon monitoring is also planned for the DRE tests. Operating parameters to ensure good operation of the waste firing system will be based on manufacturer's specifications.

For the DRE determination, it is not possible to demonstrate maximum waste feed rates for all feed streams simultaneously. Therefore, four (4) DRE test conditions are necessary. The four DRE test conditions are designated as DRE 1, DRE 2, DRE 3, and DRE 4 in Table A.2-1. During each of the test conditions, maximum feed rates for different individual waste streams will be demonstrated, while maintaining a relatively constant maximum total thermal input to the PCC and total system (the unit is designed for 40 million (MM) Btu/hr thermal input to the PCC and 80 MM Btu/hr for the total system). Minimum combustion temperatures and maximum combustion gas velocity will also be maintained throughout the four test conditions. The maximum individual waste feed rate to be demonstrated during each condition follows:

- DRE 1 - Maximum organic liquid feed rate to the PCC
  - Maximum bulk solids feed rate to the PCC
  - Maximum container feed rate (mass basis) to the PCC
  - Maximum organic liquid feed rate to the SCC
- DRE 2 - Maximum container feed rate (thermal input basis) to the PCC
- DRE 3 - Maximum aqueous feed rate to the PCC
  - Maximum organic sludge feed rate to the PCC
- DRE 4 - Maximum aqueous feed rate to the SCC

The demonstration for containerized feeds encompasses two test conditions (DRE 1 and DRE 2). The containerized wastes at Facility Y are fed in 55-gallon drums weighing 100 to 200 pounds each, and can be highly variable. Containerized feeds can range from soil remediation waste (with high moisture and no heating content) to high-heating-value, highly volatile organics sorbed onto a solid matrix.

In the DRE 1 test condition, Facility Y will demonstrate maximum containerized feed rate, as well as

maximum total solids feed rate (for both the containerized and bulk feeds combined). Both feeds will consist of contaminated, moist soils with no heating value (this type of material is representative of the bulk solids which are normally burned, and is representative of materials which are sometimes burned in containers). These conditions represent a challenging DRE test because of the heavy loading of solid material forming a heat sink in the rotary kiln. The maximum containerized feed rate for the DRE 1 condition will be 9,000 lbs/hr, and the maximum container size will be 200 lb/hr, resulting in a feeding frequency of 45 drums per hour.

A separate test condition, DRE 2, is necessary to represent containerized feeds consisting of high-heating-value, highly volatile organics. For DRE 2, drums with a total heat content of 2 MM Btu each will be prepared by adding a glass jar of highly volatile, high-heating-value liquid organics to a wood chip/plastic pellet mixture. The drums will weigh 125 pounds each, and will be fed at the maximum rate allowed by the thermal design capacity of the kiln (40 MM Btu/hr). This results in a feeding frequency of 20 drums per hour. The DRE 2 test will be performed at a higher PCC temperature than the other DRE tests, because the higher kiln temperature ensures a maximum volatilization rate. The higher PCC temperature, in combination with the minimum SCC temperature, still represents a worst-case condition for organic destruction for containerized feeds. In addition, combustion gas velocity for the DRE 2 condition will be slightly lower than the other DRE conditions, since excess air to the PCC will be minimized in an attempt to minimize excess oxygen at the location where the containers are fed.

Several batch/containerized feed parameters will not be demonstrated during the testing. Maximum batch size (200 pounds) will be demonstrated during the DRE 1 condition, and maximum batch charge heat content (which is the more important indicator of a situation that could overwhelm the combustion system) will be demonstrated in the DRE 2 condition. However, maximum container feeding frequency will not be demonstrated in either test, because Facility Y cannot simultaneously demonstrate maximum size (or maximum batch charge heat content) and maximum feeding frequency. Larger batches fed less frequently are considered to be worse than smaller batches fed more frequently, within the total targeted feed rate limits for the containerized feeds of 9,000 lbs/hr and 40 MM Btu/hr for the DRE 1 and DRE 2 tests, respectively. In addition, demonstration of maximum kiln rotation speed is not necessary, since the method of introducing volatile liquids in glass jars will ensure a maximum rate of volatilization and puff intensity.

During the DRE 1 and DRE 4 test conditions, maximum total ash feed rate and maximum atomized ash feed rate will be demonstrated. Therefore, stack sampling for particulate matter will be performed during these test conditions.

System Removal Efficiency Test Condition

In anticipation of future MACT compliance, Facility Y adds a test condition to demonstrate system removal efficiencies (SREs) for semivolatile and low-volatile metals (arsenic, beryllium, cadmium, chromium, and lead). Stack determinations for hydrogen chloride (HCl) and chlorine (Cl_2) are also planned for the SRE test, since chlorine will be maximized during this test and worst-case operating conditions for the spray dryer will be demonstrated.

Maximum semivolatile and low-volatile metal feed rates will be achieved by spiking one metal from each of the two volatility groups to the SCC organic liquid feed. Facility Y will base their total metal feed rate limits only on metals in the SCC feed stream, so that separate feed rate limits on total and pumpable feed streams will not be needed (metals fed as liquids to the SCC constitute a worst-case test).

The SRE demonstration will be conducted at a maximum SCC combustion temperature of 2,200 °F to achieve a maximum inlet fabric filter inlet temperature of 400 °F. Other control parameters to be demonstrated during the SRE test condition include: 1) maximum combustion gas velocity; 2) maximum chlorine feed rate; and 4) worst-case operating conditions for air pollution control parameters (to the extent possible).

The permit writer and Facility Y discuss whether two SRE test conditions should be performed to resolve conflicting parameters. Demonstration of the maximum combustion gas velocity control parameter conflicts with demonstration of minimum pressure differential for the fabric filter. (In fact, this conflict exists for all of the DRE test conditions as well, including the DRE 1 and DRE 4 conditions where compliance with the particulate matter standard will be demonstrated.) Facility Y wishes to avoid duplicating multiple test conditions, since the test program is already quite extensive, and observes that the MACT rule allows limits for minimum (and maximum) fabric filter pressure differential to be established based on manufacturer's specifications. The permit writer agrees with this approach in lieu of expanding the test program further.

For mercury, Facility Y wishes to avoid spiking and will not demonstrate a maximum mercury feed rate during the SRE test. Facility Y plans to conservatively assume that 100% of the mercury fed to the unit is emitted.

Risk Burn Determinations

To complete a site-specific risk assessment, Facility Y recognizes that stack emissions determinations are needed for: dioxins/furans (D/Fs); organics other than D/Fs; the eighteen toxic metals listed in Section 2.3; particle-size distribution; and HCl/Cl_2 Facility Y incorporates these determinations into the test plan as follows:

D/Fs

The primary operating parameters related to D/F formation for Facility Y are fabric filter inlet temperature and combustion parameters, including: 1) minimum PCC and SCC combustion temperatures; 2) maximum combustion gas velocity; 3) maximum waste feed rate for each location; 4) limitations on waste feed composition and batch/containerized feeds; and 5) maximum flue gas carbon monoxide and/or total hydrocarbon concentrations.

D/Fs can be expected to be maximized at the maximum fabric filter inlet temperature of 400 °F, which will be demonstrated during the SRE test. However, the SRE test is not designed to be a challenging test with respect to combustion of organics. Facility Y operates under challenging combustion scenarios which could promote D/F precursor formation, and which should be preferentially targeted for D/F testing, including: 1) transient conditions; 2) operation with containerized feeds; and 3) high carbon monoxide (greater than 100 ppm) situations. These conditions are already represented by the DRE test scenarios. Therefore, Facility Y decides to adjust the spray dryer operation to demonstrate the maximum fabric filter inlet temperature of 400 °F during the DRE tests. D/F stack emissions determinations are added to those tests.

Adjusting the DRE test conditions to demonstrate a maximum fabric filter inlet temperature causes another potential conflicting parameter situation with respect to operation of the spray dryer. To

achieve the maximum 400 °F fabric filter inlet temperature at the lower SCC combustion temperatures planned for the DRE tests, the lime slurry feed rate will have to be lowered from the feed rate planned for the SRE test (which is supposed to represent the minimum). The permit writer and facility agree that this is acceptable, as long as the permit limit for minimum spray dryer slurry feed rate is based on the higher rate demonstrated during the SRE test.

Non-D/F Organics

The feed and operating conditions that influence organic products of incomplete combustion (PICs) are already represented during the DRE test conditions. Therefore, the facility adds PIC and total organic stack emissions determinations to the DRE test conditions. In addition, Facility Y arranges for the sampling contractor to provide a temporary total hydrocarbon continuous emissions monitor during the DRE/PIC testing.

Metals

The SRE test already involves stack determinations for the five toxic metals identified in the MACT rule, and Facility Y has performed a preliminary risk assessment which indicates that the MACT emission standards for semivolatile and low-volatile metals should be sufficiently protective. Therefore, Facility Y simply expands the planned analytical determinations for the SRE test to encompass eighteen metals. The non-MACT metals will be fed at normal feed rates, since Facility Y is capable of defining and maintaining normal conditions for these metals.

Particle-Size Distribution

At Facility Y, the fabric filter will be the primary determinant of particle-size distribution. Therefore, significant variation in particle-size distribution between the different test conditions is not expected. Facility Y suggests that the particle-size distribution determination be performed during the SRE test condition. However, the permit writer is concerned that a particle-size determination during the SRE test could be biased due to the absence of solid feeds, as well as the high temperatures and metals spiking. Therefore, the parties agree that the particle-size determination will

be performed at the conclusion of the risk burn after the facility returns to normal operation.

HCl and Cl_2

Determinations for HCl and Cl_2 are already included in the SRE test, and this data can also be used for the risk assessment.

TABLE A.2-1

FACILITY Y TEST CONDITIONS

	TEST CONDITIONS AND EMISSIONS DETERMINATIONS				
	POHCs, PICs, D/Fs, TOE, Total Hydrocarbons, Carbon Monoxide PM (DRE 1 and 4 only)				Metals, HCl/Cl_2, Carbon Monoxide
	DRE 1	**DRE 2**	**DRE 3**	**DRE 4**	**SRE**
PCC combustion temperature	1,400 °F	1,800 °F	1,400 °F	1,400 °F	1,800 °F
SCC combustion temperature	1,800 °F	1,800 °F	1,800 °F	1,800 °F	2,200 °F *
Fabric filter inlet temperature	400 °F	400 °F	400 °F	400 °F	400 °F *
PCC organic liquid feed rate	**Maximum**	Minimal	Minimal	High	Maximum
PCC aqueous liquid feed rate	Minimal	Minimal	**Maximum**	Minimal	N/A
PCC organic sludge feed rate	Normal	Minimal	**Maximum**	Normal	N/A
PCC bulk solids feed rate	**Maximum**	Minimal	Minimal	Minimal	N/A
PCC container feed rate - total lb/hr - lbs/drum - drums/hr - MM Btu/drum - MM Btu/hr	**Maximum (mass input)** 9,000 200 45 0 0	**Maximum (thermal input)** 2,500 125 20 2 40	Minimal	Minimal	N/A
SCC organic liquid feed rate	**Maximum**	High	High	High	Maximum
SCC aqueous liquid feed rate	Minimal	Minimal	Minimal	**Maximum**	N/A
Thermal input, MM Btu/hr - PCC - SCC - Total	 42 41 83	 45 33 78	 45 35 80	 42 40 82	N/A
Combustion gas velocity	Maximum**	High **	Maximum**	Maximum**	Maximum**
Ash feed rate	Maximum total ash	N/A	N/A	Maximum atomized ash	N/A
Chlorine feed rate	Above average	Above average	Above average	Above average	Maximum

TABLE A.2-1

FACILITY Y TEST CONDITIONS (continued)

	TEST CONDITIONS AND EMISSIONS DETERMINATIONS				
	POHCs, PICs, D/Fs, TOE, Total Hydrocarbons, Carbon Monoxide PM (DRE 1 and 4 only)				Metals, HCl/Cl_2, Carbon Monoxide
	DRE 1	DRE 2	DRE 3	DRE 4	SRE
Spiked metal feed rates	N/A	N/A	N/A	N/A	Maximum
Other metal feed rates	N/A	N/A	N/A	N/A	Normal
Lime slurry feed rate	Minimum	Minimum	Minimum	Minimum	As low as possible *
Lime slurry properties (minimum percent lime and lime absorbent properties)	Minimum	Minimum	Minimum	Minimum	Minimum
Fabric filter differential pressure	Within manufacturer specifications **	Within manufacturer specifications **	Within manufacturer specifications **	Within manufacturer specifications **	Within manufacturer specifications **

Notes:

* = conflicting parameters related to spray dryer operation
** = conflicting parameters related to fabric filter operation

D/Fs = Dioxins/furans
DRE = Destruction and removal efficiency
hr = Hour
lb = Pounds
MM Btu = Million British thermal units
N/A = Not applicable
PCC = Primary combustion chamber
PICs = Products of incomplete combustion
PM = Particulate matter
POHCs = Principal organic hazardous constituents
SCC = Secondary combustion chamber
SRE = System removal efficiency
TOE = Total organic emissions

Site-Specific Risk Assessment

Facility Y performs the tests according to the approved test plan. Emissions data are consolidated from the test conditions for evaluation in four (4) separate multi-pathway human health and ecological site-specific risk assessment scenarios corresponding to each of the DRE 1, DRE 2, DRE 3 and DRE 4 test conditions as follows:

- D/F emissions and organic PIC emissions from each DRE test condition are evaluated, together with . . .
- Metals emissions (18 metals) from the SRE test condition, and . . .
- HCl and Cl_2 emissions from the SRE test condition.

Total chronic risks for all four risk scenarios are determined to be below target levels.

An acute risk evaluation is also performed to assess inhalation risks associated with maximum potential one-hour emissions. Maximum one-hour emissions for the acute evaluation are estimated for D/Fs , other organics, and HCl/Cl_2 based on the test data listed above, with an upward adjustment to reflect upsets. However, for metals, the test data are not representative of maximum potential one-hour emissions. For the metals represented by the spiked metals (arsenic, beryllium, cadmium, chromium, and lead), the facility uses an approved extrapolation procedure to estimate maximum one-hour emission rates based on maximum anticipated one-hour feed rates and the SREs demonstrated during the testing. The extrapolated emissions estimates are then adjusted further to reflect upsets. For the remaining metals, the facility estimates maximum emissions based on maximum anticipated one-hour feed rates and an assumption of zero SRE. Further upward adjustment for these metals is not necessary, since the "zero SRE" assumption already represents the most conservative estimate. Acute risks associated with these maximum emissions estimates are determined to be below target levels.

Finally, Facility Y performs a "post-MACT scenario" chronic risk evaluation. This evaluation is based on emissions estimates for D/Fs, mercury, semivolatile metals, low-volatile metals, and HCl/Cl_2, where emissions are determined assuming that Facility Y emits at the allowable MACT standard for these pollutants. These emission estimates are combined with the organic PIC emissions measured during the DRE

tests, as well as the metals emissions for the non-MACT metals measured during the SRE test. Total chronic risks from these consolidated emissions are determined to be below target levels.

Final Permitted Emission Rates

As summarized in Table A.2-2, maximum emission rate limits are established in the RCRA permit for D/Fs, metals, and HCl/Cl_2 based on the levels needed to achieve target risk levels. The limits are established for the purpose of periodic verification testing to ensure that emissions remain below those evaluated in the risk assessment. If emissions increases occur above the permitted levels, then the permit calls for the risk assessment to be repeated. Since none of the non-D/F organics were found to be risk drivers, emission limits for individual non-D/F organic compounds are not established in the permit.

The "post-MACT scenario" risk evaluation showed that the MACT standards for D/Fs, metals, and HCl/Cl_2 will be sufficiently protective. Therefore, the RCRA permit includes "sunset" provisions on the emission limits for these pollutants in the RCRA permit. In this instance, the sunset provisions are structured so that the RCRA emission limits will no longer apply once the facility has documented compliance with MACT, and once the regulatory agency has completed a finding of compliance. Emission limits for the non-MACT metals (aluminum, antimony, barium, cobalt, copper, manganese, nickel, selenium, silver, thallium, vanadium, and zinc) will remain in the RCRA permit.

Final Permit Limits for Control Parameters

Table A.2-2 provides the final permit limits on relevant control parameters for Facility Y. During the DRE test conditions, carbon monoxide levels were greater than 100 ppm and total hydrocarbon levels were less than 10 ppm on an hourly rolling average basis. The permit writer establishes the RCRA permit limit for carbon monoxide as the average of the test run averages (i.e., a value greater than 100 ppm). Since carbon monoxide and total hydrocarbon spikes appeared to track pretty closely, the permit writer determines that there is no need to specify continued total hydrocarbon monitoring as a RCRA permit condition prior to MACT. However, after MACT, the facility will comply with a total hydrocarbon limit of 10 ppm instead of with the limit on carbon monoxide.

With the exception of mercury, quarterly average metals feed rate limits are established in the RCRA permit based on the feed rates demonstrated during the SRE test. For mercury, a risk-based feed rate limit is conservatively calculated from the risk-based emission limit by assuming zero SRE (i.e., 100% of the mercury fed to the unit is emitted).

Short-term metal feed rate limits are not necessary for the RCRA permit, because acute risks were determined to be negligible (considering the range of inputs for metals at Facility Y). Although the SRE tests were performed for the purpose of establishing short-term metal feed rate limits for arsenic, beryllium, cadmium, chromium, and lead, these limits will apply in the future pursuant to MACT and are not a RCRA concern.

The RCRA permit is written with sunset provisions for all control parameters except for the quarterly average feed rate limits on the non-MACT metals, and except for limits on containerized feeds which are not required to be established under the MACT rule. Although MACT will limit total mass feed rate for containers (as well as total hydrocarbons), the historical operating data for Facility Y suggests that preventive controls are needed to preclude overcharging of highly volatile, high-Btu containers. Therefore, the limits on "maximum Btu/drum" and "maximum total containerized thermal input" established based on the DRE 2 test will be retained in the RCRA permit. The RCRA permit may be modified to delete these provisions if similar limitations are placed in the Title V permit for this facility in the future.

TABLE A.2-2

FINAL RCRA PERMIT LIMITS FOR FACILITY Y

Parameter	Value	Basis		Sunset
		Test	Established As:	
Summary of Performance Standards and Emission Limits				
DRE	99.99% for POHCs	N/A	Regulatory Limit	Yes
Maximum PM Emissions	0.08 gr/dscf	N/A	Regulatory Limit	Yes
HCl	Larger of 99% removal or 4 lbs/hr	N/A	Regulatory Limit	Yes
Maximum HCl and Cl_2 emissions	Inhalation risk-based limits	N/A	Target levels from risk assessment	Yes
Maximum D/F emissions	Multi-pathway risk-based limit	N/A	Target level from risk assessment	Yes
Maximum emissions (arsenic, beryllium, cadmium, chromium, lead and mercury)	Multi-pathway risk-based limits	N/A	Target levels from risk assessment	Yes
Maximum emissions (aluminum, antimony, barium, cobalt, copper, manganese, nickel, selenium, silver, thallium, vanadium, zinc)	Multi-pathway risk-based limits	N/A	Target levels from risk assessment	No
Group A Control Parameters - Interlocked with AWFCO				
Minimum PCC combustion temperature	1,400 °F, HRA	DRE	Avg. of the test run averages	Yes
Minimum SCC combustion temperature	1,800 °F, HRA	DRE	Avg. of the test run averages	Yes
Maximum combustion gas velocity	cfm, HRA	DRE/ SRE	Avg. of the test run averages [1]	Yes
Maximum PCC organic liquid feed rate	lbs/hr, HRA	DRE 1	Avg. of the test run averages [1]	Yes
Maximum PCC aqueous feed rate	lbs/hr, HRA	DRE 3	Avg. of the test run averages [1]	Yes

TABLE A.2-2

FINAL RCRA PERMIT LIMITS FOR FACILITY Y (continued)

Parameter	Value	Basis		Sunset
		Test	Established As:	
Maximum PCC organic sludge feed rate	lbs/hr, HRA	DRE 3	Avg. of the test run averages [1]	Yes
Maximum PCC bulk solids feed rate	lbs/hr, HRA	DRE 1	Avg. of the test run averages [1]	Yes
Maximum PCC container feed rate	9,000 lbs/hr, HRA	DRE 1	Avg. of the test run averages [1]	Yes
Maximum PCC container heat content	2 MM Btu/drum	DRE 2	As demonstrated during DRE 2	No/Yes [2]
Maximum total containerized thermal input	40 MM Btu/hr	DRE 2	As demonstrated during DRE 2	No/Yes [2]
Maximum SCC organic liquid feed rate	lbs/hr, HRA	DRE 1	Avg. of the test run averages [1]	Yes
Maximum SCC aqueous liquid feed rate	lbs/hr, HRA	DRE 4	Avg. of the test run averages [1]	Yes
Maximum fabric filter inlet temperature	400 °F, HRA	DRE/ SRE	Avg. of the test run averages	Yes
Minimum and maximum fabric filter pressure differential	inches water column, HRA	N/A	Manufacturer's specifications	Yes
Minimum spray dryer slurry feed rate	gpm, HRA	SRE	Avg. of the test run averages	Yes
Maximum stack carbon monoxide concentration	Site-specific limit greater than 100 ppm at 7% oxygen, dry basis, HRA	DRE	Avg. of the test run averages [3]	Yes
Maximum combustion chamber pressure	inches water column, vacuum, instantaneous limit	N/A	As necessary to maintain negative pressure	Yes

TABLE A.2-2

FINAL RCRA PERMIT LIMITS FOR FACILITY Y (continued)

Parameter	Value	Basis		Sunset
		Test	Established As:	
Group B Control Parameters				
Limits on most difficult-to-burn POHCs	Allowable Appendix VIII constituents	DRE	Based on POHCs which achieved 99.99% DRE	Yes
Maximum chlorine feed rate	lbs/hr, HRA [4]	SRE	Avg. of the test run averages	Yes
Maximum ash feed rate - total - atomized	lbs/hr, HRA [5]	 DRE 1 DRE 4	Avg. of the test run averages [5]	Yes
Maximum feed rates (arsenic, beryllium, cadmium, chromium, and lead)	lbs/hr, quarterly average [4]	SRE	Avg. of the test run averages	Yes
Maximum mercury feed rate	lbs/hr, quarterly average [6]	N/A	Feed rate calculated from the risk-based emission limit assuming zero SRE [6]	Yes
Maximum feed rates (aluminum, antimony, barium, cobalt, copper, manganese, nickel, selenium, silver, thallium, vanadium, and zinc)	lbs/hr, quarterly average	SRE	Avg. of the test run averages	No
Lime slurry properties (minimum percent lime and lime absorbent properties)	percent	SRE	Avg. of the test run averages	Yes
Group C Control Parameters				
Maximum total heat input	80 MM Btu/hr	N/A	Design basis	Yes

TABLE A.2-2

FINAL RCRA PERMIT LIMITS FOR FACILITY Y (continued)

Parameter	Value	Basis		Sunset
		Test	Established As:	
Burner/atomizer: - Maximum viscosity - Maximum turndown - Maximum solids - Minimum atomizing pressure differential	 - centipoise - gpm range - percent solids - psig (interlocked with AWFCO)	N/A	Manufacturer's recommendations	Yes
Minimum spray dryer nozzle pressure	psig, HRA (interlocked with AWFCO)	N/A	Manufacturer's recommendations	Yes

Notes:

AWFCO	=	Automatic waste feed cutoff system	MM Btu	=	Million British thermal units
Avg.	=	Average	N/A	=	Not applicable
Btu/hr	=	British thermal units per hour	PCC	=	Primary combustion chamber
cfm	=	Cubic feet per minute	PM	=	Particulate matter
D/F	=	Dioxin/furan	ppm	=	Parts per million
DRE	=	Destruction and removal efficiency	psig	=	Pounds per square inch, gauge
gal/cfm	=	Gallons per cubic feet per minute	POHC	=	Principle organic hazardous constituent
gpm	=	Gallons per minute			
gr/dscf	=	Grains per dry standard cubic foot	SCC	=	Secondary combustion chamber
HRA	=	Hourly rolling average	SRE	=	System removal efficiency
lbs/hr	=	Pounds per hour			

1 Under MACT, the limit will be based on the average of the maximum hourly rolling averages for each run.

2 For some systems, these parameters may be critical to passing the DRE performance standard under MACT and would therefore be incorporated into the Title V permit. If these limitations are placed in the Title V permit, then the provisions may be sunset or deleted from the RCRA permit.

3 Under MACT, total hydrocarbon monitoring to demonstrate compliance with a 10 ppmv limit will be performed instead of carbon monoxide monitoring.

4 Under MACT, the averaging period will be 12 hours.

5 Under MACT, the averaging period will be 12 hours and the limit will be based on the average of the maximum hourly rolling averages for each run.

6 Under MACT, the averaging period will be 12 hours and the limit will be based on the maximum theoretical emission concentration assuming that all mercury from all feed streams is emitted.

APPENDIX B

SAMPLING AND ANALYSIS

(139 pages)

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ACRONYM LIST

µg	Microgram
µm	Micron
$\mu g/m^3$	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/HighResolution 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.

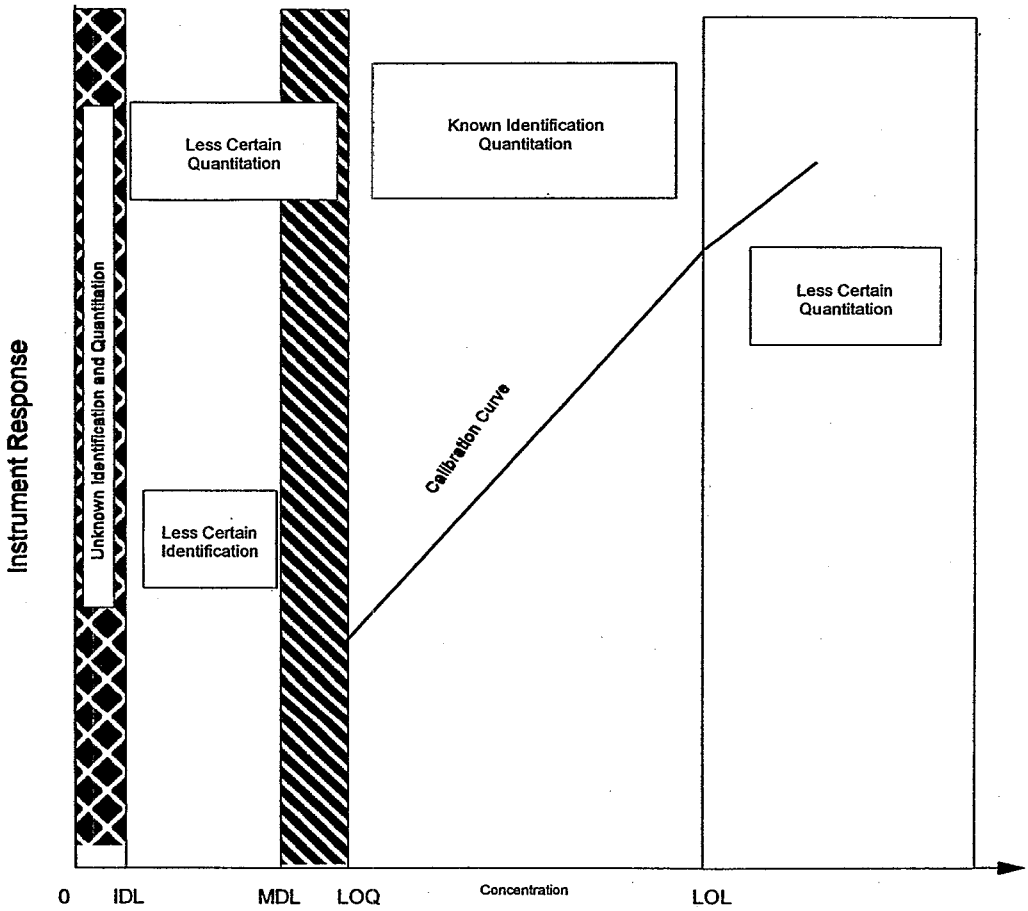
B.1.2.1 Detection Limits, Quantitation Limits, and the Range of Linearity

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

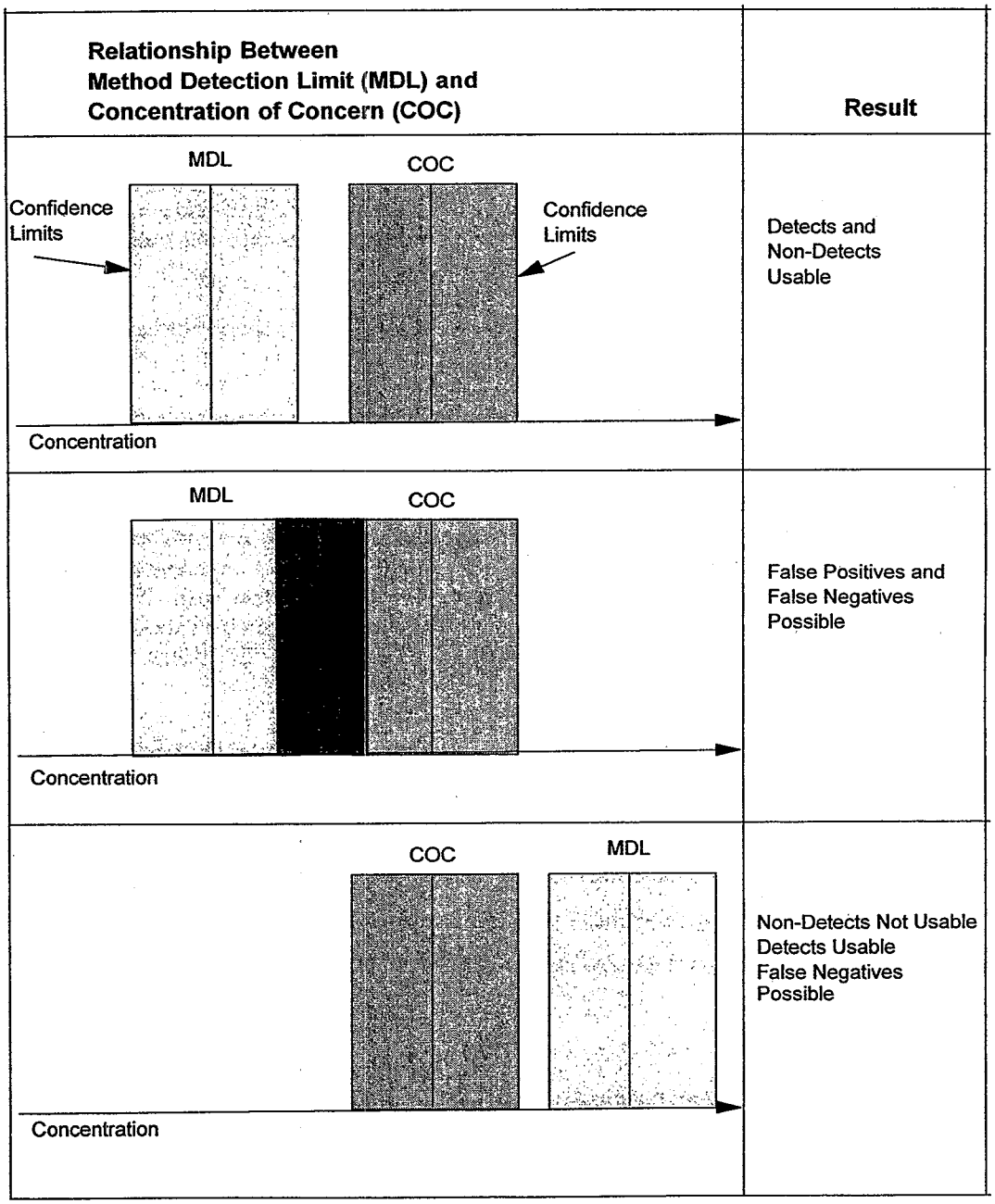


FIGURE B.1-2. IMPACT OF DETECTION LIMIT AND CONCENTRATION OF CONCERN ON DATA PLANNING

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

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* (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

*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 ($\mu g/m^3$). 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 $\mu g/m^3$ 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 $\mu g/m^3$, 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 $\mu g/m^3$. 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 $\mu g/m^3$ 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 °C)	5041A/8260B GC/MS	• Volatile target analyte list, per Table B.2-1 • 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	• Volatile target analyte list, per Table B.2-1 • 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 °C	3542/8270C GC/MS	• Semivolatile target analyte list, per Table B.3-1 • TICs, per Section B.11	Generally applicable	
Chlorobenzenes/ Chlorophenols	M0010	GC/MS	• CBs/CPs in Table B.4-1	Generally applicable	Analysis of the M0010 extract for CBs/CPs is recommended.
PAHs	M0010	CARB 429[2]	• 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: • Pesticides per Table B.10-1 • Herbicides per Table B.10-2 • Nitroaromatics • 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 °C	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 °C.
	M0010	GC/FID	Total organic mass (µg) for organics boiling between 100-300 °C		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 °C		
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:

- 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.

- 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.

- 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:

- 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 30°C and 100°C, although performance may be adequate for compounds with boiling points up to 121°C. If the boiling point of a POHC of interest is less than 30°C, the POHC may break through the sorbent under the conditions of the sample collection procedure. Many compounds that boil above 100°C (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 -15°C and 121°C. Field application for VOCs with boiling points less than 0°C 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).

- 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 121°C, 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 °C), 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 °C), 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, °C[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, °C[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 30°C 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 100°C, 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

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 > 100°C:

- 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 100°C.

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);

- A sorbent trap section (combined with both filter holder back half rinse and condenser rinse after water separation; Soxhlet extraction; dried; concentrated for analysis);
- Condensate and condensate rinse (methylene chloride extraction with water separation; dried; concentrated for analysis); and
- 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 100-150°C) 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 >100°C	
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 100°C and 150°C 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)

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
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:

- 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.

- 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.

- 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 100°C) 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:

- 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 <100°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 100°C and 300°C, and the GRAV fraction determines organics with boiling points >300°C.

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:

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

  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 $\mu g/m^3$ 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 $\mu g/m^3$, the following equation (based on the Ideal Gas Law at Standard Temperature and Pressure) is used:

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

where:

$C_{\mu g/m3}$	=	concentration of each hydrocarbon expressed in $\mu g/m^3$;
C_{ppm}	=	concentration of each hydrocarbon expressed in ppm;
GMW	=	gram molecular weight of each hydrocarbon.
24.04	=	liters/gram-mole ideal gas @ 293°K; 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 $\mu g/m^3$.

Step 3. Sum the concentrations of each of the components in $\mu g/m^3$ 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 $\mu g/m^3$) are summed, and total mass (ÓC $_{\mu g/m3}$ 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 $\mu g/m^3$ 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 ($\mu g/mL$). 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.

- TCO Fraction (Boiling Point between 100°C and 300°C)

  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:

  - 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.

  - 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.

– 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 100°C and 300°C 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).

- GRAV Fraction (Boiling Point > 300°C)

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:

- 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 ($\mu g/m^3$)
C_i	=	stack concentration of the ith identified organic compound ($\mu g/m^3$)

(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 300°C). 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 1300°F) 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 2000°F, 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 160°F 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 $\bar{n}_p$, 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.

- 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.

- 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.

- 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 (170°C [338°F]) 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 200°C (400°F) 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 350°F 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?	f1 f4l3	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	fl	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	fl, f2	3542 8270C	
79-00-5	1,1,2-Trichloroethane	0010 0030/0031 0040	fl, f2 fl fl	3542 8270C 5041A 8260B 8260B	
79-01-6	Trichloroethylene	0030/0031	fl	5041A 8260B	a.k.a. trichloroethene
95-95-4	2,4,5-Trichlorophenol	0010	fl	3542 8270C	
88-06-2	2,4,6-Trichlorophenol	0010	fl, 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 fl	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 fl	5041A 8260B 5041A 8260B 8260B GC/MS	
75-01-4	Vinyl Chloride	0030 kp 0031? kp 0040 M106	fl, f4, l1 f4 l1 fl 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	fl/fl fl l5	5041A 8260B 8260B GC/MS	a.k.a. 1,1-dichloroethene. a.k.a. 1,1-dichloroethylene
1330-20-7	Xylenes(mixture)	0010	fl	3542 8270C	Determine individual xylenes, not total.
95-47-6	*o*-Xylene	0010	fl	3542 8270C	
108-38-3	*m*-Xylene	0010	fl	3542 8270C	
106-42-3	*p*-Xylene	0010	fl	3542 8270C	

CAS No.	Chemical Name	Sampling Method	S. Code	Analysis Method	Comments
-	Antimony Compounds	M29 0060	fl	6010 6020 7000	
-	Arsenic Compounds	M29 0060	fl	6010 6020 7000	Also Method 108 & 108A
-	Beryllium Compounds	M29 0060	fl	6010 6020 7000	Also Method 103 & 104
-	Cadmium Compounds	M29 0060	fl	6010 6020 7000	
-	Chromium Compounds	M29 0060	fl	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	fl	6010 6020 7000	Also Method 12
-	Manganese Compounds	M29 0060	fl	6010 6020 7000	
-	Mercury Compounds	M29 0060	fl	7470	Also Methods 101,101A,102. For speciation research see references 50 & 55.
-	Mineral Fibers				
-	Nickel Compounds	M29 0060	fl	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	fl	6010 7000	

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