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Guidance on Collection of Emissions Data to Support Site-Specific Risk Assessments at Hazardous Waste Combustion Facilities

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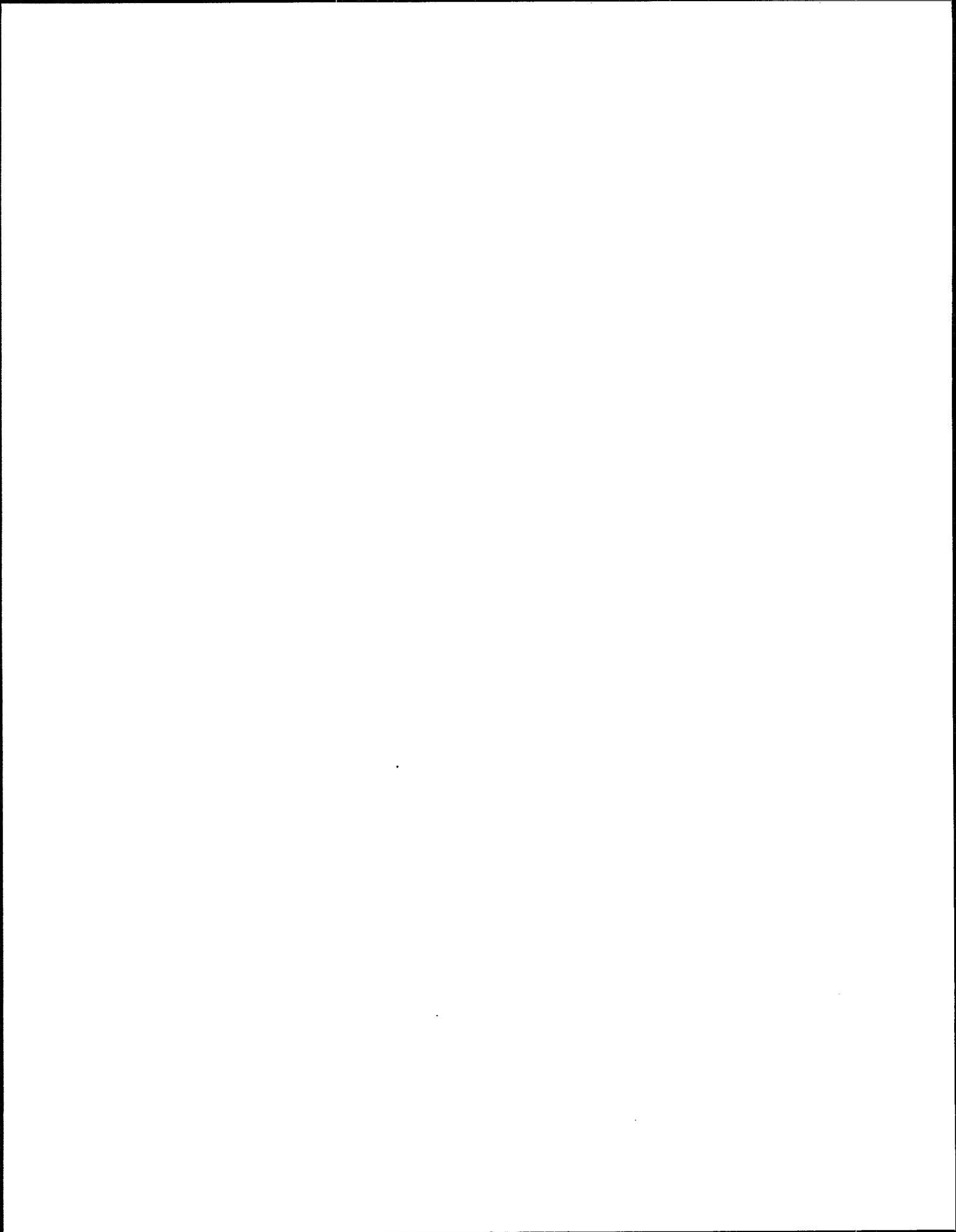
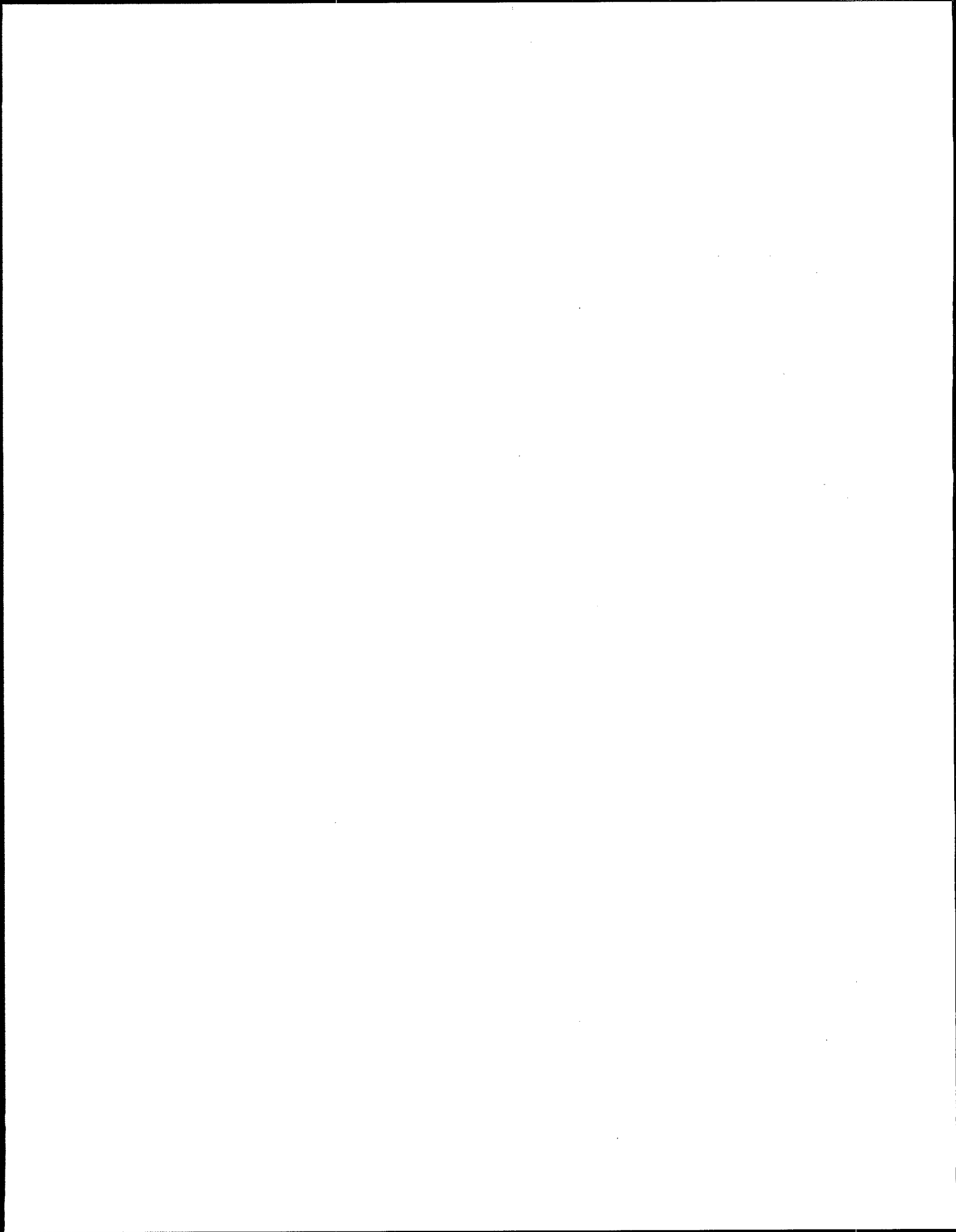# GUIDANCE ON COLLECTION OF EMISSIONS DATA TO SUPPORT SITE-SPECIFIC RISK ASSESSMENTS AT HAZARDOUS WASTE COMBUSTION FACILITIES

Risk Burn Guidance

PEER REVIEW DRAFT

OFFICE OF SOLID WASTE AND EMERENCY RESPONSE
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DISCLAIMER

This document provides guidance to EPA and states on how best to implement RCRA and EPA's regulations to facilitate permitting decisions for hazardous waste combustion facilities. It also provides guidance to the public and the regulated community on how EPA intends to exercise its discretion in implementing its regulations. The document does not substitute for EPA's regulations, nor is it a regulation itself. Thus, it cannot impose legally binding requirements on EPA, states, or the regulated community, and may not apply to a particular situation based upon the circumstances. EPA may change this guidance in the future, as appropriate.

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ACRONYM LIST

µg/dL	Micrograms per deciliter
µg/m^3	Micrograms per cubic meter
APCD	Air pollution control device
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
AWFCS	Automatic waste feed cutoff system
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	Dioxins and furans
DNA	Deoxyribonucleic acid
DQO	Data quality objective
DRE	Destruction and removal efficiency
EDL	Estimated detection limit
EER	Energy and Environmental Research Corporation
ELCR	Excess lifetime carcinogenic risk
EMPC	Estimated maximum possible concentration
EPA	U.S. Environmental Protection Agency
ESP	Electrostatic precipitator
GC	Gas chromatography
grains/dscf	Grains per dry standard cubic foot
HCl	Hydrogen chloride
HEAST	Health Effects Assessment Summary Tables
HEPA	High efficiency particulate air
HRA	Hourly rolling average

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ACRONYM LIST (Continued)

HWC	Hazardous waste combustion
HWI	Hazardous waste incinerator
IRIS	Integrated Risk Information System
LWAK	Light weight aggregate kiln
MACT	Maximum achievable control technology
mg/dscm	Milligrams per dry standard cubic meter
mg/kg	Milligrams per kilogram
MS	Mass spectrometry
ng/dscm	Nanograms per dry standard cubic meter
NAAQS	National Ambient Air Quality Standard
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PCC	Primary combustion chamber
PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofuran
PIC	Products of incomplete combustion
PM	Particulate matter
POHC	Principal organic hazardous constituent
ppm	Parts per million
ppmv	Parts-per-million volume
RAC	Reference air concentration
RCRA	Resource Conservation and Recovery Act
RDL	Reliable detection limit
RfC	Reference concentration
RfD	Reference dose
RME	Reasonable maximum exposure
SCC	Secondary combustion chamber
SRE	System removal efficiency
SSRA	Site-specific risk assessment
TCDD	Tetrachlorodibenzo-p-dioxin
TEQ	Toxic equivalents

ACRONYM LIST (Continued)

TO   Total organic

TRV   Toxicity reference value

U/BK   Uptake/biokinetic

WESP   Wet electrostatic precipitator

1.0 INTRODUCTION

This document provides guidance on collection of stack emissions data to support multi-pathway, site-specific risk assessments (SSRA) at hazardous waste combustion (HWC) facilities. HWC facilities include hazardous waste incinerators (HWI) and boilers and industrial furnaces (BIF) that burn hazardous waste for energy or material recovery. Multi-pathway human health and ecological SSRAs may be performed for these facilities to determine potential direct and indirect risks from:

- Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), known collectively as dioxins and furans (D/F)

- Organic emissions (volatile, semivolatile, and nonvolatile) other than D/Fs, often referred to as products of incomplete combustion (PIC)

- Metals that are potentially toxic to human or ecological receptors

- Hydrogen chloride (HCl) and molecular chlorine (Cl_2)

Direct risks include risks from the inhalation exposure pathway. Indirect risks include risks resulting from long-term deposition, including contamination of soil and surface water, bioaccumulation, and food chain effects. The results of an SSRA may be used to establish additional conditions in the Resource Conservation and Recovery Act (RCRA) permit as necessary to protect human health and the environment. These additional conditions can include emissions limits for D/Fs, metals, or other site-specific compounds; additional limits on operating parameters; and expanded waste characterization and waste tracking requirements.

This guidance identifies the types of emissions data that are needed to support SSRAs. The guidance suggests operating and feed conditions that should generally be demonstrated during the testing, and identifies appropriate stack sampling and analytical techniques for collection of emissions data. In addition, the relationship between test conditions and potential RCRA permit conditions is discussed. The guidance presumes that emissions data for SSRAs will typically be collected in conjunction with RCRA trial burns. However, in some cases emissions data may be generated during other sampling events.

This guidance does not include a methodology for performing the SSRAs. The U.S. Environmental Protection Agency (EPA) is currently developing protocols for conducting human health and ecological SSRAs (EPA in press a, in press b). These or other SSRA protocols (e.g., Research Triangle Institute [RTI] 1996) should be used in conjunction with this guidance. The human health and ecological risk

protocols, in conjunction with this guidance, supersede previous EPA Office of Solid Waste guidance on combustion risk assessments (EPA 1994b).

1.1 OBJECTIVES

The objectives of this guidance are to:

- Ensure the collection of adequate data to support completion of defensible human health and ecological SSRAs. Specific data needs of the SSRA 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 Section 2.0, and sampling and analytical procedures are discussed in Appendix B.

- Provide flexibility in the trial burn process by allowing (as appropriate) the option for a separate test conducted exclusively for collection of SSRA data. The separate test (which can be referred to as a risk burn) may be performed at conditions representing long-term average, or normal, operations. Selection of appropriate test conditions for collection of SSRA data is discussed in detail in Section 3.0

- Identify key operating parameters that can influence emissions of D/Fs, organics other than D/Fs, and metals. These operating parameters should be demonstrated during SSRA emissions testing and may be limited by the final permit. This guidance also recognizes inherent design differences between HWIs, boilers, cement kilns, and light weight aggregate kilns (LWAK), and accounts for these differences in recommending operating parameters to be limited under RCRA. Key operating parameters related to emissions of D/Fs, organics other than D/Fs, and metals are discussed in Sections 4.0, 5.0, and 6.0, respectively. The significance of particle-size distribution and HCl and Cl_2 emissions are addressed in Section 7.0.

- Explain how emissions data may be evaluated in the SSRA, and identify additional emissions and operating parameters that might be limited in the final RCRA permit based upon results of the SSRA. These issues are discussed in Section 8.0 and are illustrated by the example in Appendix A.

- Identify ongoing waste feed and operation evaluations that may be needed to ensure that the SSRA remains representative of existing and future facility operations. These issues are briefly discussed in Section 9.0.

This guidance focuses on the data needs specified in the first bullet of this section (page 2), above. Other data needs of the SSRA should be addressed on a site-specific basis, and could include compounds such as radionuclides or other criteria pollutants not specifically addressed in this guidance. Additional discussion of some of these other compounds can be found in EPA (in press a).

This guidance supplements, but does not supersede, existing guidance and regulatory requirements pertaining to performance testing. Although general guidelines are provided, permit writers are

encouraged to consider facility-specific circumstances that are not fully addressed. Overall, this guidance should be regarded as a living document and may be updated as additional technical issues arise.

EPA Region 6 has also developed additional guidance for reviewing trial burn plans, RCRA Part B permit applications, and documents such as quality assurance project plans (EPA 1997f, 1997g, 1997h, 1997i, and 1997j). These documents may also be helpful when reviewing permit applications, trial burn plans, and related documents. These documents are available from EPA Region 6 on their Internet web site at http://www.epa.gov/earth1r6/6pd/rcra-c/manual/manual.htm#A.

The remainder of this section provides background information on RCRA performance standards and existing trial burn guidance. Potential limitations of current EPA regulations are identified, and the use of SSRAs to supplement current regulatory controls is also discussed. Finally, this section briefly discusses EPA's proposed Maximum Achievable Control Technology (MACT) standards for HWC facilities (EPA 1996a) and discusses their relevance to this guidance.

1.2 REVIEW OF RCRA TRIAL BURN PROVISIONS

This section reviews RCRA trial burn provisions and it provides the framework for issues discussed later in the document. The review discussion is minimal, and the cited references should be consulted for more detail.

Performance standards for HWIs 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 (POHC) of 99.99 percent, or 99.9999 percent for dioxin-listed wastes; (2) particulate matter (PM) 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. The trial burn is used to define the operating range (or envelope) that assures the required DRE of the selected POHCs. Trial burns for a HWI typically are conducted at extreme "worst-case" conditions for time, temperature, and turbulence in the combustion chamber. This involves at least one performance test condition at a minimum combustion temperature to demonstrate DRE. Additional test conditions may be required to resolve potential conflicts between operating parameters.

Ongoing compliance with the three performance standards is assured by developing limits for the following operating parameters:

- Minimum combustion temperature in the primary combustion chamber (PCC) and secondary combustion chamber (SCC)
- Maximum flue gas flow rate (or velocity) and maximum waste feed rate
- Carbon monoxide concentration in exhaust gas
- Other operating requirements as necessary to ensure that performance standards are met

Guidance pertaining to these operating parameters has been provided previously (EPA 1983, 1989). EPA's (1989) guidance also addresses the importance of establishing operating parameters for air pollution control devices (APCD), including wet and dry scrubbers, fabric filters, and electrostatic precipitators (ESP). APCD parameters include minimum and maximum pressures, temperatures, flow rates, pH, and power.

Standards for BIFs, including boilers, cement kilns and LWAKs 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. BIFs are required to comply with a DRE performance standard as well as emission standards for metals, HCl, Cl_2, PM, carbon monoxide, and total hydrocarbons. BIFs are also required to comply with general requirements applicable to all HWIs, 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 chromium are based on an aggregate (all carcinogenic metals) maximum potential excess lifetime carcinogenic risk (ELCR) 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 (RfD) converted to reference air concentrations (RAC) or published reference concentrations (RfC) 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 corresponding RACs. Since 1992, nickel and selenium emissions have also been limited as necessary to protect human health and the environment (EPA 1992a).

Organic emissions from BIFs are controlled using a DRE standard and by limiting carbon monoxide (and in some cases total hydrocarbon concentrations) in stack gas (EPA 1992b). The BIF rule also recognizes that HWC facilities with dry APCDs operating between 450 and 750 °F may emit higher concentrations of D/Fs than HWC facilities with other types of APCDs. SSRAs are required for BIFs with dry APCDs operating at 450 to 750 °F to demonstrate that the ELCR from 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, conducted at a high combustion temperature, in order to maximize metal volatility. Thus, under the BIF rule, the operational envelope is generally defined by a low-temperature test to demonstrate DRE and a high-temperature test to demonstrate system removal efficiency (SRE) for up to 12 metals. Operating limits to control metals are based on SRE conditions that include maximum combustion temperature, maximum metals feed rates, and appropriate APCD operating parameters (e.g., temperature, pressure, or power). Maximum metal and chlorine feed rates for BIFs are 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 establish maximum feed rates. This ensures that sufficiently flexible metal and chlorine feed rate limits will be incorporated into the facility's operating permit. Similar provisions have been implemented at HWIs as necessary to protect human health and the environment.

EPA trial burn and technical guidance documents for HWIs and BIFs (EPA 1989, 1992b, 1997f) describe control parameters typically monitored during trial burn testing. These operating parameters (monitored during DRE or SRE conditions) are defined as Group A, B, or C. Short-term limits, such as hourly rolling averages (HRA) and instantaneous limits, are typically set for these operating parameters in the facility's RCRA permit. The Group A, B, and C designations are also used in this document, and are discussed below.

Group A operating parameters are linked with automatic waste feed cutoff system (AWFCS) limits. This means that waste feed is automatically cut off when specified limits are exceeded. Group A operating parameters must be continuously monitored while hazardous waste is being fed to the HWC unit. Examples of Group A parameters include maximum and minimum PCC and SCC temperatures; maximum

combustion gas velocity, waste feed rate, carbon monoxide concentration, and combustion chamber pressure; and minimum venturi scrubber differential pressure, scrubber liquid to gas ratio and pH, baghouse differential pressure, and wet ESP (WESP) power input and liquid flow rate.

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

Group C operating parameters are set independently of trial burn conditions, and limits are generally 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 require continuous monitoring and interlocks with AWFCS; 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 required to demonstrate compliance with permitted operating conditions.

The Group A, B, and C designations are used throughout this document. These designations are applied to the operating parameters discussed in Sections 4.0 through 7.0, Tables 4-1 and 4-2, and Appendix A.

1.3   RISK ASSESSMENTS AT HWC FACILITIES

The performance standards described in Section 1.2 were developed to control potential inhalation risks from HWC units. Requirements for HWIs were promulgated during 1981, and requirements for BIFs were promulgated during 1991. Since these requirements were developed, additional concerns regarding combustion of hazardous waste have been identified. These concerns relate to potential indirect effects (including uptake through the food chain) from long-term deposition of metals, D/Fs, and other organic compounds in soils and surface water. The current regulations do not directly address potentially significant risks via these indirect exposure pathways.

The U.S. Congress and EPA have recognized that emissions of compounds such as D/Fs and mercury are especially toxic and have the propensity to cause significant human and ecological effects through bioaccumulation in the food chain. This includes contamination of beef and dairy cattle, as well as pork

and poultry, on agricultural lands and fish in aquatic ecosystems. Potential indirect risks from these types of compounds often exceed potential risks from the direct inhalation pathway. Additional information on these contaminants can be found in the Mercury Study Report to Congress (EPA 1997e), EPA's proposed MACT standards (EPA 1996a), and EPA's protocols for human health and ecological risk assessments (EPA in press a, in press b).

Based on available data summarizing notable D/F and mercury emissions from HWC facilities (EPA 1996a, EPA 1997k), EPA has prioritized the identification of potential human health and ecological risks due to HWC emissions (EPA in press a, in press b), and implementation of appropriate controls (EPA 1996a). In addition, EPA recognizes that significant uncertainty may exist regarding potential risks due to organic emissions other than D/Fs. SSRAs provide a mechanism for assessing potential risks and uncertainties, and for determining protective emission rates. Therefore, EPA recommends that SSRAs be completed as part of the RCRA permitting process for HWC facilities as necessary to protect human health and the environment (EPA 1993, 1994c, 1996a).

Section 3005(c)(3) of RCRA and 40 CFR Part 270.32(b)(2) provide EPA with the responsibility to establish additional permit conditions on a case-by-case basis as necessary to protect human health and the environment. These provisions are generally referred to as EPA's omnibus authority. Under 40 CFR Part 270.10(k), EPA may use its omnibus authority to require a permit applicant to submit additional information necessary to establish protective permit conditions. Collection of additional emissions data and completion of SSRAs can provide the information necessary to determine what, if any, additional permit conditions are necessary for maintaining risks within acceptable levels. Any decision to add permit conditions based on an SSRA must be justified in the administrative record for each facility, and the implementing agency must explain the basis for the additional conditions.

1.4   EPA'S MACT STANDARDS

EPA'S MACT standards for HWC facilities propose technology-based limits for D/Fs; organic emissions other than D/Fs; low-volatile, semivolatile, and volatile metals; Cl_2 and HCl; and PM (EPA 1996a). These standards have been proposed under joint authority of RCRA and the Clean Air Act. The MACT standards will apply to several categories of HWC facilities including HWIs, hazardous waste burning cement kilns, and hazardous waste burning LWAKs. Emission standards for hazardous waste burning boilers are anticipated in a future MACT standards rulemaking.

EPA (1996a) recommends that SSRAs continue to be part of the RCRA permitting process, prior to implementation of final MACT standard requirements. Updated policy regarding the use of SSRAs in setting permit conditions is expected at the time the MACT standards are promulgated. If, in the future, MACT standards are promulgated that are more stringent than the existing site-specific risk-based standards, then the MACT standards would take precedence.

2.0 EXPANDED SCOPE OF THE TRIAL BURN

Specific data needs of the SSRA that should be considered during trial burn planning 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 section summarizes the significance of these data needs with respect to protection of human health and the environment.

Results of the SSRA for human health will be used to determine whether potential risks exceed acceptable levels as specified by the regulatory authority. It is important that all toxicological data concerning a constituent be evaluated for all known effects. Some constituents have effects on multiple organs, and thus have a collective harmful effect on the receptor.

Prior to data collection, information should be developed for the trial burn plan and associated quality assurance project plan to ensure that analytical methods will be adequately sensitive so that risks are not driven by non-detected constituents. Analytical detection limits should be compared with the data needs of the SSRAs (EPA in press a, in press b), and as appropriate, be compared with those found in EPA (1996g). Detection limits may need to be reduced to achieve target risk levels. Detection limits and data analysis are discussed in greater detail in EPA (in press a), and in Section 8.2 and Appendix B of this document.

2.1   DIOXINS AND FURANS

D/Fs should be addressed in SSRAs because they can pose significant risks through both direct and indirect exposure pathways. Their propensity to partition to adipose (fat) tissue and to bioaccumulate can make food chain effects particularly significant. According to EPA (1995b) the air-to-plant-to-animal exposure pathway is a primary exposure route for humans. Other significant exposure pathways include source-to-surface water-to-fish. Human exposures would then 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 carcinogenicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) 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 1995b). As described in Section 4.0, the formation of D/Fs in HWC facilities is highly dependent on 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-

TCDD toxic equivalents (TEQ). For the purpose of this guidance, TEQs are calculated using the procedure in 40 CFR Part 266, Appendix IX.

2.2 ORGANICS OTHER THAN DIOXINS AND FURANS

A number of organic compounds other than D/Fs can result in increased risks from both direct and indirect exposures and should therefore be evaluated in SSRAs. The treatment of hazardous wastes in HWC facilities results in emissions of organics that include halogenated and nonhalogenated organic compounds. Chapter 2.0 of EPA (in press a) states that HWC organic emissions can include classes of compounds such as polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB). Both PAHs and PCBs are considered by EPA (1998a) as potential human carcinogens, and are considered to be toxic, persistent, and bioaccumulative. PAHs are frequently associated with PM from combustion facilities. EPA (in press a) cites data from EPA Region 10, whereby PCBs were formed as PICs during combustion of hazardous wastes. As discussed in Section 5.0 of this document, organic PICs from HWC facilities typically include compounds such as methane, propane, chlorinated alkanes and alkenes, phenols, and chlorinated aromatics (Ryan and others 1996, 1997; Midwest Research Institute and AT Kearney, Inc. 1997).

Target analyte lists for specific organics to be identified as part of SSRA data collection 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, Section 5.0 and Appendix B of this document describe a method for total organic (TO) analysis for quantifying the total mass of organic PICs based on boiling point ranges. This information is useful in indicating the level of uncertainty associated with the risk assessment.

2.3 METALS

Metal emissions can pose potential human and ecological risks and should be evaluated in SSRAs. EPA's BIF rule (40 CFR 266, Subpart H) and supporting documentation (EPA 1992a) lists the metals antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, nickel, selenium, silver, and thallium for establishing metal feed rates. Table A-1, "Chemicals for Consideration as Compounds of Potential Concern," of Appendix A of EPA (in press a, in press b) identifies the additional metals aluminum, copper, cobalt, manganese, vanadium, and zinc. Thus, these additional metals would also be considered as compounds of potential concern (COPC) during the COPC selection process. As appropriate, these metals may be carried through the risk assessment process.

Potential human cancer risks (based on the inhalation exposure pathway) are based on carcinogenic slope factors (CSF) 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, selenium, silver, thallium, and vanadium. As explained in Section 2.3.3 of this document, potential health effects from lead are modeled using an alternative approach (EPA in press a).

EPA's ecological risk assessment protocols (EPA in press b) include ecological toxicity reference values (TRV) for a number of ecosystems and receptors. This includes freshwater quality, freshwater sediment, marine and estuarine water quality, marine and estuarine sediment, and specific receptors including earthworms, terrestrial plants, mammals, and birds. TRVs 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. These metals should be considered during the COPC selection process for ecological SSRAs.

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 because these metals were not addressed in the original BIF rule (40 CFR 266, Subpart H) or supporting documentation (EPA 1992b). All of these metals (except aluminum and cobalt) have published toxicity values (RfDs and/or RfCs) in EPA's Integrated Risk Information System (IRIS) (EPA 1998a) and/or EPA's Health Effects Assessment Summary Tables (HEAST).

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 heath 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] 1992; Paasivirta 1991). In mammals, aluminum is poorly absorbed and is not readily metabolized (Ganrot 1986). From a human health perspective, aluminum

emissions do not appear to pose any toxicological concern. Therefore, aluminum is considered as a COPC only for ecological SSRAs and TRVs 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 exposures to airborne cobalt appears to result in sensitization followed by irritation and produced pulmonary effects (Doull and others 1991). TRVs for cobalt 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 (DNA) or generate free radicals.

Organisms lacking effective biological barriers to absorption are the most susceptible to copper toxicity. Aquatic organisms such as algae, fungi, certain invertebrates, and fish represent examples of this type of organism. 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). TRVs 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 1998a) 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. TRVs 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 (in press a, 1998a) states that nickel refinery dust is a potential human carcinogen. Based on this information, EPA (in press a) recommends that inhalation risks from nickel be evaluated using the CSF for nickel refinery dust. This represents a change in EPA's previous policies under the BIF rule whereby nickel was evaluated as a noncarcinogen. This may result in lower allowable nickel feed rates. Additional information on nickel speciation is found in Section 2.3.8.4 of EPA (in press a) and Section 6.1 of this document. TRVs 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, and pose a hazard to livestock and other species. In humans, selenium partitions to the kidneys and liver and is excreted though 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. Based on available data, aquatic birds are potential sensitive receptors. TRVs 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 kidney. TRVs 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). TRVs have been developed for zinc.

2.3.2   Issues Related to Indirect Risks from Mercury

Control of mercury emission and feed rate limits to protect against potential indirect risks will generally result in lower limits compared to those established under the BIF rule, 40 CFR 266, Subpart H and EPA (1992b). Mercury has significant potential to biotransfer up the food chain through water and sediments to fish to human receptors. Thus, indirect exposure pathways may drive potential risks from mercury to human and ecological receptors.

Default exposure assumptions for speciated mercury are found in EPA (in press a, in press b). However, a facility may wish to collect site-specific data to address mercury speciation. Additional information on mercury speciation is found in Section 2.3.8.3 of EPA (in press a), and in Section 6.1 and Appendix B of this document.

2.3.3   Issues Related to Indirect Risks from Lead

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, both air and soil lead levels should be evaluated in a SSRA. Air concentrations can be modeled, and soil levels can be calculated based on modeled results.

Information on estimating threshold levels of lead exposure is provided in Sections 2.3.8.2 and 7.5 of EPA (in press a). Toxicity factors (CSFs and RfDs) are not available for lead. Therefore, adverse health effects for lead will be characterized through a direct comparison with media-specific health-based levels, adjusted for background exposure.

The neurobiological effects observed in children are used as the sensitive endpoint for evaluating lead toxicity from ingestion. EPA recommends 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. 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 predicts that no more than five percent of children exposed to a lead concentration in soil of 400 milligrams per kilogram (mg/kg) will have blood lead concentrations exceeding 10 μg/dL. In lieu of direct comparison to a target soil level, EPA (in press a) also provides the option of running the U/BK model.

2.4   PARTICLE-SIZE DISTRIBUTION

Information on particle-size distribution (presented as particle diameter in micrometers, referred to as microns) is needed for the air dispersion and deposition modeling that supports the SSRAs (EPA in press a). Because particle dispersion and subsequent deposition are directly related to particle size, potential risks from the indirect exposure route 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. An exception is mercury which partitions between particle and vapor phases.

Default assumptions for particle-size distribution for sources equipped with ESPs and fabric filters are provided in EPA (in press a). However, recent measurements show that the default assumptions may be overly biased towards larger particles (EPA 1998b). In addition, default assumptions are not available for facilities equipped with wet APCDs, or for facilities with no APCDs. Thus, site-specific particle-size measurements are recommended for all HWC facilities completing SSRAs.

Sampling and analysis for particle-size distribution will reflect site-specific combustion characteristics and the efficiency of the APCD; significant particle fractions with particle sizes less than one micron are not uncommon (EPA 1998b). Because a widely accepted method for determining particle-size distribution is not yet available, permit writers should work with facilities to obtain the best data possible when considering facility-specific circumstances. This issue is discussed in more detail in Section 7.0 and in Appendix B of this document.

2.5   HYDROGEN CHLORIDE AND CHLORINE

Potential risks from HCl and Cl_2 are limited to the inhalation pathway. Thus, completion of SSRAs is not expected to affect the current regulatory approach for HCl and Cl_2 from BIFs. However, EPA recommends that HWIs test their stack emissions for both HCl and Cl_2. Risk-based limits may be established in the

final permit for HWIs in lieu of the 40 CFR Part 264 technology-based limits, if the risk-based limits are more stringent. Detailed information on control of HCl and Cl_2 has been provided in previous guidance (EPA 1989, 1992a, 1996a). Therefore, this document does not address control measures for HCl and Cl_2 in detail.

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3.0 INTEGRATION OF PERFORMANCE TESTING WITH RISK-BASED DATA NEEDS

As discussed in Sections 1.0 and 2.0, collection of SSRA data at HWC facilities involves sampling and analysis for D/Fs, non-D/F organics, metals, particle-size distribution, and HCl and Cl_2. Based on the results of the SSRA, EPA may establish risk-based permit limits under omnibus authority of RCRA as described in 40 CFR 270.32(b)(2). Therefore, collection of emissions data for use in the SSRAs should be integrated with performance testing as necessary to produce a consistent set of enforceable permit conditions.

This section provides general guidelines regarding appropriate test conditions for collection of emissions data to be used in SSRAs. Data collection may be associated with (1) a low-temperature test conducted to demonstrate DRE of POHCs, (2) a high-temperature SRE test conducted to establish metal feed rates and to account for metal emissions and partitioning, and/or (3) a specially designed risk burn test (which may be conducted at normal operating conditions) specifically for the collection of risk assessment data. A flow chart (Figure 3-1) is presented to help guide permit writers and facility personnel through the decision-making process. Sections 4.0 through 6.0 build on these concepts by identifying operating parameters associated with emissions of specific contaminants (D/Fs, non-D/F organics, and metals) and specific types of HWC facilities (HWIs, boilers, cement kilns, and LWAKs). These operating parameters include many of the same Group A, B, and C parameters typically measured during DRE and SRE performance testing.

3.1 PERFORMANCE TESTING AND DEFINING AN OPERATING ENVELOPE

Section 1.0 explains that performance testing of HWC facilities involves the identification of an operational envelope based on DRE (low temperature) and SRE (high temperature) conditions. Defining a facility's operational envelope has been regarded as a way of challenging the facility's operating systems to perform under "worst-case" conditions while meeting EPA performance standards for DRE (of organic POHCs) and emission rates (of PM, metals, HCl, Cl_2, carbon monoxide, and total hydrocarbons). In some cases, wastes synthesized from pure compounds are burned during performance tests in lieu of actual wastes to help achieve these "worst-case" conditions. Synthetic wastes may also be burned during performance testing because of analytical interferences between the waste constituents and the POHCs, because of incompatibilities between the wastes and spiking materials, or because waste volumes are insufficient for completion of three runs per test condition.

These considerations influence whether collection of SSRA data can be integrated with DRE and SRE performance testing, or whether data collection during a separate risk burn test is preferred. For example, a facility may need to consider collection of SSRA emissions data during a separate risk burn test if actual wastes are not burned during the DRE and SRE tests. As discussed further in Sections 4.0 and 5.0, actual representative wastes should be burned to the extent possible during collection of SSRA emissions data for D/F and non-D/F organics. If circumstances preclude use of actual wastes during the DRE or SRE test conditions, then integration of risk-based data collection with performance testing may not be an option. Additional information on balancing the use of real wastes versus synthetic wastes is found in Section 5.1 of this document.

3.2   TEST CONDITIONS FOR RISK-BASED DATA COLLECTION AND RISK BURN

Data for the SSRA may be collected during DRE or SRE test conditions if issues regarding the use of actual representative wastes can be resolved. However, estimating potential risks based on emissions from worst-case DRE and/or SRE conditions could be overly conservative, given that a facility will not operate at the edges of its operating envelope all of the time. For example, the SRE test condition may involve spiking to increase metal feed rates above normal levels, resulting in high metal emissions. From a risk assessment standpoint, a case can be made for using emissions data generated during average, or normal operation of the HWC unit. SSRAs assess potential risks of operations over 30 or more years. Therefore, for contaminants such as metals, emissions during normal operations (as compared to emissions during DRE or SRE conditions) may be more directly related to the risk posed by the HWC facility over its operating life.

If a facility requests that emissions data be collected under normal or average operating conditions (for consideration in the SSRA), then an additional test condition is specified in the trial burn plan. This additional risk burn is optional and is performed by the facility on a voluntary basis. However, the facility may feel that a test condition at average operating conditions is more representative of long-term emission rates. Evaluation of emissions data generated under normal operating conditions in an SSRA (in conjunction with or instead of data generated during a DRE or SRE test) may be considered by the permitting authority on a case-by-case basis. If an agreement with the facility can be reached, then an extra layer of permit conditions 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.

3.3   DEFINING AVERAGE OR NORMAL OPERATING CONDITIONS

Collecting emissions data under normal or average operating conditions may result in lower emission rates and lower, but more representative, potential risks. However, every HWC facility may not be eligible for using risk data collected under normal operating conditions in the SSRA. Relevant criteria include the following:

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

    EPA (1997f) states that data collection for SSRAs under normal operating conditions will only be considered if the facility burns wastes that have little temporal variation in chemical and physical properties, at nearly constant rates, and under operating conditions that do not fluctuate widely. Facilities that cannot meet these criteria, including facilities that burn highly variable wastes, should perform the risk testing under DRE and SRE conditions. Similar logic also should be applied to fuels and raw materials used in cement kilns and LWAKs. For example, mercury in coal can contribute to potential risks and should be considered in the feed characterization.

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

    Facilities choosing to use SSRA data collected under normal operating conditions will likely be subject to additional permit conditions. The purpose of the additional conditions is to ensure that ongoing feeds and operating conditions remain within the boundaries represented by the risk assessment (feeds include hazardous waste and, as appropriate, raw materials and auxiliary fuels such as coal). These permit conditions may be based on long-term (monthly, quarterly, semiannual, and/or annual) averages for operating parameters, or they might involve waste tracking and record keeping. The facility should propose a permitting approach to ensure that normal conditions are maintained. The permit may require that significant changes be reported to the permitting authority. These changes may be subject to review and determination of the need for possible retesting.

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

    A facility may be required to use emissions data collected under DRE and/or SRE conditions in the SSRA because of other circumstances, such as acute risk concerns.

An example of a situation meeting the criteria for use of emissions data collected under normal operating conditions would be a BIF facility that can provide historical data to establish average metal feed rates, and that proposes to comply with both HRA and monthly-average metal feed rate permit limits. The testing and permitting approach would be as follows:

*   ***SRE Test:*** The SRE test would be conducted at maximum metals feed rates, and could involve metals spiking. Emissions from the SRE test would need to be below the BIF

allowable emissions limits (which are based only on inhalation risks). HRA metal feed rate limits would be established based upon this test.

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

An example of a situation that may not meet the criteria for data collection under normal operating conditions would be a commercial HWC facility with a diverse customer list that randomly burns any hazardous waste available on the test day. This facility may not be able to make a case as to why the specific waste represents normal operations, or may not commit to a waste inventory tracking scheme and long-term averaging to assess whether the test waste remains representative. In this case, emissions data from "worst-case" DRE and SRE tests should be evaluated in the SSRA.

Emission rates (and related operating parameters and conditions) that are evaluated in the SSRA should clearly correspond to the permit terms and conditions. These risk-based terms and conditions should serve as a constraint to prohibit operations outside of the operating boundaries evaluated in the SSRA. The permit writer should work closely with the facility to determine the appropriate test condition(s) for collection of the SSRA data.

3.4 RISK-BASED DATA COLLECTION, EXAMPLE LOGIC

Figure 3-1 provides example logic for permit writers and facility personnel to use in determining appropriate test conditions for risk-based data collection. The first step involves determining whether data collected under DRE and SRE conditions are anticipated to meet target risk levels, as specified by the regulatory agency. This question can be answered by evaluating existing emissions data, by conducting "miniburns" (as allowed by existing permit or interim status conditions), or by evaluating data from similar facilities in a preliminary SSRA. Miniburns involve collection of emissions data prior to trial burn testing. Miniburns can be used for determining potential compliance with risk-based limits, and for establishing risk-based detection limits.

Based on preliminary data analysis, a facility may anticipate that emissions data collected during performance testing (DRE and SRE conditions) will meet target risk levels. The permit writer would then work with the facility to determine whether the operating parameters identified in Sections 4.0 through 6.0 of this document can be demonstrated under DRE and SRE test conditions. If so, then the SSRA

FIGURE 3-1

SITE SPECIFIC RISK ASSESSMENT DATA COLLECTION FLOW CHART

No ← — Are emissions from DRE/SRE performance tests likely to pass the site-specific risk assessment? → Yes

Yes — Can normal operating conditions be defined and maintained?

Implement process changes to reduce emissions.

Yes — Are the appropriate operating parameters (Section 4.0) demonstrated during performance tests?

No → Can adjustments be made to define normal operating conditions? — No

No → Add test conditions as necessary to establish limits for appropriate operating parameters.

Yes → Adjust operating parameters and conduct engineering analysis to achieve normal operating conditions.

Testing:
Perform additional test conditions at normal conditions for collection of D/F, non-D/F organic, and metals data for evaluation in the site-specific risk assessment.

Testing:
Collect D/F, non-D/F organic, and metals data for evaluation in the site-specific risk assessment in conjuction with performance tests.

Permit Limits:
- Operating Limits — Establish long-term average permit limits and/or a compliance monitoring plan for important operating parameters for:
  - D/F
  - Non-D/F organics
  - Metals
  Establish HRA or instantaneous limits from DRE/SRE tests.

- Emission Limits — Normal Test Emission Rates ≤ Allowable Permit Limits≤ for D/Fs and Metals — Lower of Risk-Based Limit or Existing Regulatory Standard

Permit Limits:
- Operating Limits — No long-term average permit limits needed. Establish HRA or instantaneous limits per existing guidance from DRE/SRE tests.

- Emission Limits — Perf. Test Emission Rates ≤ Allowable Permit Limits≤ for D/Fs and Metals — Lower of Risk-Based Limit or Existing Regulatory Standard

Normal or Average Operating Conditions   **Performance Test Conditions**

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emissions data may be collected in conjunction with the DRE and SRE test conditions. If not, then extra test conditions may be needed. For example, a trial burn plan for a boiler equipped with a dry APCD would not include a maximum temperature SRE test condition if the waste feed did not contain metals. Section 4.1.1 identifies maximum inlet temperature to a dry APCD as a primary operating parameter related to D/F emissions. Therefore, the facility would evaluate whether maximum APCD temperature could be achieved during the DRE test. If the boiler could not establish a maximum APCD inlet temperature during the DRE test (because of an inability to control APCD temperature independently of combustion temperature), then an extra test condition would be added to the test plan specifically to demonstrate maximum APCD temperature while sampling for D/Fs.

In some cases, the preliminary data analysis might suggest that emissions data collected during performance testing (DRE and SRE conditions) will not meet target risk levels. Facilities that cannot meet target risk levels for emissions data collected during performance testing at DRE and SRE operating conditions have two options (1) demonstrate that average conditions can be defined and maintained and collect data at normal or average operating conditions, or (2) implement process changes to reduce emissions and meet risk-based requirements under DRE and SRE conditions. Process changes can include changes to improve combustion efficiency (including burner design and methods of feeding wastes) or the addition of control systems such as carbon injection.

Facilities that demonstrate the ability to define and maintain normal operating conditions will likely be subject to additional permit conditions based on long-term averages of appropriate waste feed rates, temperatures, and other appropriate operating parameters. These facilities may also be required to submit a compliance monitoring plan that demonstrates how long-term averages will be maintained and tracked.

4.0 DIOXIN AND FURAN EMISSIONS

This section summarizes specific operating and waste feed parameters to be considered for collection of D/F emissions data to support human health and ecological SSRAs. COPC emission rates are dependent on several operating parameters, most of which are monitored during DRE and SRE tests. Operating parameters may also vary between types of HWC facilities (HWIs, boilers, cement kilns, and LWAKs). Separate subsections are included to further discuss the relevance of the operating parameters as they relate to each type of HWC facility. The MACT database (EPA 1996a, 1996b, 1996c, 1996d, 1996e, 1997a, and 1997l) is used as a reference to describe operations and APCD performance in HWIs, cement kilns, and LWAKs. MACT data on boilers are limited and are not considered fully representative of the entire boiler universe within the United States.

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 potential situation. Permit writers should always evaluate facility-specific operating trends and information against the underlying principles of the recommendations in this document.

The subject of D/F formation is both complex and extensive, and this section starts with general information and becomes progressively more specific. Formation mechanisms are discussed in Section 4.1, key operating and waste feed parameters are reviewed and summarized in Section 4.2, and the relevance of the parameters for each industry category are discussed in Sections 4.3 through 4.6. Finally, Tables 4-1 and 4-2 summarize the recommendations by industry category.

4.1 DIOXIN AND FURAN FORMATION MECHANISMS

D/F formation mechanisms, emission rates, and potential control measures in combustion systems have been studied since the late 1970s with increased efforts in the United States over the past 10 years. D/Fs are formed as the result of many complex side reactions that occur in a combustion system (Townsend and others 1995). These side reactions occur primarily in the post-furnace (downstream) regions of the HWC facility. D/Fs can result from a combination of formation mechanisms depending on combustion conditions, the type of APCD, and waste feed characteristics.

D/F formation in HWC facilities is believed to include three possible mechanisms. Depending on waste feed, design, APCD, and operating characteristics, one or more of the following mechanisms may predominate:

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1. Homogeneous gas-phase formation was one of the earliest D/F formation mechanisms observed in combustion systems (Sidhu and others 1994). However, gas phase formation is believed to play a relatively minor role in D/F formation in HWC facilities.

2. The term *de novo* synthesis is commonly used for heterogeneous, surface-catalyzed D/F formation from flyash-based organic material coupled with flyash-based metal catalysts (such as copper). This mechanism is likely to occur in HWC facilities.

3. Heterogeneous D/F formation from gas-phase precursors and flyash-based metal catalysts is also considered a likely formation mechanism in HWC facilities.

Gas-phase D/F formation from trichlorinated phenols was observed to occur at temperatures of 570 to 1,475 °F by Sidhu and others (1994). Their data indicated that the kinetic model developed by Shaub and Tsang (1983) underestimated potential D/F emissions by a factor of approximately 50. The model developed by Sidhu and others (1994) is dependent on the presence of halogenated phenols which are recognized as D/F precursors. Sidhu and others (1994) concluded that pure gas-phase formation of D/Fs in combustion systems is possible given the presence of halogenated hydrocarbons that form halophenols.

The kinetic model for gas-phase formation developed by Shaub and Tsang (1983) failed to account for all the D/F emissions from a municipal waste incinerator, and subsequent work focused more on heterogeneous, surface-catalyzed reactions. Subsequently, over the past 15 years, research has focused on *de novo* synthesis of D/Fs and synthesis from gas-phase precursors.

Early studies on municipal waste incinerators indicated that organic compounds in the gas coupled with high flyash concentrations promote chlorination reactions and subsequent synthesis of D/Fs (Bruce 1993; Townsend and others 1995). Bruce (1993) and Griffin (1986) theorized that this synthesis involves the Deacon reaction:

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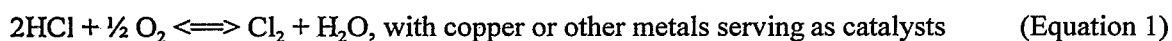
where:

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

The free chlorine formed by the reaction then chlorinates D/F precursors, including halogenated aromatics, through substitution reactions. Sulfur has been shown to interfere with the Deacon reaction, and thereby decreases D/F formation (Griffin 1986; Bruce 1993; Raghunathan and Gullet 1994). Researchers have

theorized that sulfur may affect these results by (1) reducing the Cl_2 to HCl (Equation 2), and (2) altering the copper in the Deacon reaction (Equation 3) (Bruce 1993):

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

where:

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

and:

$$CuO + SO_2 + \tfrac{1}{2} O_2 \Longleftrightarrow CuSO_4 \qquad \text{(Equation 3)}$$

where:

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

De novo synthesis of D/Fs involves many complex reactions that can occur at several stages in the combustion process. However, all *de novo* formation mechanisms appear to depend on solid phase chemistry (Townsend and others 1995). Historically, D/F emissions were believed to be controlled by ensuring good combustion and by controlling temperature, oxygen, and PM (carbon monoxide concentration has been used as a surrogate for good combustion). Recent studies indicate that even in systems achieving good combustion (with low carbon monoxide concentrations), D/F reformation may occur in cooler zones downstream of combustion chambers (Santoleri 1995). Critical operating parameters related to D/F formation in downstream zones include (1) presence of particulates, which allow for solid-phase, metal-catalyzed reactions, (2) appropriate temperature window (approximately 400 to 750 °F), (3) presence of Cl_2 and other precursors, including chlorinated aromatics, and (4) particulate residence time. Poor combustion can increase D/F formation through increased PM (which serves as the reaction site for D/F formation), increased formation of PICs (which could serve as D/F precursors), and increased gas-phase formation of D/Fs.

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Santoleri (1995) summarizes several operating conditions and parameters that are relevant to D/F formation and control as follows:

- Combustion temperatures lower than approximately 1,800 °F or higher than 2,250 °F can lead to higher free Cl_2 emissions and subsequent D/F formation. A rapid quench is recommended to quickly lower the temperature and improve the conversion of Cl_2 to HCl.

- Sulfur and sulfur dioxide have been observed to be effective in reducing Cl_2 to HCl, thereby reducing D/F emissions.

- Downstream zones that potentially collect PM (including boiler tubes, ESP plates, and fabric filters) provide reaction sites that promote D/F formation. More rapid cycling of cleaning processes can shorten the residence time for D/F formation, and decrease D/F emissions.

Overall, researchers have concluded that D/F formation mechanisms in HWC facilities are extremely complex and cannot be predicted accurately with kinetic models or surrogate monitoring parameters such as carbon monoxide or total hydrocarbons (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 1990; 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 chlorinated phenols) 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 or not a given HWC facility will have significant D/F emissions. Therefore, it is anticipated that all HWC facilities will need to test for D/Fs. The remainder of this section discusses key operating parameters that should be considered for D/F testing.

4.1.1   Particulate Hold-Up Temperatures

Several studies have demonstrated the importance of identifying critical operating parameters associated with D/F emissions. Data described in Altwicker and others (1990), Harris and others (1994), Lanier and others (1996), and EPA (1994a, 1996a, 1997a) indicate the importance of inlet temperatures for HWC units equipped with dry APCDs (such as ESPs, fabric filters, or possibly high efficiency particulate air [HEPA] filters). 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 temperature. Thus, dry APCD inlet temperature is a critical operating parameter. The lower temperature of 400 °F, versus 450 °F as prescribed by the current BIF regulations, has been emphasized in evaluations conducted for the MACT standards (EPA 1996a, 1997a).

Additional data indicate that any particulate holdup areas (including boiler tubes and long runs of ductwork) can serve as reaction sites for D/F formation if the temperature profile falls within the D/F formation window. Santoleri (1995), 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. The proposed mechanism is a result of boiler tube corrosion as the tubes trap ash and form deposits. As HCl gas passes over these deposits, the deposits and iron within the tubes react to form Cl_2 and iron chlorides, resulting in conditions conducive for D/F formation. The D/F emissions trend for waste heat recovery boilers is further supported by EPA (1997a), who found that incinerators equipped with recovery boilers have significantly higher D/F emissions than other incinerators. EPA (1997a) noted that the heat recovery boilers preclude rapid temperature quench of combustion gases to a temperature of less than 400 °F. Acharya and others (1991) hypothesized that D/Fs in a boiler could be minimized by only cooling combustion gases to about 800 °F. Although energy recovery might be reduced, this would keep the gases outside of the 400 to 750 °F range.

EPA (1997a) also found elevated D/F emission rates at some LWAKs where formation apparently occurred in extensive runs of ductwork connecting the kilns to the fabric filters. 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 dewpoint prior to the fabric filter.

Results of these studies indicate that, for D/F testing, the relatively low temperature (approximately 400 to 750 °F) areas of particulate holdup downstream of the combustion zone should be emphasized. These areas are conducive to surface-catalyzed D/F formation through mechanisms such as *de novo* synthesis. Available data indicate that PM provides the substrate to act as a chemical reactor, given the appropriate temperature, time, and presence of Cl_2. Thus, any particulate holdup area (including fabric filters, ESPs, HEPA filters, heat recovery boilers, and extensive runs of ductwork) can serve as a reactor for D/F formation.

Particulate holdup temperatures should be considered very carefully in determining the appropriate test condition for D/F testing. Unless the temperature fluctuation across the PM holdup device is negligible, D/F testing should not be performed at normal or average holdup temperatures. D/F formation has been observed to increase exponentially with increases in temperature over the range of approximately 400 to 750 °F (EPA 1994a, 1996a; Lanier and others 1996). Thus, a long-term average temperature limit will not

necessarily ensure that D/Fs remain below the levels observed during a normal temperature test (i.e., the D/F emissions from one minute of operation at 100 °F above normal could not be offset by one minute of operation at 100 °F below normal). Unless a facility can provide a monitoring scheme that will reliably ensure that D/Fs can be maintained below the levels observed during testing at average holdup temperatures, then D/F emissions data should be collected while the facility is operating under maximum particulate holdup temperatures.

4.1.2   Rapid and Partial Liquid Quench Systems

Ullrich and others (1996) describe the reduction of D/F emissions through the use of a rapid liquid quench, which decreases residence time in the D/F formation window. A liquid quench involves rapid quenching (on the order of milliseconds) from combustion temperatures to saturation temperatures of approximately 170 to 185 °F. HWC facilities that provide for rapid flue gas quenching 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 (1997) observed significant increases in D/F levels in the flue gas as post-partial-quench temperatures increased from 711 to 795 °F (prior to the full quench). The observed residence time between the partial quench and full quench chamber 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.

Based on this information, it appears that operating limits on rapid quench systems are unnecessary for the control of D/Fs. However, limits on post-quench temperatures from partial-quench systems are potentially important.

4.1.3   Combustion Conditions

This section provides general information regarding the impact of combustion conditions on D//F emissions. Further industry-specific discussion is provided in Sections 4.3 through 4.6. These discussions are based on the underlying assumption that HWC facilities must operate under combustion conditions that meet or exceed 99.99 percent DRE.

Combustion conditions and associated quality can play a key role in minimizing the formation of D/F precursors, and thus, in potentially minimizing D/F emissions (EPA 1994a, 1996a). Berger and others (1996) describe an increase in D/F, carbon monoxide, and total hydrocarbon emissions through poor combustion in HWIs. High D/F emissions were observed only during the same incineration processes that

included high total hydrocarbon emissions. Gullett and Raghunathan (1997) observed substantial increases in D/F emissions under conditions of poor combustion and carbon monoxide levels greater than 2,000 parts per million (ppm).

In order to assure combustion quality, EPA (1996a) has indicated that the following combustion parameters should be demonstrated during D/F testing and controlled (during facility operation) to minimize D/F precursors:

- Minimum PCC and SCC combustion temperatures
- Maximum combustion gas velocity
- Maximum waste feed rates
- For batch feeds,
    - maximum feeding frequency
    - maximum batch size
    - minimum oxygen concentration
- Maximum carbon monoxide
- Maximum total hydrocarbons

Unfortunately, it is often difficult to determine a direct correlation between an individual combustion parameter and D/F emissions. Combustion processes involve complex physical and chemical interactions. A change in a single independent variable can simultaneously impact several dependent variables. These changes may or may not impact D/F emissions, and the most influential combustion parameters may not always be the ones listed above. These points are demonstrated by the following two examples.

The first example involves minimum combustion temperature. Operating conditions associated with DRE testing, including minimum combustion temperature, are generally believed to result in higher PIC formation (and thus, potentially higher D/F emissions). This should be the case for most systems. However, the opposite has been shown for incinerators feeding containerized wastes. For these units, pilot testing shows that PIC emissions can be minimized by operating at *lower* PCC temperatures (Lemieux and others 1990). Higher PCC temperatures and higher kiln rotation speeds result in rapid heating and rupturing of the containers. Evolution of waste gases from the containers can exceed the rate at which the stoichiometric amount of oxygen can be supplied, resulting in increased organic emissions rates. Lower temperatures may lead to more gradual rupture of waste containers, and less disruptive transients. (The tern "transient" refers to frequent changes in combustion conditions. These changes may be indicated by recurring temperature, carbon monoxide, or total hydrocarbon spikes, or by frequent changes in

combustion pressure.) The impact of this phenomenon on D/F emissions has been confirmed during at least one trial burn at a HWC facility burning containerized wastes. At this facility, dioxin yields were higher at maximum PCC temperatures than at minimum temperatures (EPA 1998c).

The second example involves oxygen concentration. Oxygen concentration is not specifically addressed during many trial burns. In fact, it often varies considerably between test conditions when excess air is used to simultaneously achieve minimum combustion temperature and maximum combustion gas velocity. However, D/F emission rates may be impacted by oxygen levels. Gullett and Lemieux (1994) performed a pilot study to investigate the impact of oxygen concentrations (as well as several downstream parameters) on dioxin yields. Intermediate levels of oxygen (4.7 percent) were found to produce greater dioxin yields than extreme levels (1.7 and 8.9 percent). In addition, oxygen significantly affected the partitioning between dioxins and furans. Increases in oxygen favored formation of dioxins over furans.

These examples illustrate that the relationship between individual combustion parameters and D/F emissions is not necessarily intuitive or readily demonstrated. Key parameters are likely to vary by facility, and the facility-specific key parameters may or may not be those identified in EPA (1996a). Because of these uncertainties, it is recommended that D/F emissions be determined during all of the planned test conditions (e.g., DRE and SRE) at a HWC facility 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 the combustion parameters that should be limited in the RCRA permit to control D/F emissions.

The recommendation for D/F sampling during all test conditions 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 have been conducted in advance of the sampling effort to collect SSRA data, or stack sampling ports may not accommodate all of the necessary sampling trains for consolidated testing. 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 above 100 ppm

As appropriate, permit conditions for the combustion parameters listed in Tables 4-1 and 4-2 should be established based on testing under the conditions indicated above. In addition, a facility-specific review of trial burn and historical operating data should be performed to determine whether transient operations correlate with other operating or feed parameters. If so, then the correlating parameters may be limited in the permit in addition to, or in lieu of, the specific parameters listed in Tables 4-1 and 4-2.

Some HWC units do not operate under the scenarios identified above. For example, a liquid injection incinerator feeding a single high-British thermal unit (Btu) waste stream may sustain very constant temperatures and extremely low carbon monoxide concentrations. Ideally, D/F testing performed in conjunction with the DRE test will demonstrate the combustion parameters indicated in Tables 4-1 and 4-2. However, if this is not possible then historical operating data for the appropriate combustion parameters should be reviewed. Demonstration of absolute maximum or minimum values for combustion parameters during D/F testing may be less critical if the review indicates steady-state operations with very few fluctuations. For this situation, consideration may be given to testing under normal combustion conditions. Periodic reporting to confirm continued absence of transients may be appropriate in lieu of specific permit limits for the parameters listed in Table 4-1. When D/F testing is not performed in conjunction with the DRE test, caution should be exercised to ensure that combustion parameters are not substantially different from levels demonstrated during the DRE test.

The remainder of this section provides additional information on transient conditions, combustion of containerized or batch wastes, and operating at high carbon monoxide levels for units with carbon monoxide limits above 100 ppm.

4.1.3.1   Transient Conditions

The permit writer should review historical operating data to determine whether a facility experiences routine transients, and, if so, the waste feed or operating conditions that cause the spikes should be determined. The feeds or operating conditions causing transients represent candidate conditions for D/F testing. Particular attention should be given to data indicating transients for combustion temperatures, combustion chamber pressure, carbon monoxide, and total hydrocarbons. Instantaneous data may be more useful in defining transients than rolling average data, which inherently dampen spikes.

During D/F testing, the facility should treat difficult-to-burn wastes under operating extremes that may challenge combustion quality. Actual wastes (and not surrogate wastes synthesized from pure compounds) should be used whenever possible. Candidate wastes should be selected based upon a review of the wastes handled at a particular facility. Special consideration should be given to those wastes burned at commercial facilities due to their variation and complexity. Examples of wastes that can cause transients 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
- Batch feeds with high moisture, volatility, or instantaneous oxygen demand

4.1.3.2   Containerized or Batch Wastes

Transient operations due to batch waste feeds are fairly common. D/F testing during batch feed conditions should be performed regardless of carbon monoxide concentrations (which are generally measured downstream of the SCC and which may or may not reflect the transients experienced in the PCC). Based upon EPA (1996a) and Lemieux and others (1990), the following batch feed parameters should be demonstrated during D/F testing:

- Maximum feeding frequency
- Maximum batch size
- Maximum PCC combustion temperature
- Maximum kiln rotation speed
- Minimum oxygen concentration

A trial burn plan for a batch-fed facility should include a description of the procedures used to maintain adequate oxygen while feeding batch or containerized wastes. Unless the oxygen demand from the batch waste is insignificant compared to the oxygen demand of other fuels (e.g., 1-gallon containers fed to the hot end of a cement kiln), EPA (1996a) suggests establishing a minimum oxygen limit at the end of the combustion chamber into which the batch is fed, at the time the batch is fed. Implementation of minimum

oxygen limits at the exit of the PCC on rotary kilns can sometimes be difficult, due to potentially significant gas-phase stratification (Cundy and others 1991). If this is a problem, alternate monitoring locations may need to be considered. Minimum oxygen limits for HWC facilities other than batch-fed units are generally not necessary because emission limits for carbon monoxide will ensure that wastes are not fed to the unit while excess air is at too low a level. However, if a HWC facility operates at conditions that frequently exceed the carbon monoxide limits, the permit writer may consider establishing either a minimum oxygen limit from the trial burn, or requiring an automatic control system to maintain fuel-to-air ratios. Carbon monoxide may not always be a good indicator of combustion efficiency for cement kilns, as discussed later in Section 4.5.

The physical and chemical composition of the batch waste is also important. Key characteristics include volatility, instantaneous oxygen demand, moisture content, and heating value. Historical information on operating trends and AWFCS events should be reviewed in an effort to determine which batch characteristics are most likely to cause transients for a particular HWC 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 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.

4.1.3.3   High Carbon Monoxide

Units with carbon monoxide limits above 100 ppm should perform D/F emissions testing while carbon monoxide levels are maximized. EPA (1994a) evaluated D/F emissions data by normalizing the data for APCD inlet temperature and carbon monoxide. Low carbon monoxide levels (less than 100 ppm) were associated with very low D/F emissions (less than 1 nanogram per dry standard cubic meter [ng/dscm] on a total basis). For carbon monoxide levels greater than 100 ppm, temperature-normalized dioxin emissions were significantly higher (in the range of 10 to 100 ng/dscm on a total basis).

4.1.4   Feed Composition

In addition to the physical waste characteristics that can cause poor combustion, there are several chemical characteristics that can potentially influence D/F emissions. These include chlorine concentration, the presence of metals (such as copper, iron, and nickel) that can act as catalysts in D/F production

mechanisms, the presence of D/F precursors (such as chlorobenzenes and chlorophenols), and the presence of D/F inhibitors (such as sulfur and ammonia). Each of these is discussed below.

4.1.4.1 Chlorine

While the presence of chlorine is necessary for the formation of D/Fs, 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 in full-scale HWC 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. Obviously, no D/Fs could be formed without the presence of chlorine. However, other parameters, such as APCD inlet temperature, are more statistically significant and any potential effect of chlorine feed input is effectively masked.

EPA (1996a) is not proposing to limit the amount of chlorine fed to the HWC facility to ensure compliance with the proposed D/F MACT standards. For D/F testing, chlorine feed rates should be maintained at normal levels (i.e., chlorine should not be biased low). For purposes of this guidance, the term chlorine feed rate refers to total chlorine from all sources, including both organic and inorganic forms. Chlorinated wastes are preferred over non-chlorinated wastes, where the choice exists. However, specific HRA limits on total chlorine are not anticipated based upon the D/F testing.

4.1.4.2 Metal Catalysts

Abundant pilot-scale and fundamental research has shown that certain metals, such as copper, may catalyze the formation of D/Fs. This phenomenon has not been observed during full-scale testing (Lanier and others 1996); however, the testing may have been conducted in a system that was influenced by other, more dominant factors. EPA (1996a) is not proposing to limit the amount of catalytic metals to ensure compliance with the future D/F MACT standards. Wastes or other feed materials containing copper are preferred over feeds without copper during the D/F testing, where the choice exists. However, specific limits on copper (or other catalytic metals) are not anticipated based upon the D/F testing.

4.1.4.3 D/F Precursors

Some HWIs that burn D/F precursors, including chlorobenzenes, chlorophenols, and PCBs, have been shown to have high D/F emissions. EPA (1996a) compared a limited number of facilities that feed known D/F precursors to those that do not feed D/F precursors. This limited study suggested no strong correlation between the level of precursors and D/F formation; however, the issue has not been examined in detail. If a facility burns wastes with significant quantities of D/F precursors, these wastes are preferred over wastes without precursors for D/F testing. Although specific permit limits on D/F precursors are not anticipated, the permit writer may require waste profile tracking to determine whether increased quantities of precursor wastes warrant retesting.

4.1.4.4 D/F Inhibitors

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. Raghunathan and Gullett (1994) and Raghunathan and others (1997) conducted bench and pilot-scale tests of municipal solid waste combustion facilities and concluded that co-firing with coal can effectively reduce D/F emission rates. Significant decreases in D/F emission rates were observed at a sulfur to chlorine ratio of 0.64 (Raghunathan and Gullett 1994). Depletion of active chlorine by sulfur dioxide through a gas-phase reaction appears to be a significant inhibition mechanism, in addition to sulfur dioxide deactivation of copper catalysts. In reviewing the D/F test protocol, the permit writer should ensure that the facility will not burn a high sulfur waste or fuel in greater quantities than during normal operation. The permit writer may require waste and fossil fuel tracking to determine whether burning decreased quantities of sulfur warrant retesting.

4.1.4.5 Other Factors

Other waste feed components may also 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 1998; Lemieux and Ryan in press). Although the effects of the presence of bromine has not been clearly established during full-scale testing, permit writers should be aware of its potential when selecting waste feeds for trial burns, particularly if the facility burns brominated waste during normal operations.

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4.1.5   D/F Control Technologies

Some facilities may install specific D/F control technologies. These include carbon injection, carbon beds, catalytic oxidizers, and D/F inhibitor technologies. If a facility uses one of these technologies, then permit limits on key operating parameters should be established during D/F testing. Relevant operating parameters are identified in EPA (1996a, 1996d).

4.2   OPERATING PARAMETERS ASSOCIATED WITH D/F PRODUCTION

Based on a review of existing information, this guidance prioritizes operating parameters and conditions associated with D/F formation as primary, secondary, or tertiary. These hierarchial designations should not be considered absolute, but are intended to emphasize the relative importance of demonstrating various operating parameters during D/F testing and limiting those parameters in the final RCRA permit. Parameters related to combustion conditions are categorized as primary; however, this designation should be tempered by the previous discussion for steady-state systems. A description of primary, secondary, and tertiary operating parameters follows:

- Primary operating parameters are those that have shown the highest correlation with D/F emission rates during full-scale testing, and are expected to dominate D/F formation. These parameters should always be demonstrated during the D/F test, and should be limited in the permit by specific quantitative limits. These operating parameters relate to either surface-catalyzed D/F formation, or the use of specific D/F control technologies and include:

  - Inlet temperature to dry APCDs
  - Temperature profiles over particulate holdup areas (including long runs of ductwork, economizers, and boiler tubes)
  - Key operating parameters for specific D/F control technologies
  - Combustion parameters listed in Tables 4-1 and 4-2

- Secondary operating 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 need to be demonstrated during the D/F test and limited in the permit, depending on the significance of these parameters for a given system configuration and the presence or absence of dominant primary parameters. Secondary parameters include:

  - Conditions other than combustion quality that could lead to the formation of organic precursors (such as organics from raw materials in cement kilns and LWAKs)
  - Flue gas temperatures due to partial quenching

- Tertiary operating parameters are those that relate to feed composition. These operating parameters have been the subject of fundamental and pilot-scale research on D/F

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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 are not expected to be limited in the permit by specific feed rate limits. Tertiary 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)

The following subsections discuss critical D/F operating parameters in more detail as they relate to specific types of HWC facilities.

4.3   D/F EMISSIONS FROM HWIS

HWIs include rotary kiln, liquid injection, fluidized bed, and fixed hearth designs. Commercial HWIs typically accept hazardous waste from generators throughout the United States. Waste feeds to these units can be highly variable, for example waste feed material may include low- and high-Btu liquids, as well as solids from laboratory packs and soils contaminated with low levels of RCRA hazardous wastes. Large chemical complexes may operate captive HWIs that treat waste feeds generated on site and from corporate affiliates off site. These wastes may also be highly variable, especially if the facility burns a number of wastes from different production operations and does not have the capability to blend the wastes to a consistent specification. Small chemical companies may generate only one or two waste streams. These wastes are typically more predictable and homogeneous.

HWIs are generally associated with two-stage APCDs (EPA 1996a) that first cool hot flue gases and then remove PM, metals, and organics. Most HWIs use wet APCDs (three were cited that use dry scrubbers). Typical APCDs include (1) packed towers, spray dryers, or dry scrubbers for temperature reduction and acid gas control and (2) venturi scrubbers, wet or dry ESPs, or fabric filters for PM, metal, and organics control. Some new technologies are being developed, and several facilities are injecting activated carbon in the spray dryers for control of D/Fs, non-D/F organics, and mercury (EPA 1996a). Some HWIs may have heat recovery boilers that affect D/F emissions.

The level of D/F emissions from HWIs 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 4.1 apply to HWIs.

Table 4-1 summarizes operating parameters associated with D/F emissions from HWIs. Recommended averaging periods are discussed further in Section 8.0. Depending on the system configuration, demonstration of operating parameters associated with D/F formation may coincide with both the DRE and SRE test conditions. If dry APCD equipment or heat recovery devices are present in the HWI system, the temperature profile across these systems is recognized as a primary operating parameter directly related to D/F formation. Therefore, for these systems, D/F data collection may be performed in conjunction with SRE testing (unless the facility can adjust inlet temperature to obtain the requisite temperature profiles during DRE testing). Demonstration of operating parameters affecting combustion efficiency (especially for transient operations, units burning containerized wastes, or high carbon monoxide situations) will most likely coincide with the DRE test condition.

Facilities with more predictable, homogeneous waste feeds, few operating fluctuations, and no particulate holdup devices may opt to collect D/F emissions data during a risk burn conducted under normal operating conditions. Waste feed selection is based on a representative waste stream, with a preference for D/F precursors such as chlorophenols and minimal amounts of D/F inhibitors (such as sulfur).

4.4 D/F EMISSIONS FROM BOILERS

General boiler designs are discussed by EPA (1994a), and requirements for boilers burning hazardous waste are defined in 40 CFR Part 266.100 et seq. Boilers recover the heat from hazardous waste combustion to pressurize water. The three most common boiler designs used for treating hazardous waste include firetube boilers, watertube boilers, and stoker-fired boilers. Most boilers treating hazardous waste are on-site units at chemical production facilities. Most boilers do not have APCDs. Historically, emissions tests from boilers have focused on metals and PM, and the database for D/F emissions from boilers is not as extensive as it is for D/F emissions from HWIs and cement kilns.

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 operating parameters associated with D/F and other organic emissions from boilers. Recommended averaging periods are discussed further in Section 8.0. Depending on the system configuration, demonstration of operating parameters associated with D/F formation in boilers may coincide with both the DRE and SRE test conditions.

TABLE 4-1

OPERATING PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM HWIS AND BOILERS

	Operating Parameters	Most Likely Achieved During	Parameter Type/Suggested Averaging Periods*	How Limit is Established	Other Considerations
PRIMARY OPERATING PARAMETERS					
Surface-Catalyzed Formation: (Dry APCD) Surface-catalyzed formation is a predominant D/F formation mechanism for post-combustion dry APCD particulate holdup areas operating at temperatures between 400-750 °F.	Maximum dry ESP inlet temperature	SRE test, unless a variable quench is used	Group A: Dual 10 minute/1 hour	Average of three maximum 10-minute RAs/Average of three maximum HRAs	Particulate loading should not be biased low during the test, based upon a review of: - ash feed rate - combustion gas velocity - APCD operation Ongoing PM control is assured by limits on APCD operating parameters established during the PM test.
	Maximum FF inlet temperature				
	Maximum HEPA filter inlet temperature				
	Boiler exit temperature	Any test that achieves the critical temperature window	Group A: Dual 10 minute/1 hour	Average of three minimum or maximum 10-minute RAs/Average of three minimum or maximum HRAs (depending on which edge of the boiler operating range is in the critical temperature window)	
D/F-Specific Control Technology: D/F-specific control technologies include carbon injection, carbon bed, and inhibitor technologies.	If a specific control technology is used to limit D/F emissions, operating limits should be established per EPA (1996a, 1996d).				

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TABLE 4-1

OPERATING PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM HWIS AND BOILERS (Continued)

	Operating Parameters	Most Likely Achieved During	Parameter Type/Suggested Averaging Periods*	How Limit is Established	Other Considerations
PRIMARY OPERATING PARAMETERS (Continued)					
Combustion Conditions Related to Formation of D/F Precursors: (*These parameters should also be limited to control non-D/F organics, as discussed in Section 5.1*) Operating parameters to limit D/F precursors from poor combustion are most critical for transient operations.	Minimum combustion temperature, each chamber Exception: Maximum PCC temperatures should be demonstrated for units burning containerized wastes	DRE	<u>Group A:</u> Dual 10-minute/1 hour	Average of three minimum 10-minute RAs/Average of three minimum HRAs	
Transient operations may be identified by frequent temperature, carbon monoxide, oxygen, or total hydrocarbon spikes.	Maximum combustion gas velocity	DRE/ SRE	<u>Group A:</u> 1 hour	Average of three maximum HRAs	
Operating parameters related to good combustion may be less critical for steady-state operations. Although demonstration of these operating parameters during DRE conditions is preferred whenever possible, D/F testing at normal combustion conditions may be considered for some steady-state units. Record keeping and periodic reporting to confirm continued absence of transients may be considered in lieu of HRAs or 10-minute averages.	Maximum waste feed rate, each location	DRE	<u>Group A:</u> 1 hour	Average of three maximum HRAs	Limits should be established for: - maximum organic liquids to PCC - maximum aqueous liquids to PCC - maximum sludges to PCC - maximum solids to PCC - maximum organic liquids to SCC - maximum aqueous liquids to SCC

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TABLE 4-1

OPERATING PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM HWIS AND BOILERS (Continued)

	Operating Parameters	Most Likely Achieved During	Parameter Type/Suggested Averaging Periods*	How Limit is Established	Other Considerations
PRIMARY OPERATING PARAMETERS (Continued)					
Combustion Conditions Related to Formation of D/F Precursors: (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.		Wastes with physical properties that can cause combustion transients (as discussed in Section 4.1) should be selected.
	Batch feed conditions: - batch size - batch frequency - minimum oxygen level - maximum PCC temperature - maximum kiln rotation speed	DRE	<u>Group B:</u> Per batch <u>Group A:</u> 1 hour	Batch: - size demonstrated during test - frequency demonstrated during test - oxygen level demonstrated during test Average of three maximum HRAs	Test wastes with high volatility and oxygen demand.
	Maximum carbon monoxide and total hydrocarbons	DRE	<u>Group A:</u> 1 hour	Average of three maximum HRAs, or 100 ppm carbon monoxide, whichever is higher	None

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TABLE 4-1

OPERATING PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM HWIS AND BOILERS (Continued)

	Operating Parameters	Most Likely Achieved During	Parameter Type/Suggested Averaging Periods*	How Limit is Established	Other Considerations
SECONDARY OPERATING PARAMETERS					
Rapid High Temperature Formation: (Wet APCD) May be a concern for partial quench situations with post-partial quench gas temperatures between 570-800 °F. Not a concern for rapid wet quench systems that cool gases to saturation temperatures within milliseconds.	Maximum post-partial quench gas temperature	Any test condition that achieves the critical temperature window for D/F formation	Group A: Dual 10-minute/1 hour	Average of three maximum 10-minute RAs/Average of three maximum HRAs	None
TERTIARY OPERATING PARAMETERS					
Feed Composition: Wastes should be chosen based on consideration of chlorine and D/F precursors, catalysts, and inhibitors.	Total Chlorine D/F Precursors D/F Catalysts 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 4.1.

Notes:
APCD	= air pollution control device	FF	= fabric filter	RA	= rolling average
D/F	= dioxins and furans	HEPA	= high efficiency particulate air	SCC	= secondary combustion chamber
DRE	= destruction and removal efficiency	HRA	= hourly rolling average	SRE	= system removal efficiency
EPA	= U.S. Environmental Protection Agency	PCC	= primary combustion chamber		
ESP	= electrostatic precipitator	PM	= particulate matter		

* = Hourly and 10-minute rolling averages are specified as examples, but other averaging periods and techniques may be considered. When establishing permit limits that are based on the average of the three highest (or lowest) rolling averages, it is important to ensure that the test is conducted in a manner that only allows for normal variability about a central value. For example, it would not be acceptable to conduct the test at 15 minutes of artificially high carbon monoxide concentrations, with the remainder of the test at normal levels. One way to avoid this is to establish the permit limit as the time-weighted average over all runs. Averaging periods are also discussed in Section 8.0

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As explained in Section 4.1, boiler tubes may serve as particulate holdup areas and lead to D/F emissions. D/Fs may form when boiler flue gases are within the D/F formation temperature window. Because boilers typically have no rapid quench, the time and temperature window for D/F formation may be large. Therefore, boiler exit temperature (which can include temperatures at heat exchangers and economizers) is considered a primary operating parameter for D/F formation and control. Collection of D/F emissions data for boilers is recommended during conditions that achieve boiler exit temperatures in the upper end of (but well within) the 400 to 750 °F range. For example, for a facility with boiler exit temperatures ranging from 350 to 550 °F, D/F testing at the boiler exit temperature of 550 °F would be preferred over testing at the exit temperature of 350 °F. Boiler 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.

Demonstration of parameters related to combustion quality 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 be evaluated by the permit writer prior to trial burn to determine the potential for transients. Demonstration of operating parameters affecting combustion efficiency will most likely coincide with the DRE test condition.

Demonstrating key operating parameters related to combustion quality can sometimes be problematic for boilers based on potential test condition conflicts (Schofield and others 1997). For example, a facility with a fixed combustion air flow rate burning a single high-Btu waste stream will not be able to demonstrate minimum combustion temperature and maximum feed rate simultaneously. Thus, two test conditions may be needed to demonstrate all of the key control parameters related to combustion. However, if combustion air can be controlled, then temperature could be minimized and feed rate could be maximized simultaneously by adjusting the amount of combustion air.

In some cases, D/F testing during the DRE condition may not be possible for reasons discussed in Section 4.1 (e.g., because of sampling port limitations, or because the risk testing is being performed separately from performance testing). In these situations, a facility with predictable, homogeneous waste feeds and few combustion transients may opt to test during a test condition that represents normal combustion conditions. The facility would still need to demonstrate boiler exit temperatures in the upper end of the 400 to 750 °F range.

In general, facilities with highly variable operations should collect D/F emission samples during DRE conditions and any other condition that is necessary to achieve boiler exit temperatures in the upper end of

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the 400 to 750 °F window. This could result in multiple test conditions. Facilities with more predictable, homogeneous waste feeds and few combustion transients may need to test only during the test condition achieving the requisite boiler exit temperatures.

Permit writers should also be aware of soot blowing practices at boilers because high particulate loading due to this practice could affect D/F emissions. The permit writer should determine normal sootblowing procedures from the facility's operating record. Sootblowing should be performed during D/F testing to capture the potential impact of higher particulate loading on D/F emissions. However, sootblowing should not be performed on a more rapid cycle than normal, because this could potentially shorten the residence time for D/F formation, and decrease D/F emissions (Santoleri 1995). EPA (1992b) provides guidance on structuring test runs to reflect sootblowing practices.

4.5   D/F EMISSIONS FROM CEMENT KILNS

Background information on potential D/F emissions from cement kilns is summarized by EPA (1994a, 1996a). Cement kilns may use hazardous waste as a supplementary fuel while producing a salable product. In general, the operating envelope of cement kilns is dictated in large part by the American Society for Testing and Materials (ASTM) requirements for their final product. Cement kilns also have regions that operate at high temperatures approaching 3,000 °F. Based on these characteristics, issues related to good combustion and minimum combustion temperatures are less relevant, as compared to HWIs and boilers. Also, because of the chemical composition of the raw materials, carbon monoxide and total hydrocarbon concentrations may not always serve as indicators of good combustion. According to EPA (1996a) all hazardous waste burning cement kilns use either fabric filters or ESPs as APCDs.

Table 4-2 summarizes operating parameters associated with D/F and other organic emissions from cement kilns and LWAKs. Data presented by Harris and others (1994) and Lanier and others (1996) demonstrate that D/F emissions from cement kilns increase exponentially with increases in inlet temperatures to the dry APCD while within the D/F formation window (400 to 750 °F). Given these conditions, maximum inlet temperature to the dry APCD system is the primary operating parameter related to D/F emissions for cement kilns. Collection of D/F emission data should occur during conditions that achieve maximum APCD inlet temperatures. These conditions may coincide with the SRE test if the APCD inlet temperature cannot be independently controlled from combustion temperature.

TABLE 4-2

OPERATING PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM CEMENT KILNS AND LWAKS

	Operating Parameters	Most Likely Achieved During	Parameter Type/Suggested Averaging Periods*	How Limit is Established	Other Considerations
PRIMARY OPERATING PARAMETERS					
Surface-Catalyzed Formation: (Dry APCD)	Maximum dry ESP inlet temperature	SRE	Group A: Dual 10 minute/ 1 hour	Average of three maximum 10-minute RAs/Average of three maximum HRAs	Ongoing PM control is assured by limits on APCD operating parameters established during the PM test.
Surface-catalyzed formation is a predominant mechanism for post-combustion dry particulate holdup areas operating at temperatures between 400-750 °F.	Maximum FF inlet temperature				
	LWAKS: Maximum inlet temperature to extensive runs of ductwork	SRE	Group A: Dual 10 minute/ 1 hour	Average of three maximum 10-minute RAs/Average of three maximum HRAs	
D/F-Specific Control Technology: D/F-specific control technologies include carbon injection, carbon bed, and inhibitor technologies.	If a specific control technology is used to limit D/F emissions, operating limits should be established per EPA (1996a and 1996d).				

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TABLE 4-2

OPERATING PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM CEMENT KILNS AND LWAKS (Continued)

	Operating Parameters	Most Likely Achieved During	Parameter Type/Suggested Averaging Periods*	How Limit is Established	Other Considerations
SECONDARY OPERATING PARAMETERS					
Good Combustion to Control D/F Precursors: *Note: These parameters should also be limited to control non-D/F organics, as discussed in Section 5.2* Applicable only to kilns that feed wastes at locations other than the hot end of the kiln.	Batch feed conditions: - batch size - batch frequency - feed location - minimum oxygen - maximum temperature at feed location	Any test	<u>Group B</u>: Per batch	Batch: - size demonstrated in test - frequency demonstrated in test - location demonstrated in test - oxygen level demonstrated in test - temperature demonstrated in test	Test wastes with high volatility/oxygen demand. Kiln rotation speed is generally limited by the production process and need not be limited for cement kilns.
Control of Precursors from Raw Material Organics: *Note: These parameters should also be limited to control non-D/F organics, as discussed in Section 5.2* Total hydrocarbons originating from raw materials may lead to formation of chlorinated organics that could potentially serve as D/F precursors.	Maximum total hydrocarbons, as measured at both the main and bypass stacks, not to exceed 20 ppmv per BIF	SRE	<u>Group A</u>: 1 hour	20 ppmv, regulatory limit, at the monitoring location used for BIF compliance. Limits for other locations will be considered based on the results of the SSRA.	Temporary total hydrocarbon monitors may be needed if the facility does not normally measure total hydrocarbons.

TABLE 4-2

OPERATING PARAMETERS ASSOCIATED WITH D/F EMISSIONS FROM CEMENT KILNS AND LWAKS (Continued)

	Operating Parameters	Most Likely Achieved During	Parameter Type/Suggested Averaging Periods*	How Limit is Established	Other Considerations
TERTIARY OPERATING PARAMETERS					
Feed Composition: Total chlorine and the presence of D/F inhibitors such as sulfur in coal should be considered during selection of wastes and other fuels.	Total Chlorine		These are not continuously monitored parameters, but pertain to selection of wastes and fuels for the testing. Conditions for waste profile tracking may be specified by the permit writer.		Normal to high levels of total chlorine should be maintained during the D/F testing.
	D/F Inhibitors				Coal should not be fed at higher than normal rates during the D/F testing, and low-sulfur coal is preferable if the facility uses coal with varying sulfur content.

Notes:

APCD	=	air pollution control device	ESP	=	electrostatic precipitator	ppmv	=	parts per million volume
BIF	=	boiler and industrial fur	FF	=	fabric filter	RA	=	rolling average
D/F	=	dioxins and furans	HRA	=	hourly rolling average	SRE	=	system removal efficiency
EPA	=	U.S. Environmental Protection Agency	PM	=	particulate matter			

* = Hourly and 10-minute rolling averages are specified as examples, but other averaging periods and techniques may be considered. When establishing permit limits that are based on the average of the three highest (or lowest) rolling averages, it is important to ensure that the test is conducted in a manner that only allows for normal variability about a central value. For example, it would not be acceptable to conduct the test at 15 minutes of artificially high carbon monoxide concentrations, with the remainder of the test at normal levels. One way to avoid this is to establish the permit limit as the time-weighted average over all runs. Averaging periods are also discussed in Section 8.0.

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The operating parameters in Table 4-2 related to combustion conditions are limited to situations where kilns feed hazardous waste at locations other than the hot end of the kiln. Controls on waste charging rate and kiln oxygen concentration are recommended because wastes injected at mid- or feed-end locations may not experience the same elevated temperatures and long residence times as those wastes injected 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).

Table 4-2 does not establish control parameters related to combustion of hazardous wastes introduced to the hot end of kilns. 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 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. However, facility-specific DRE testing should be sufficient to reveal design problems.

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. The chlorination of these hydrocarbons is a potential source of chlorinated hydrocarbon emissions, including D/F precursors such as monochlorobenzene (Dellinger and others 1993). Therefore, D/F testing should 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 20 parts-per-million volume (ppmv) at the monitoring location used for BIF compliance. 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 and others (1993) observed an inverse relationship between total hydrocarbons and stack oxygen concentrations. The organic content of the raw material can also significantly influence hydrocarbon levels, but the raw materials are not easily controlled for the purpose of testing. If total hydrocarbon levels increase substantially due to changes in raw materials, then re-testing may be necessary. Organic emissions from LWAKs are generally expected to be less than those from cement kilns. This is because the feed material is usually shale or slate with low organic carbon content. However, the objectives for maximizing total hydrocarbons still apply, consistent with those provided for cement kilns.

In the context of D/F and other organic testing, total hydrocarbons are used as an operating 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 as an indicator of good combustion or combustion efficiency. The SSRA quantifies risks from organic emissions from the HWC facility, regardless of source. Therefore, facilities that only monitor carbon monoxide under the BIF regulations (some LWAKs), or cement kilns that only monitor carbon monoxide or total hydrocarbons in a bypass stack, may need to install temporary total hydrocarbon monitors on the main stack prior to and during the D/F and other organic tests to ensure that total hydrocarbon emissions are being maximized. The need for permanent total hydrocarbon monitoring is assessed by the permit writer after the SSRA is completed and potential risks are compared to target risk levels. Carbon monoxide may not always be a good indicator of organic emissions from cement kilns. Carbon monoxide is generated during the calcining of calcium carbonate, and may also be formed at the kiln exit where some of the total hydrocarbons from the raw materials are oxidized.

Normal levels of chlorine in wastes should be maintained during D/F and other organic emissions testing. It has been proposed that the highly alkaline environment in a cement kiln scavenges available chlorine, making it unavailable for chlorination of organics. However, equilibrium calculations show lower chlorine capture at high temperatures and conversion of HCl to Cl_2. Thus, even a highly basic chemical species such as calcium hydroxide would not be expected to effectively control chlorinated hydrocarbon formation (including D/Fs) at temperatures above 400 °F (Dellinger and others 1993).

Naturally occurring D/F inhibitors, such as sulfur, are expected to be present in the coal used for co-firing a cement kiln. During the D/F testing, coal should not be fed at higher-than-normal rates, and low sulfur coal is preferred if a facility uses several coal suppliers. Other potential D/F inhibitors, such as calcium, are already present in the raw materials.

Metal catalysts in the waste are not expected to be relevant to D/F testing at cement kilns. Spiking wastes with copper were 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 studied as D/F catalysts (iron and aluminum) are major ingredients in cement kiln raw materials.

D/F precursors at cement kilns are expected to be dominated by precursors in the raw material, and not by precursors in the waste. However, if a facility burns wastes with significant quantities of D/F precursors, these would be preferred over wastes without the precursors.

4.6 D/F EMISSIONS FROM LWAKS

The operation of LWAKs is similar to cement kilns in that (1) the operating temperature range is dictated by ASTM consideration of the final product and (2) temperature at the hot end varies from 2,050 to 2,300 °F (EPA 1996a). Combustion gas exit temperatures vary from 300 to 1,200 °F depending on the feed and system design. LWAKs typically burn only high-Btu, liquid fuel, and do not burn wastes at locations other than the hot end. According to EPA (1996a), all LWAKs using hazardous waste as a fuel use fabric filters for PM control.

Table 4-2 summarizes operating parameters associated with D/F and other organic emissions. As with cement kilns, dry APCD inlet temperature is the primary operating parameter related to D/F formation. The need to demonstrate combustion parameters should be evaluated on a case-by-case basis. As appropriate, permit writers may also wish to consider combustion parameters as permit conditions. LWAKs do not operate at combustion temperatures as high as those in cement kilns. However, the potential for combustion transients may be minimized because LWAKs typically only burn high-Btu, liquid wastes in the flame zone.

An additional concern for some LWAKs is the use of long runs of duct work (between the kiln, fabric filter, and stack) that can lead to particle entrainment and high D/F emissions. This particulate holdup area should be evaluated as a primary issue related to D/F formation. D/F emission data collection is most appropriate during the upper end of the temperature operating envelope (SRE) due to the importance of the inlet temperature to the dry APCD and duct work.

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5.0   ORGANIC EMISSIONS OTHER THAN DIOXINS AND FURANS

Completion of human health and ecological SSRAs includes the evaluation of organic emissions other than D/Fs (EPA in press a, in press b). EPA has conducted research to identify the types and quantities of organics emitted from HWC facilities (EPA 1997c; Ryan and others 1996, 1997; and Midwest Research Institute and A.T. Kearney 1997). These research efforts indicate frequent detection of volatile and semivolatile organics including chloro-, bromo-, and mixed bromochloro-alkanes, alkenes, alkynes, aromatics, polyaromatics, and D/Fs; nitrogenated and sulfonated organics; and short-chain alkanes (such as methane and propane). Additional semivolatile compounds detected include oxygenated compounds (PAHs and heterocycles), phthalates, phenols, halogenated mono- and polyaromatics, and nitrogenated and sulfonated compounds. EPA (1997c) 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 supports ongoing research to improve the identification and quantification of organic emissions. However, uncertainty remains regarding the full suite of organic emissions from HWC facilities and associated potential risks. Therefore, it is anticipated that all HWC facilities will need to test for organic emissions to assess potential risks on a site-specific basis.

Testing for organic emissions should accomplish the following two 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

- Completion of a mass balance for total organics (including nontoxic organics) to reduce and evaluate the uncertainty associated with the risk assessment process

Target analyte lists for identifying specific organics during laboratory analysis are provided in Appendix B of this document. Standard EPA methods (1996g) can be used to identify and quantify many organics that are potentially toxic, persistent, and bioaccumulative, such as PCBs and PAHs. For volatile and semivolatile organic compounds, SW-846 Methods 8260 and 8270 gas chromatography/mass spectrometry (GC/MS) procedures are preferred (EPA 1996g). Finally, a MS library search to tentatively identify nontarget compounds is recommended. Tentatively identified compounds that could significantly contribute to risk should be confirmed and quantified through the use of known standards.

The EPA methods, as written, are intended as guidance and should be used as starting points for the development of standard operating procedures that will actually be used. For collection of SSRA emissions data, method flexibility is allowed and guidance on appropriate method modifications is

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provided in SW-846. (Refer to Chapter 2 of EPA [1996g] and the applicable methods.) However, the facility must be able to demonstrate and document that the methods used to generate the data meet the data quality objectives (DQO) for the particular application. Other methods not found in SW-846 may also be used provided that the user can demonstrate and document the methods used to generate data that meet the appropriate DQOs.

Unfortunately, only a limited number of organic compounds can be accurately identified and quantified using standard stack gas sampling and analysis methods. The mass of organic emissions that cannot be readily identified and quantified using standard EPA (1996g) methods is estimated using the TO procedure which sums organic fractions determined for three boiling point ranges (EPA 1996f). The TO procedure is discussed further in Appendix B. TO values can be good indicators of uncertainty in the SSRAs because they serve as a measure of the fraction of TO mass that has not been identified and quantified (TO mass minus the total mass of speciated compounds). Thus, a TO determination should be performed to supplement the organic emissions testing at each HWC facility.

An additional consideration in developing planned sampling and analytical procedures is that many organics lack EPA toxicity values, or they may not be toxic. These compounds are typically not included on standard target analyte lists. However, an important advantage of detecting, identifying, and quantifying as many organics as possible is the reduction of uncertainties associated with the risk assessment process. Determinations for methane, propane, and other short-chain aliphatics add little cost to the emissions testing, and can potentially alleviate concerns about the percentage of the total organic mass that might be toxic. This is discussed in more detail in Appendix B.

Operating parameters and conditions affecting organic emissions are expected to vary between different types of HWC units. The following sections provide some guidelines regarding differences in operating parameters for HWIs, boilers, cement kilns, and LWAKs.

5.1   ORGANIC EMISSIONS FROM HWIS AND BOILERS

The generation of organic PICs from HWIs and boilers is generally associated with poor combustion (conditions related to time, temperature, and turbulence). Berger and others (1996) documented the effects of inefficient burner operation and oxygen control in the PCC and SCC of HWIs. These conditions led to incomplete combustion and subsequent increases in flyash and carbon monoxide and total hydrocarbon concentrations. In general, adequate design and operation of the combustion zone operating parameters

ensure the availability of excess oxygen and destruction of combustion gases in the SCC. Historically, levels of oxygen, carbon monoxide, and total hydrocarbons have been used as surrogates of good combustion to minimize PIC emissions.

Mixing (turbulence) with oxygen also is critical in order to minimize production of fly ash and PM, which can be correlated to PIC production (Berger and others 1996). Different organic wastes will vary in their tendency to form flyash and PM and PICs. Other examples of operating conditions that could lead to increased PIC formation are as follows:

- 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 conditions of low oxygen and incomplete combustion

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

- Insufficient temperatures in either the PCC or SCC leading to incomplete combustion

These types of operating issues typically are addressed during performance testing under DRE conditions. Historically, DRE tests have included operating conditions that result in minimum combustion temperatures in the PCC and SCC, maximum carbon monoxide emissions, maximum flue gas velocity or flow, and maximum feed rate of each waste type (EPA 1989, 1997f). Therefore, a successful DRE test should result in the maximum organic PIC emissions for HWIs and boilers.

The operating parameters associated with organic emission testing for HWIs and boilers are the same as those identified in Table 4-1. These parameters include:

- Combustion temperature
- Combustion gas velocity
- Waste feed rates
- Waste composition
- Carbon monoxide and total hydrocarbon levels

These parameters are usually demonstrated in conjunction with the DRE test condition; however, there may be situations where collection of non-D/F organic emissions data would occur during a separate risk burn test at normal operating conditions. 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. Facilities may request that the permitting authority allow testing at normal conditions provided that the facility can establish a

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monitoring plan and is willing to accept permit conditions to ensure that the test conditions are representative of long-term operations. In all cases, the permit writer has a responsibility to ensure that permit condition based on the non-D/F organic testing will be protective. Therefore, a permit writer's decision to approve testing during normal (or average) conditions will depend on the extent to which those conditions represent potential emissions and risks over the permitted operating range. 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.

Waste selection for PIC testing at HWIs and boilers can be very important, because the types of organic PICs may relate directly to the chemical composition of the waste. Actual wastes, and not surrogate wastes synthesized from pure compounds, should be used whenever possible. However, 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. For example, a commercial facility burning containerized wastes may only have a few drums from each generator. A combination of real waste and simulated wastes should be used in this situation. In the case of containerized wastes, it will generally be more important to focus on maximizing the amount of volatile material within each container, as discussed in Section 4.1.3.2, than to use a real waste with less oxygen demand.

When choosing actual wastes, the emphasis should be on high quantity, routine, and recurring waste streams. 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 location into the HWC 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 each feed location into the HWC unit over a given period for:
  - heating value
  - percentage total chlorine
  - percent ash
  - percent water
  - percent solids
  - viscosity (as appropriate)
  - percent sulfur
  - concentrations for each metal of concern

Candidate wastes for organic emissions testing should be recommended and justified 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 trial burn. Efforts should be made to schedule the trial burn for a time period when the target wastes will be available. However, waste selection may need to be evaluated a few weeks prior to the trial burn based on actual waste stockpiles or scheduled waste receipts.

The facility should also provide protocols for monitoring and tracking waste stream information on an ongoing basis. The protocols should include methods and procedures for comparing future waste characteristics to the wastes burned during the organic emissions testing. This information may be used to determine the potential need for retesting.

5.2   ORGANIC EMISSIONS FROM CEMENT KILNS AND LWAKS

Sections 4.5 and 4.6 describe how conditions related to good combustion are less relevant for cement kilns and LWAKs than for HWIs and boilers. This also applies to emissions of organics other than D/Fs. The design basis of a cement kiln rarely leads to poor combustion. However, naturally occurring organics are driven out of the raw materials at the cold end of the kiln.

The operating parameters associated with organic emissions from cement kilns and LWAKs are the same as those identified in Table 4-2. Conditions relative to good combustion are applicable only to cement kilns and LWAKs that feed wastes at locations other then the hot end of the kiln. Conditions relative to raw material organics are most likely to be achieved during a high temperature or SRE test.

Selection of wastes burned at the hot end of a cement kiln or a LWAK is expected to be less complex than for HWIs and boilers, because wastes are blended to meet fuel specifications. However, the waste

characterization information discussed in Section 5.1 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, an alternate ranking scheme would need to be developed to reflect the most prevalent waste codes and toxic, persistent, and bioaccumulative constituents in the blended fuel. The information on minimum, maximum and average physical and chemical characteristics would be provided for the as-blended fuel.

6.0 METAL EMISSIONS

Metal emissions from HWC facilities are primarily dependent on metal volatility and APCD type, rather than type of HWC facility. Therefore, this subsection focuses primarily on volatility groupings and APCDs and associated PM controls. Metals are currently regulated under EPA's BIF rule (40 CFR 266 Subpart H) and under omnibus authority of Section 3005(c)(3) of RCRA and 40 CFR 270.32(b)(2). Additional information on approaches for establishing permit limits for metals is found in EPA (1992b, 1997f, 1997g, 1997h, 1997i, and 1997j). In general, HRA metal feed rate limits are established in RCRA Part B permits based on either a BIF Tier I approach, or high temperature (SRE) test results. The BIF Tier I approach assumes no removal of metals. The SRE test involves quantifying metal contents of waste feeds, spiking with specific metals during SRE testing, stack gas sampling and analysis, and determining risk-based limits based on potential human health risks through the direct exposure (inhalation) pathway. The 10 BIF metals originally listed in 40 CFR 266 Subpart H include antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, silver, and thallium. Nickel and selenium were later regulated through omnibus authority of RCRA (EPA 1992a). While antimony, arsenic, and selenium typically exhibit only weak metallic properties and may commonly be referred to as metalloids, they are defined here as metals for simplicity.

The traditional approach of establishing HRA feed rate limits based on either a BIF Tier I approach or from an SRE test is required for BIFs and is recommended for most HWIs. However, the emission rates associated with maximum SRE or Tier I metal feed rates could exceed target risk levels when evaluated in multi-pathway SSRAs. Because the SSRAs include direct and indirect exposure routes for all contaminants, it is expected that metal emission limits (in the final RCRA permits) will be lower than those based on BIF air modeling approaches and the direct inhalation pathway. Lower limits are especially likely for mercury, because of its propensity to bioaccumulate, and for nickel, because it will now be evaluated as a potential carcinogen through the direct inhalation exposure route (EPA 1998a, in press a).

A facility has two options for achieving the target risk levels using feed rate controls if the emission rates corresponding to a BIF Tier I approach or from an SRE test are likely to exceed target risk levels. First, the facility should determine how far the emission and feed rates should be lowered to meet target risk levels. In some cases, the SRE test may be expanded to include more metals, or spiking of wastes with specific metals may no longer be appropriate (in general, spiking with mercury is discouraged). Next, the facility should evaluate whether compliance with the reduced feed rate limits can be achieved on an HRA

basis. If so, the net result of the SSRA would simply be to lower the HRA metal feed rate permit limits from those established using BIF procedures.

If lower HRA feed rate limits will not allow sufficient operating flexibility, the facility may opt to conduct a separate risk burn at normal metal feed rates to establish long-term feed rate limits, in addition to the traditional HRA limits. Facilities that wish to use metals emissions data collected during normal operating conditions in the SSRA will be subject to a dual testing and permitting scheme. Permit conditions will be based on the following tests:

- A SRE test, to establish HRA limits and to demonstrate that maximum emissions meet BIF emission limits (or risk-based emission limits considering only inhalation for HWIs)

- A normal test, to establish long-term average operating limits and to generate emissions data for evaluation in the multi-pathway SSRAs

The short-term HRA limits are required for BIFs, and are necessary for HWIs in order to alleviate concerns regarding short-term, high emission spikes that would not be controlled by long-term limits. Limiting the potential for short-term spikes based on an inhalation pathway evaluation is a conservative and reasonable approach (in the absence of acute health benchmarks) since indirect effects and bioaccumulation are not factors for the inhalation pathway. Additional information on acute inhalation risks is found in EPA (in press a). The long-term limits are used to assure that operating conditions evaluated in the SSRA remain representative.

In addition to the original 10 BIF metals, metals that will be considered as COPCs for the SSRA will include aluminum, cobalt, copper, manganese, nickel, selenium, vanadium, and zinc (EPA in press a, in press b). Summaries of specific human health and ecological concerns related to these metals are found in Section 2.3 of this document. With the possible exception of nickel (which is considered as a potential carcinogen) it is generally anticipated that feed rates of these non-BIF metals will not need to be limited on an HRA basis. In addition, testing for these metals will not typically involve spiking. However, tracking could be required to monitor potentially significant changes in feed rates that would warrant re-evaluation in the SSRA, or long-term average feed rate limits may be established.

Specific operating parameters related to control of metal emission rates are expected to be consistent with operating parameters previously identified by EPA (1989, 1992b, 1994a, 1997f, 1997g, 1997h, 1997i, and 1997j). Most of these operating parameters are summarized in Section 6.3 of this document. Technical support documents related to EPA's proposed MACT standards (EPA 1996a) provide additional

information on control technologies and effectiveness of APCDs (EPA 1996b, 1996c, 1996d, 1996e). Thus, a significant body of knowledge exists on metals and PM control, operation of APCDs, and specific APCD operating parameters. This document relies on this accumulated information.

Overall, metal behavior (and potential risks) in HWC facilities is influenced by issues related to metal speciation, metal volatility, and system operating conditions (EPA 1992b, 1996a). These issues include (1) higher volatility of metal chlorides than metal oxides, (2) thermodynamic considerations related to temperature profiles, (3) metal valence and phase, (4) removal efficiencies for specific types of APCDs, and (5) system-specific operating parameters such as cement kiln dust recycling rate (EPA 1996a). Additional information on metal speciation, volatility, system operating conditions, and control measures are discussed below.

6.1 METAL SPECIATION

Speciation is important for the volatile metal mercury and the low-volatile metals chromium and nickel. Currently, EPA's human health and ecological risk assessment protocols (EPA in press a, in press b) do not rely on analytical methods for quantifying metals speciation. The model associated with the protocols includes default assumptions to partition the various forms of the elements. Based on the conservative nature of these assumptions, a facility may want to perform speciation sampling or present other information to replace the default assumptions with site-specific data.

Mercury can be present in the divalent (oxidized) form or the elemental (reduced) form. 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 will tend to drive indirect ecological risks and food chain risks to humans. Divalent mercury emission can be reduced through the use of a wet scrubber or other APCD. Elemental mercury emissions are more difficult to control, and are more likely to become part of the global mercury cycle. Mercury speciation is discussed in greater detail in EPA (in press a). EPA (in press a) assumes that mercury is partitioned as 80 percent vapor phase, and 20 percent particle-bound. The 80 percent vapor phase is segregated into 20 percent elemental and 60 percent divalent. Of the 20 percent particle-bound, all of it is assumed to be divalent. Potential sampling methods for mercury speciation are discussed in Appendix B of this document.

Chromium exists in multiple valance states. The trivalent form has relatively low toxicity based on indirect exposure pathways, while the hexavalent form is carcinogenic to humans via the direct inhalation route. The hexavalent form typically occurs as either chromate or dichromate. Other chromium valence states are not considered in the SSRA. EPA (in press a) initially assumes all chromium to be emitted in the hexavalent (carcinogenic) form. However, the risk model can be adjusted to show indirect effects and ecological uptake through the trivalent form. Laboratory work by Linak and others (1996) and Linak and Wendt (in press) 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. 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. EPA (1996g) provides an in-stack emissions method (Method 0061) for differentiating between trivalent and hexavalent chromium.

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 as potential human carcinogens. Currently, EPA (in press a, 1998a) recognizes nickel emissions from HWC facilities as a potential human carcinogen via the direct inhalation exposure pathway based on data collected on nickel refinery dust. Overall, this assumption is fairly conservative because emissions of carcinogenic forms of nickel by HWC facilities is unproven. Based on this, a facility may present data indicating the absence of carcinogenic nickel refinery dust components or the presence of noncarcinogenic species such as soluble salts. Standard EPA sampling methods for nickel speciation do not exist at this time. For exposure pathways other than direct inhalation, nickel is assumed to be in the noncarcinogenic soluble form.

6.2 METAL VOLATILITY GROUPINGS

Metals can be grouped as volatile, semivolatile, or low volatile. Volatile metals are defined by EPA (1992b, 1996a, 1996b, 1996c, 1996d, 1996e) and Energy and Environmental Research Corporation (EER) (1996a, 1996b) 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 of HWC facilities. Because of variable removal efficiencies in the APCD, emissions of volatile metals are highly dependent on feed rate.

Semivolatile metals typically have higher vapor pressures at combustion temperatures and lower vapor pressures at APCD temperature (EER 1996a, 1996b). This leads 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, 1996c, 1996d). Emissions of semivolatile metals are a function of both feed rate and APCD removal efficiency (EPA 1996a).

Low-volatile metals vaporize at a lesser extent at combustion temperatures and partition to a greater extent to bottom ash, other residue, cement kiln clinker, or entrained flue gas PM (EPA 1996a, 1996b, 1996c). Low-volatile metal emissions are more strongly related to the operation of the APCD than to feed rate. Evaluations conducted by EER (1996a, 1996b) indicate that SRE of metals increases strongly with increasing feed rate for similar types of facilities, and that this relationship is stronger for semivolatile as compared to low-volatile metals.

Figure 6-1, reproduced from Clark and Sloss (1992), provides a representation of metals volatility groups. 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. However, based on vapor pressures and information found in Dellinger (1993) aluminum would be expected to be low volatile as an oxide. As a chloride, aluminum could be semivolatile to volatile. Based on the species expected to be formed within combustion environments, silver would likely be classified as low volatile.

It is important to note that definitions of volatile, semivolatile, and low-volatile metals will vary among studies, test conditions, and type of HWC facility (EPA 1996a, 1996b, 1996c 1996d, 1996e; EER 1991, 1996a, 1996b; Cesmebasi and others 1991; Linak and Wendt in press). Moreover, metal volatility is affected by design differences in the HWC unit (such as differences among kilns, liquid injection, and controlled air designs), APCD PM removal efficiency, raw materials (for cement kilns and LWAKs), the presence of chlorine (which increases metal volatility), and fuel (natural gas, fuel oil, or coal). The figure reproduced from Clark and Sloss (1992) may not fully represent the behavior of certain metals in cement kilns. For example, EER (1996a, 1996b) found that the metals antimony and arsenic, exhibited low volatility in cement kilns (probably due to their affinity for the cement matrix).

Specific issues related to volatile, semivolatile, and low-volatile metals and their expected behavior in HWIs, cement kilns, and LWAKs are described in the following sections. These discussions are provided in order to establish a general framework regarding metals behavior. However, this guidance does not

recommend that permit limits be established based upon volatility groups (rather than individual metals). The divisions between volatility groups are not absolute, and metals must be modeled individually in the SSRA. In addition, the following discussions should not be construed as superseding current BIF regulatory requirements for metals. Deviations from the traditional BIF approach may only be considered in the context of permitting conducted pursuant to EPA's omnibus authority (e.g., SRE tests for HWIs, or metals tests conducted at normal conditions for SSRAs).

FIGURE 6-1

METAL VOLATILITY GROUPS
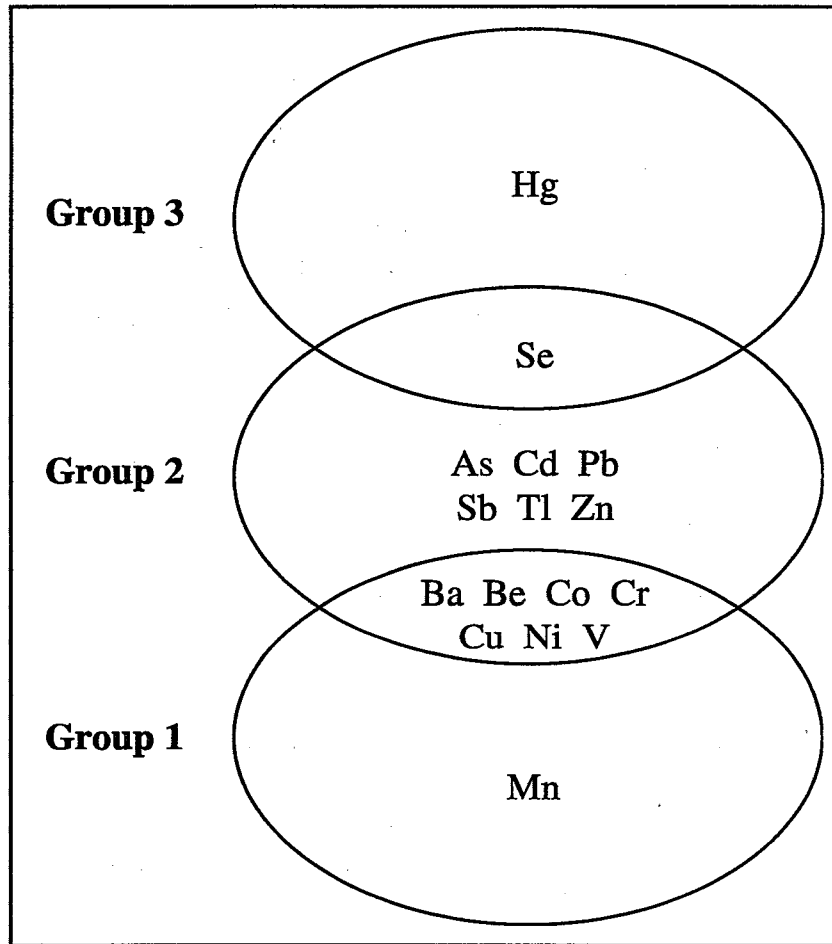
6.2.1 Volatile Metals (Mercury and Selenium)

EER (1996a, 1996b) and Clarke and Sloss (1992) identify mercury and selenium as volatile metals. These metals tend to vaporize completely at combustion temperatures. Mercury may remain volatile in the APCD, while selenium is more likely to condense out. Further considerations related to mercury are provided below.

EPA (1996a, 1997e) and the U.S. Congress consider mercury to be a high priority hazardous air pollutant with the potential to cause significant human health and environmental effects. 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 1997e). At temperatures found in RCRA-permitted HWC facilities, nearly all mercury volatilizes to form gaseous mercury that includes both elemental (reduced) and divalent (oxidized) forms (EPA in press a). The divalent form is more likely to adsorb to PM and to be removed in the facility's APCD. EPA (in press a) has found that partitioning between elemental and divalent mercury during combustion is dependent on fuel and physical characteristics of the source. For combustion sources containing relatively high concentrations of mercury and chlorine, mercuric chloride is expected to be the dominant form of mercury (EPA 1996a).

Operating parameters related to mercury emissions from HWC facilities include the following (EPA 1996d):

- Mercury emissions increase with increasing mercury feedrate. Permit limits should be established for total maximum mercury feedrate (including hazardous waste, raw materials, and fossil fuels). No separate limit is recommended for pumpable hazardous wastes, since mercury is highly volatile in any form.

- Chlorine feedrate 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 also not necessary, 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. However, experimental results indicate that conversion of elemental mercury to mercuric chloride increases with temperature up to approximately 1,600 °F (EPA 1996d).

- Wet scrubbers have been demonstrated to be effective at controlling water soluble forms of mercury. Operating parameters associated with wet scrubbers (such as pressure drops,

liquid feed pressure, pH, and ratio of liquid to flue gas) should be established as permit conditions. Gaspar and others (1997) observed that rapid quenching of hot flue gases from municipal waste incinerators reduced mercury removal in wet scrubbers. They believed the lower temperatures affect the equilibrium reactions and shift equilibrium towards elemental mercury. Similar observations have been made by EPA (1997d) at several HWC facilities.

Mercury emissions from HWIs are currently controlled by limiting waste feed rates and using wet scrubbers designed for acid gas removal. As described above, wet scrubbers are effective in removing water soluble forms of mercury including mercuric chloride. EPA (1996a) also states that additional alternative controls including carbon injection and carbon bed technologies would increase mercury removal from HWIs up to 90 to 99 percent (EPA 1996d).

Cement kilns are currently regulated by BIF requirements, and they control mercury emissions by limiting mercury feedrate. Raw materials and coal (as an auxiliary fuel) can add to the mercury emissions. EPA (1996a) states that additional removal may be achieved by quenching the flue gases, followed by treatment with carbon injection or carbon beds. Mercury can exit the kiln as volatile emissions, or partition to the clinker product or cement kiln dust. According to EPA (1996a), all existing cement kilns rely on dry APCDs that are either fabric filters or ESPs. Mercury is volatile at the operating temperature of these units, and removal efficiencies are highly variable, ranging from zero to 90 percent (EPA 1996a).

Similar to cement kilns, LWAKs are currently regulated by BIF requirements, and mercury emissions are controlled by limiting mercury feedrate. According to EPA (1996a), all LWAKs rely on fabric filters to control PM emissions, although one facility uses a spray dryer, venturi scrubber, and wet scrubber in addition to the fabric filter. The range of mercury emission rates is similar to that observed for cement kilns. The raw material used by LWAKs seems to contribute to the total emissions rate. EPA (1996a) states that additional removal may be achieved by quenching the flue gases, followed by treatment with carbon injection or carbon beds.

6.2.2 Semivolatile Metals

Several operating parameters affect semivolatile metal emissions from HWC facilities. A summary of operating parameters for the semivolatile metals based on EPA (1992b, 1996a, 1996d) follows:

- Semivolatile metal emission rates increase as the metal feedrate increases. Permit limits should be established for total maximum feedrates (including hazardous waste, raw materials, and fossil fuels). A separate limit for pumpable feedstreams 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. An operating limit on maximum chlorine fed to the HWC unit is recommended. The limit is based on total chlorine from all sources, including organic and inorganic chlorine sources.

- Maximum combustion chamber temperature traditionally is 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 HWC facilities. For semivolatile metals, typical combustion temperatures are generally high enough to volatilize all of the metals in the combustion chamber.

- APCD type and operating parameters are recognized as critical to the control of semivolatile metals, and limits on APCD parameters should be established as permit conditions. In addition, the operating temperature of the APCD may also be important. At higher temperatures, a larger portion of some metals will be in the vapor phase. The establishment of a maximum limit on the inlet temperature to the dry APCD is recommended to control emissions from semivolatile metals.

- Cement kilns and LWAKs that recycle collected PM require special consideration to ensure that emissions reach steady-state prior to testing, as described in EPA (1992b).

Semivolatile metals are volatile at the high temperatures found within the combustion chamber, but typically condense onto the fine particulates within a dry APCD such as a baghouse or ESP. Control of semivolatile metals is most directly associated with PM control. However, these metals tend to condense onto fine PM (less than 1 micron) (EPA 1996b), which is controlled less effectively than larger PM. Therefore, removal efficiencies of particulates associated with semivolatile metals are lower than removal efficiencies for total PM. EPA (1996a) also observed that venturi and wet scrubbers are effective in controlling emissions of semivolatile metals. However, venturi scrubbers are generally considered most effective for larger particulates (greater than 1 micron diameter). Wet scrubbers are designed for acid gas removal and are also only effective in removing large particulates. Thus, fabric filters and ESPs would be considered the most effective in removing smaller particulates (Clarke and Sloss 1992; EER 1991).

6.2.3   Low-Volatile Metals

Operating parameters associated with the low-volatile metals are consistent with those described for the semivolatile metals in Section 6.2.2 (EPA 1996d), with the following exceptions:

- A separate limit for low-volatile metals in pumpable feed streams is recommended, since these may partition at a higher rate to the combustion flue gas.

- Low-volatile metals are less apt to vaporize completely at typical combustion temperatures. Thus, a limit on maximum combustion temperature may be more important

for low-volatile metals than for semivolatile metals. However, maximum combustion chamber temperature is most likely less important than APCD operating parameters. The amount of additional vaporization at slightly higher temperatures could be negligible compared to the amount of metals contained in entrained flue gas PM, especially for kilns and pulverized coal boilers.

Similar to the semivolatile metals, EPA (1996a) observed that operation of the APCD is critical to removal of low-volatile metals. Also, some low-volatile metals can behave as semivolatile metals in the presence of chlorine or under reducing conditions. Venturi and wet scrubbers, ESPs, and fabric filters were all found to be effective in controlling low-volatile metals. However, fabric filters and ESPs would be considered the most effective in removing smaller particulates.

6.3   OPERATING CONDITIONS AND PARAMETERS FOR METALS

In general, metals emissions data are collected during high temperature (SRE) conditions as explained in the BIF rule (40 CFR 266 Subpart H) and EPA (1992b, 1997f, 1997g, 1997h, 1997i, 1997j). As appropriate, metal emissions data for SSRAs may also be collected during normal operating conditions, as explained in Section 3.0 of this document. Operating parameters related to collection of metals emission data are summarized in the documents cited above, as well as in Appendix A of this document. RCRA permit limits for metal feed rates will generally be based on HRAs for BIF metals and, as appropriate, long-term averages for any additional metals.

Operating parameters related to high temperature testing of BIF metals have traditionally included:

- Maximum combustion temperatures
- Maximum flue gas flow rate or velocity, or production rate for cement kilns and LWAKs
- Maximum metal feed rates (total feed rates, total hazardous waste, and total pumpable hazardous waste)
- Maximum total chlorine feed rates

As explained previously, metal emissions are dependent on operation of APCDs and associated PM controls. Specific operating parameters related to APCDs with wet scrubbers include:

- Minimum pressure drops across the scrubber
- Minimum liquid feed pressure
- Minimum liquid pH
- Minimum liquid/flue gas ratio

- Maximum scrubber blowdown or maximum suspended solids

Specific operating parameters related to APCDs with dry systems include:

- Maximum inlet temperature for fabric filters and ESPs
- Minimum pressure drop across fabric filters
- Minimum power input to ESPs
- Minimum caustic feed rate to dry scrubbers

7.0 PARTICLE-SIZE DISTRIBUTION AND HYDROGEN CHLORIDE AND CHLORINE EMISSIONS

This section addresses data collection requirements and operating parameters for particle-size distribution, HCl, and Cl_2. Particle-size distribution is used in the air dispersion modeling completed as part of the SSRAs, as described by EPA (in press a, in press b). HCl and Cl_2 emissions are relevant to the direct inhalation pathway of the SSRA.

7.1 RELATIONSHIP BETWEEN PARTICLE SIZE AND POTENTIAL EMISSIONS

Quantification of indirect human health and ecological risks in the SSRAs is dependent upon annual deposition rates at actual and reasonable future exposure scenario locations (EPA in press a). In general, most semivolatile and low-volatile metals and some semivolatile and low-volatile organics occur only in the particle phase (mercury is partitioned between vapor and particulate phases by the model associated with the human health and ecological SSRAs). Particle size is the primary variable associated with the transport of emitted particles (this includes wet and dry removal processes and subsequent deposition). Particle terminal velocity is based on particle diameter and density.

Particle-size distribution information is necessary in order to perform air dispersion and deposition modeling for the SSRA. Required inputs to the model include (1) particle density, (2) mass distribution by particle-size category, and (3) surface area distribution by particle-size category. 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.

A particle-size distribution that is more heavily weighted towards larger particles will result in higher deposition near the source, and reduced concentration and deposition further away from the source. A particle-size distribution which is more heavily weighted towards smaller particles will decrease deposition near the facility and increase 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 potential risks. Receptor locations relative to maximum deposition are a critical factor when quantifying potential risks.

In most cases, the effectiveness (and associated removal efficiency) of the APCD is the primary determinant of particle size and total particle mass emitted from HWC facilities. Advances in air pollution

control technology have led to particulate removal and removal efficiency improvements. However, removal efficiencies are typically expected to decrease as particle size decreases. For example, according to 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 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 1996b). Based on these observations, a well-operated APCD greatly decreases the potential mass and mean particle size emitted from HWC facilities.

7.2   MEASURING PARTICLE-SIZE DISTRIBUTION

EPA (in press a) provides a nine-category particle-size default assumption which represents the particle-size categories emitted from sources equipped with ESPs or fabric filters. The default particle-size diameters range from less than 0.7 to greater than 15.0 microns. However, recent measurements of particle sizes by HWC facilities for the purpose of conducting SSRAs have shown that the default distributions may be overly biased towards larger particles. Much of the actual monitoring data are showing a majority of the particle mass at less than 1 or 2 microns. In addition, the default assumptions would not be appropriate for facilities equipped with wet APCDs, or facilities with no APCD. Thus, site-specific particle-size measurements are recommended for each HWC facility.

Particle-size distribution may be determined using devices such as cascade impactors or by analysis of PM deposited on filters using scanning electron microscopy (EPA 1998b). Preliminary data collected and analyzed using these methods (EPA 1998b) indicate a large amount of uncertainty, especially for particle sizes less than 1 micron. EPA (1997b) recognizes the inherent problems associated with measuring very low masses of particulates and recommends modified Method 5 (Method 5I) to improve accuracy, precision, and representativeness by significantly reducing the variability and potential errors. Method 5I includes improved sample collection, elimination of possible contamination, and improved sample analysis (EPA 1997b). Although Method 5I was not written specifically for particle-size determinations, it is possible that use of 5I procedures in conjunction with the cascade impactors for particle-size determinations could help reduce analytical uncertainty. A facility equipped with fabric filters or ESPs may also be able to conduct preliminary modeling to demonstrate a reduced need for site-specific particle-size information.

EPA recognizes the inherent uncertainties associated with collecting particle-size distribution data, given (1) the removal efficiencies of APCDs, (2) the small particle sizes emitted, and (3) the practical difficulties associated with measuring these particles using currently available techniques. Permit writers should work with facilities to obtain the best data available under the circumstances. Additional guidance regarding particle-size determinations is provided in Appendix B.

7.3 OPERATING CONDITIONS AND PARAMETERS FOR COLLECTION OF PARTICLE-SIZE DISTRIBUTION DATA

EPA recommends that particle-size data be collected under normal or other operating conditions (as defined by the facility) where ash spiking is not performed. Ash spiking will bias the particle-size distribution and results would not be representative of actual combustion conditions.

7.4 HYDROGEN CHLORIDE AND CHLORINE EMISSIONS

HCl limits for HWIs are found in 40 CFR Part 264.343. Appendix IV of 40 CFR Part 266 provides direct inhalation RACs for total Cl_2 and HCl emissions from BIFs (including cement kilns, LWAKs, and boilers). Since potential risks from HCl and Cl_2 are limited to the inhalation pathway, completion of multi-pathway SSRAs is not expected to affect the current regulatory approach for HCl and Cl_2 emissions from BIFs. However, it is now recommended that HWIs test their stack emissions for both HCl and Cl_2. Risk-based limits may be established in the final permit for HWIs in lieu of the technology-based emissions limits found in 40 CFR 264.343 if the risk-based limits are lower.

Continuous emissions monitoring systems (CEMS) for HCl are available; however, HCl and Cl_2 are controlled typically by limiting the feed rate of total chlorine in all feed streams and by establishing appropriate APCD operating parameters for wet and dry scrubbers as listed previously in Section 6.3.

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8.0   DATA ANALYSIS AND PERMIT CONDITIONS

As explained in Section 1.0 of this document, additional RCRA permit conditions may be established based on the collection of emissions data (including D/Fs, organics other than D/Fs, metals, and HCl and Cl$_2$) from HWC facilities and subsequent evaluation of these data in SSRAs. These data will be collected during the appropriate test condition (as described in Section 3.0), and by relying on the appropriate operating parameters (as discussed in Sections 4.0 through 6.0) for HWIs, boilers, cement kilns, and LWAKs. The data are evaluated in the SSRAs to provide reasonable maximum exposure (RME) estimates of potential risks to human and ecological receptors (EPA in press a, in press b). Final RCRA permit conditions will ultimately depend on the operating practices, emissions levels, and SSRA results specific to each facility. This section identifies information that should be included in the trial burn plan to clearly communicate the relationship between the planned test protocol and potential permit conditions. In addition, this section describes how trial burn data should be consolidated for evaluation in the SSRA. Further examples regarding the relationship between test protocols and permit conditions are provided in Appendix A of this document.

Consistent with existing EPA trial burn guidance (EPA 1989, 1992b, 1997f, 1997g, 1997h, 1997i, and 1997j) it is assumed that three operating runs are conducted at each test condition, and that trial burn testing frequently includes three test conditions (DRE, SRE, and normal test conditions). In certain cases, additional test conditions may be required for a facility to develop the appropriate operating envelopes for a variety of operating scenarios. This could be the case for facilities that burn wastes from different production runs in discrete campaigns, facilities that cannot simultaneously maximize all of their feeds during one test condition, or facilities that need to perform multiple tests to resolve conflicting operating parameters.

Conflicting parameters are key operating 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 operating parameters for risk testing (identified in Sections 4.0 through 6.0) with the key operating parameters for traditional DRE and SRE testing. To overcome a conflict, a facility may need to perform duplicate tests as follows:

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

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

8.1   PERMIT LIMITS FOR KEY OPERATING PARAMETERS

The key operating parameters that could be limited in a facility's RCRA permit based on collection of SSRA data are identified in Sections 4.0 through 6.0. Many of these parameters are assigned primary, secondary, and tertiary hierarchial designations to indicate their relative significance. These designations, together with consideration of site-specific operating practices and final SSRA results, should all be considered by the permit writer in determining which operating parameters require final permit limits. Also, depending on the significance of a specific operating parameter for the facility, a final permit limit might be quantitative (such as an HRA limit), or it could involve periodic monitoring and reporting (for permit limits based on normal operating conditions).

Compliance averaging periods for key operating parameters should also be considered. Frequently, permit limits are established using HRA averaging periods. However, EPA (1996a) states that shorter averaging periods (such as instantaneous or 10-minute rolling averages) may be appropriate in situations where short-term perturbations outside of a certain operating range could result in high emission rates that cannot be offset by lower emission rates during periods of more normal operations. The short-term average limit, used to control perturbations, would be used in conjunction with an HRA limit to control average emissions. For the operating parameters in Tables 4-1 and 4-2, EPA (1996a) suggests that short-term limits are appropriate for minimum combustion temperatures and maximum post-combustion temperatures.

Alternatively, EPA (1996a) acknowledges that averaging periods longer than an hour may be appropriate for situations where control of longer-term average emissions is the only concern. Examples include metals and chlorine feed rate limits. Long-term averages may be considered for any operating parameter where short-term perturbations are not a concern, and where an averaging period is not already prescribed by regulation. Control charts, similar to those used for industrial quality control, provide an alternate means of assessing ongoing operations to ensure that the SSRA remains representative over the long term. 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. EPA (1996a, 1997j) provide further information on averaging periods and control charts.

Early communication and coordination between the permit writer and facility is essential, because an understanding of how the final permit limits will be developed is integral to the design of the test protocol. The facility owner/operator is ultimately responsible for assuring that the trial burn provides adequate data to support permit conditions that are acceptable to the facility. The following recommendations identify specific types of information that should be provided by the facility to facilitate this process:

- A summary matrix (for each test condition) should be provided listing the planned emissions data to be collected and proposed operating limit for each relevant operating parameter. Operating parameters include those listed in Sections 4.0 through 6.0, as well as the operating parameters that must be demonstrated during the traditional DRE, SRE, PM, and HCl and Cl_2 demonstrations.

- A list of conflicting parameters (key operating parameters that cannot be maximized or minimized simultaneously) and a detailed explanation of the reasons for the conflict should be provided. This should include a summary to explain the two or more test conditions that will be performed to resolve the conflict, and to identify changes in other operating parameters that may be necessary to resolve the conflict.

- A complete list of operating and waste feed parameters which are expected to be limited in the permit should be provided. This list should be consistent with the proposed test conditions and the following information should be included for each waste feed and operating 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 BIF Tier I for metals).

  - Specific information on how each permit limit will be established based on trial burn results. This 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 operating parameter will be monitored and recorded to demonstrate compliance with the permit limit (i.e., whether the operating 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 AWFCS, and the corresponding proposed setpoint.

Appendix A includes a detailed list of final permit limits for an example HWI. The example facility is a liquid injection incinerator with a heat recovery boiler and an APCD system consisting of a fabric filter and venturi scrubber.

8.2 APPLICATION OF TRIAL BURN DATA IN THE SSRA

In addition to information on key operating parameters, the trial burn plan should indicate how the emissions data from the various test conditions will be analyzed and consolidated for evaluation in the SSRA. Data analysis for each test condition involves several steps, including evaluation of non-detected constituents, final COPC selection, and determination of COPC emission rates as described in Section 2.3 of EPA (in press a). Consolidation of data from multiple test conditions can also encompass a range of options, depending on how the test conditions are structured and how the data will be presented for comparison to target risk levels. For example, separate risk values can be quantified based on different test conditions to provide a risk range. Alternatively, a single risk estimate might be calculated by combining the highest emission rates from multiple tests. These options should be considered carefully prior to establishing test conditions and subsequent data collection.

Data analysis starts with decisions regarding treatment of non-detected constituents. Section 2.4.2 of EPA (in press a) provides a recommended procedure. Several terms for non-detected constituents apply. These include reliable detection limits (RDL) for constituents analyzed with non-isotope dilution methods, estimated detection limits (EDL) for constituents analyzed with most isotope dilution methods, and estimated maximum possible concentrations (EMPC) associated with SW-846 Method 8290 (EPA 1996g) or other appropriate method.

Constituents that are not detected during any of the test runs should be re-evaluated for inclusion in the SSRA, consistent with the final COPC selection process (and associated flowchart) found in EPA (in press a). As part of the final COPC selection process, some constituents that are not detected during any of the test runs will be eliminated from further consideration in the SSRA. However, care should be taken not to eliminate non-detected constituents that will be limited in the final RCRA permit based on the SSRA results. This is because compliance with an emission rate limit of zero cannot be determined. Pollutants that may be limited in the final permit based on SSRA results include D/Fs, specific metals, HCl and Cl_2, and significant waste constituents (e.g., chemical agents). If these pollutants are not detected, then the full RDLs, EDLs, or EMPCs (as appropriate) should be used in the emissions calculations. As appropriate, permit limits may be considered for other contaminants that are found to be risk drivers during the risk assessment process. However, emission limits are not expected to be routinely established for individual organics, other than D/Fs.

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For COPCs detected in at least one run of the test (as well as for COPCs that may be limited in the final permit) the RME emission rate is calculated as the 95th percentile of the arithmetic test mean, or the maximum value from the three test runs, whichever is lower (EPA in press a). RDLs, EDLs, or EMPCs (as appropriate) should be used in the calculations when a COPC is not detected during a test run.

Next, consolidation of results from multiple test conditions must be considered. Possible options include (1) calculation of risk ranges corresponding to specific test conditions (e.g., DRE and SRE), (2) consolidation of the highest emissions data from the various test conditions for calculation of a single high-end risk value, (3) combining test data with estimates of emission rates of COPCs to calculate high-end risks, or (4) some combination of these. Unless all emissions determinations (D/Fs, other organics, and metals) are conducted during each operating test condition, then consolidation of data from multiple conditions must be considered. Further explanation regarding these possibilities are provided below and in Appendix A.

Calculation of Risk Ranges Corresponding to Specific Test Conditions

A facility may choose to collect emissions data for use in the SSRA in conjunction with the SRE and DRE tests, without performing a risk burn under normal operating conditions. In this case, the metals emissions are expected to be higher in the SRE test, and the organic emissions may be higher in the DRE test. If all emissions data are collected (D/Fs, other organics, and metals) during both test conditions, then the facility could evaluate the emissions data sets from each separate test condition to calculate risk ranges.

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

If the facility described above did not collect data for all COPCs during both test conditions (e.g., sampling for metals emissions was not performed during the DRE test), then the metals emissions from the SRE test and the higher of the D/F and organic emissions from either the SRE or DRE tests should be combined for calculating potential RME risk estimates.

Combining Test Data with Emissions Estimates

For either of the above approaches, the facility may not have spiked mercury during the SRE test. Instead, the facility estimated maximum mercury emissions by assuming zero SRE at a maximum mercury feed rate. This maximum mercury emissions estimate could be combined with measured emissions data for calculation of either a risk range or a single risk estimate.

Combined Approach

It is likely that metals emissions would not be determined during the DRE test, because of stack port constraints or to limit metals spiking. In addition, it is likely that the facility would not spike mercury during either test. In this case, a single RME risk estimate could be calculated by consolidating the maximum estimated mercury emissions rate (and estimated emission rates for any other Tier I metals) with the emissions data for the remaining metals collected during the SRE test, and the higher of the D/F and organic emissions from either the SRE or DRE tests. The approach for calculation of a risk range would be similar, except that separate risk calculations would be performed using the D/F and organic emissions data from the SRE test versus those from the DRE test.

Obviously, if a facility chooses to collect emissions data under additional operating test conditions, then the data management and analysis become more complex. Again, early communication and coordination between the permit writer and facility is essential.

The primary objective of SSRA data analysis and consolidation is to ensure that the trial burn (and/or risk burn, as appropriate) provide emissions data suitable for quantifying potential human and ecological risks based on RME conditions. In addition, operating conditions associated with these risks should be clearly limited by the permit terms and conditions.

Recent EPA direction in characterizing and communicating risk (EPA 1995a) to the public should also be considered during the risk assessment process. EPA (1995a) states that risk assessments should include risks based on data reflecting both RME and central tendency (average) conditions. As appropriate, SSRAs could be completed based on both average and RME 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

9.0   REPORTING CHANGES OF WASTE FEED AND OPERATING PARAMETERS

Previous sections of this document identified appropriate operating conditions and parameters for collecting risk-based emissions data for HWC facilities including HWIs, boilers, cement kilns, and LWAKs. Performance testing and Group A, B, and C operating parameters are used to define the HWC facility operational envelope and to demonstrate performance standards. Risk-based emissions data are used to establish baseline conditions for either reasonably conservative operating conditions (based on DRE and SRE testing) or normal (or average) operating conditions. These data define a facility's baseline with respect to long-term impacts, including potential effects on human health and the environment. This is especially relevant for HWC facilities that conduct emissions testing under normal operating conditions.

The trial burn and corresponding RCRA permit conditions are based on assumptions that include:

- Waste composition, physical form (liquid, solid, aqueous, or organic), and feed rates

- Operating conditions and parameters including those related to combustion conditions (temperature, turbulence, and residence time) and APCDs (pressure changes, flow rates, liquid to gas ratios, inlet temperatures, and power)

Monitoring and reporting requirements should be incorporated into the final permit to ensure that any significant changes to the facility's baseline that could affect emissions (including types of wastes treated or major changes to operating parameters) will be reported to EPA or the appropriate state agency. This information should be used to determine whether any additional risk-based data collection or risk analyses will be required.

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APPENDIX A

TRIAL BURN CONDITIONS AND PERMIT LIMITS

FOR AN EXAMPLE HWC FACILITY

(10 pages)

APPENDIX A

TRIAL BURN CONDITIONS AND PERMIT LIMITS
FOR AN EXAMPLE HWC FACILITY

This Appendix includes a detailed list of Group A, B, and C control parameters (and associated monitoring requirements) for an example hazardous waste incinerator (HWI) (Facility Z). Facility Z includes a liquid injection combustion chamber burning organic liquid and aqueous wastes, a heat recovery boiler, and an air pollution control device (APCD) system consisting of a fabric filter and venturi scrubber. Facility Z typically operates within a 1,750 ± 50 °F combustion 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. Facility Z plans to perform three test conditions (summarized in Table A-1) that consist of the following:

Destruction and Removal Efficiency Test Condition

The destruction and removal efficiency (DRE) demonstration is proposed at a minimum combustion temperature of 1,600 °F to promote maximum operating flexibility. This test also involves the key operating parameters for organic products of incomplete combustion (PIC); therefore, the facility plans to measure PICs and total organics (TO) in conjunction with the DRE performance demonstration. A temporary total hydrocarbon continuous emissions monitor (CEM) will be operational during the DRE/PIC testing. Carbon monoxide monitoring will be performed during the DRE conditions.

Dioxin/furan (D/F) testing will also be performed during the DRE test. This is because of concerns that the high combustion temperatures demonstrated during the system removal efficiency (SRE) test might not adequately represent the presence of D/F precursors formed during poor combustion conditions. In general, the formation of D/F precursors during conditions of poor combustion are not a significant concern for this system (because the historical data review indicated very constant operating temperatures, very low carbon monoxide, and very few waste feed cutoffs). In addition, 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 agreed that D/F sampling during DRE conditions would better represent the operating envelope, and the stack sampling ports could accommodate all of the necessary sampling trains for multiple determinations.

System Removal Efficiency Test Condition

Facility Z plans to demonstrate SRE for metals at maximum feed rates by spiking with arsenic, beryllium, cadmium, chromium, lead, and nickel. The SRE demonstration for nickel is necessary based upon a preliminary risk evaluation that quantifies potential carcinogenic risks from inhaled nickel emissions. The SRE demonstration will be performed at a maximum combustion temperature of 1,850 °F and a maximum inlet fabric filter temperature of 550 °F. 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.

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). D/Fs are expected to be maximized at the maximum fabric filter inlet temperature of 550 °F, and will be measured in conjunction with the SRE test. Particulate matter (PM) and hydrogen chloride (HCl) and chlorine (Cl_2) will also be measured, because the SRE test maximizes chlorine emissions, ash production, and flue gas velocity. Carbon monoxide monitoring will be performed during the SRE conditions.

Normal Test Condition

Facility Z is capable of defining and maintaining a normal operating condition. A normal test is proposed for metals, because of concerns that spiking with metals will result in risks that exceed target values. The normal test will involve normal metal feed rates, a combustion temperature of approximately 1,750 °F, and a fabric filter inlet temperature of 450 °F. Emissions testing will be performed for all 18 metals (the 12 boiler and industrial furnace [BIF] regulation metals and the six additional compounds of potential concern [COPC] metals from Table A-1 of Appendix A of EPA's "Protocol for Human Health Risk Assessment at Hazardous Waste Combustion Facilities," EPA-R6-098-002, Center for Combustion Science and Engineering, Multimedia Planning and Permitting Division, EPA Region 6, [in press]).

PM and HCl and Cl_2 emissions testing were also added to the normal test to establish minimum pressure differential limits for the fabric filter and venturi scrubber. Minimum pressure differentials conflict with the maximum combustion gas velocities demonstrated during DRE and SRE test conditions. A particle-size determination was added to the normal test, since this test does not include ash spiking. Carbon monoxide monitoring will be performed during the normal conditions.

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Site-Specific Risk Assessment

Facility Z performed the trial burn according the approved test plan. The D/F emissions, as well as the HCl and Cl_2 emissions, were highest during the SRE test condition. Emissions were consolidated from the three test conditions for evaluation in the multi-pathway human health and ecological site-specific risk assessments (SSRA) as follows:

- D/F emissions from the SRE test condition
- Metals emissions (18 metals) from the normal test condition
- Organic PIC emissions from the DRE test condition
- HCl and Cl_2 emissions from the SRE test condition

Total risks from these consolidated emissions were below target levels.

Next, a second SSRA evaluation was performed considering only the inhalation pathway, consistent with the BIF regulations. This evaluation used emissions from the SRE test condition for the spiked metals (arsenic, beryllium, cadmium, chromium, lead, and nickel), as well as emissions estimates for the remaining metals based on maximum anticipated feed rates and an assumption of zero SRE. Emission rate data for all other pollutants were unchanged. Total inhalation risks from these consolidated emissions were also below target levels.

Final Permit Limits

Table A-2 provides the final permit limits for Facility Z. For both minimum combustion temperature and maximum fabric filter inlet temperature, limits were established based on the following dual averaging periods:

- Hourly rolling averages (HRA)
- Short-term limits (10-minute rolling averages [RA]) to control temperature spikes which could result in excess D/F or organic PIC emissions

HRA feed rate limits for the six spiked metals (arsenic, beryllium, cadmium, chromium, lead, and nickel) were established based on feed rates measured during the SRE test. For two of the unspiked metals (barium and mercury), HRA feed rate limits were established using the inhalation risk-based limit (and an assumption of no SRE). For the remaining 10 unspiked metals (aluminum, antimony, cobalt, copper, manganese, selenium, silver, thallium, vanadium, and zinc), HRA feed rate limits were considered

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unnecessary because inhalation risks were either negligible or not applicable (considering the range of inputs for these metals at Facility Z). Quarterly average metals feed rate limits were established for all eighteen metals based on feed rates demonstrated during the normal test condition.

Total hydrocarbon levels were negligible during the DRE test condition. Therefore, the permit writer determined that there was no need to require continued total hydrocarbon monitoring.

Final Permitted Emission Rates

Maximum emission rate limits were established in the permit for D/Fs and Cl_2 based on multi-pathway SSRA target risk levels. The limits were established for the purpose of periodic verification testing to ensure that emissions remain below those evaluated in the SSRA. If emissions increases occur above target levels, then the SSRA would need to be redone. Both "normal" and "maximum" emission rate limits for metals were established corresponding to the multi-pathway SSRA and inhalation-only target risk levels, respectively.

TABLE A-1

FACILITY Z TEST CONDITIONS

	TEST CONDITIONS AND EMISSIONS DETERMINATIONS		
	DRE POHCs, PICs, D/Fs, TO, Total Hydrocarbons, Carbon Monoxide	**SRE** Metals, D/Fs, PM, HCl/Cl$_2$, Carbon Monoxide	**NORMAL** Metals, PM, HCl/Cl$_2$, Carbon Monoxide, Particle Size
Combustion temperature	1,600 °F, HRA (1,575 °F, 10-min. minimum RA)	1,850 °F HRA	1,750 °F HRA
Fabric filter inlet temperature	350 °F	550 °F (565 °F, 10-min. maximum RA)	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 normal	Maximum	Normal
Chlorine feed rate	Maximum	Maximum	Normal
Spiked metals (Arsenic, beryllium, cadmium, chromium, lead, and nickel)	N/A	Maximum	Normal
Other metals	N/A	Normal	Normal
Fabric filter differential pressure	Maximum *	Maximum *	Minimum
Venturi differential pressure	Maximum *	Maximum *	Minimum
Venturi liquid-to-gas ratio	Minimum	Minimum	Minimum
Venturi scrubber liquid exit pH	Minimum	Minimum	Minimum
Scrubber blowdown rate	Minimum	Minimum	Minimum

Notes:

*   =   conflicting parameters

TABLE A-2

FINAL PERMIT LIMITS FOR FACILITY Z

Operating Parameters	Value	Basis	
		Test	Established As:
Group A			
Minimum combustion temperature	1,600 °F, HRA	DRE	Avg. of the three lowest HRA temperatures during the DRE test
	1,575 °F, 10-min. RA	DRE	Avg. of the three lowest 10-min. RAs during the DRE test
Maximum combustion temperature	1,850 °F, HRA	SRE	Avg. of the three highest HRA temperatures during the SRE test
Maximum combustion gas velocity	cfm, HRA	SRE/ DRE	Avg. of the six highest HRA velocities during DRE and SRE
Maximum organic liquid feed rate	lbs/hr, HRA	DRE	Avg. of the three highest HRA feed rates during the DRE test
Maximum aqueous feed rate	lbs/hr, HRA	DRE	Avg. of the three highest HRA feed rates during the DRE test
Maximum fabric filter inlet temperature	550 °F, HRA	SRE	Avg. of the three highest HRA temperatures during the SRE test
	565 °F, 10-min. RA	SRE	Avg. of the three highest 10-min. RAs during the SRE test
Minimum fabric filter pressure differential	inches water column, HRA	Normal	Avg. of the three lowest HRA pressure differentials during the normal test
Minimum venturi scrubber differential pressure	inches water column, HRA	Normal	Avg. of the three lowest HRA pressure differentials during the normal test
Minimum venturi liquid-to-gas ratio	gal/cfm, HRA	SRE	Avg. of the three lowest HRA ratios during the SRE test
Minimum venturi scrubber liquid exit pH	pH, HRA	SRE	Avg. of the three lowest HRA pHs during the SRE test
Minimum scrubber blowdown flow rate	gpm, HRA	SRE	Avg. of the three lowest HRA flow rates during the SRE test
Maximum stack Carbon Monoxide concentration	100 ppm at 7% oxygen, dry basis, HRA	N/A	Limit based on established guidance

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Operating Parameters	Value	Basis	
		Test	Established As:
Maximum combustion chamber pressure	inches water column, vacuum, instantaneous limit (interlocked with AWFCS)	N/A	As necessary to maintain negative pressure
Group B			
POHC incinerability limits	Allowable Appendix VIII constituents	DRE	Based on POHCs which achieved 99.99% DRE
Maximum chlorine feed rate	lbs/hr, HRA	SRE	Avg. of the three highest HRA feed rates during the SRE test
Maximum ash feed rate	lbs/hr, HRA	SRE	Avg. of the three highest HRA feed rates during the SRE test
Maximum feed rates (spiked metals): - arsenic, beryllium, cadmium, chromium, lead, and nickel	lbs/hr, HRA	SRE	Avg. of the three highest HRA feed rates during the SRE test
Maximum feed rates: - barium and mercury	lbs/hr, HRA	SRE	Zero SRE; the inhalation risk-based emission limit is used as the feed rate limit
Maximum feed rates: - aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, selenium, silver, thallium, vanadium, and zinc	lbs/hr, quarterly average	Normal	Avg. over all three runs of feed rates during the normal test

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Operating Parameters	Value	Basis	
		Test	Established As:
Group C			
Maximum heat input	million Btu/hr	N/A	Design basis
Burner/atomizer: - Maximum viscosity - Maximum turndown - Maximum solids - Minimum atomizing pressure differential	- centipoise - gpm range - percent solids - psig (interlocked with AWFCS)	N/A	Manufacturer's recommendations
Minimum venturi scrubber nozzle pressure	psig (interlocked with AWFCS)	N/A	Manufacturer's recommendations
Summary of Performance Standards and Emission Limits			
DRE	99.99% for POHCs	N/A	Statutory requirement
Maximum PM emissions	0.08 gr/dscf	N/A	Regulatory limit
Maximum HCl emissions	Lower of 4 lbs/hr or inhalation risk-based limit	N/A	Regulatory limit/SSRA target level
Maximum Cl_2 emissions	Inhalation risk-based limit	N/A	SSRA target level
Maximum D/F emissions	SSRA risk-based limit	N/A	SSRA target level
Maximum emissions, each metal	Inhalation SSRA risk-based limits	N/A	SSRA target level, established for the purpose of periodic SRE verification tests at conducted at maximum metals feed rates and/or confirmation of Tier I estimates
Normal emissions, each metal	Multi-pathway SSRA risk-based limits	N/A	SSRA target level, established for the purpose of defining the baseline for the SSRA. Increases in normal metal feed rates or emission rates could require retesting and/or another SSRA

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TABLE A-2

FINAL PERMIT LIMITS FOR FACILITY Z (Continued)

Notes:

AWFCS	=	automatic waste feed cutoff system
Avg.	=	average
Btu/hr	=	British thermal units per hour
cfm	=	cubic feet per minute
gal/cfm	=	gallons per cubic feet per minute
gpm	=	gallons per minute
lbs/hr	=	pounds per hour
min.	=	minutes
N/A	=	not applicable
ppm	=	parts per million
psig	=	pounds per square inch, gauge
POHC	=	principle organic hazardous constituent
gr/dscf	=	grains per dry standard cubic foot

APPENDIX B

SAMPLING AND ANALYSIS

(51 pages)

CONTENTS

Attachment

Method 0040 Clarifications

TABLES

ACRONYM LIST

μg	Microgram
μg/m³	Microgram per cubic meter
μg/mL	Microgram per milliliter
AED	Atomic emission detection
A/K	Aldehyde/ketone
AMS	Alkaline mercury speciation
APCD	Air pollution control device
BIF	Boiler and industrial furnace
BP	Boiling point
CARB	California Air Resources Board
CAS	Chemical Abstract Services
CB	Chlorobenzene
CEM	Continuous emissions monitor
CO	Carbon monoxide
CP	Chlorophenol
D/F	Dioxin and furan
DQO	Data quality objective
ECD	Electron capture detector
EDL	Estimated detection limit
EMPC	Estimated maximum possible concentration
EPA	U.S. Environmental Protection Agency
ESP	Electrostatic precipitator
FGC	Field gas chromatography
FID	Flame ionization detector
GC	Gas chromatography
gm/cm³	Grams per cubic centimeter
GRAV	Gravimetric
HEPA	High efficiency particulate air
HHRA	Human health risk assessment
HPLC	High performance liquid chromatography
HRGC	High resolution gas chromatography
HRMS	High resolution mass spectrometry

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ACRONYM LIST (Continued)

HWC	Hazardous waste combustion
HWI	Hazardous waste incinerator
IUPAC	International Union of Pure and Applied Chemists
LC	Liquid chromatography
LRMS	Low resolution mass spectrometry
MDGC	Multi-dimensional gas chromatography
mg	Milligram
MM5	Modified Method 5
MS	Mass spectrometry
ng	Nanogram
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
ppb	Parts per billion
ppm	Parts per million
QA/QC	Quality assurance/quality control
RCRA	Resource Conservation and Recovery Act
RDL	Reliable detection limit
RRF	Relative response factor
SEM	Scanning electron microscopy
SOP	Standard operating procedure
SSRA	Site-specific risk assessment
SVOC	Semivolatile organic compound
TCO	Total chromatographable organic
TEQ	Toxic equivalent
THC	Total hydrocarbon
TIC	Tentatively identified compound
TO	Total organic
VOC	Volatile organic compound
VOST	Volatile organic sampling train

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B.1 OVERVIEW OF SAMPLING AND ANALYSIS PROCEDURES

This appendix discusses recommended procedures for collection of stack emissions data for site-specific risk assessments (SSRA). As explained previously in Section 2.0 of this document, emissions data needs for SSRAs include the following:

- Dioxins and furans (D/F)
- Non-dioxin organics and total organic (TO) mass
- Metals
- Particle-size distribution
- Hydrogen chloride and chlorine

Although the majority of this appendix focuses on the sampling and analysis procedures for obtaining this stack emissions data, recommended characterizations for process samples are also discussed briefly in Section B.17. Characterization of waste feeds, auxiliary fuels, and raw materials during the risk testing is necessary in order to establish the basis for the SSRA.

This appendix is intended to be a tool for assisting permit writers and facility managers in making informed decisions about the measurements necessary for their SSRA data needs. It identifies appropriate methods and highlights sampling, sample recovery, and analytical considerations which can influence detection limits, and therefore, the results of the SSRA. To a limited extent, it also provides method clarifications and "lessons learned" that have not been widely published elsewhere.

B.1.1   EMISSIONS TESTING OBJECTIVES

Sampling and analyses for SSRA emissions data should accomplish two primary objectives as follows:

- Achieve the most comprehensive emissions characterization possible by (1) identifying and quantifying specific toxic constituents, in order to assess their contribution to the total risk posed by the facility; and (2) identifying and quantifying as many other constituents as possible, regardless of toxicity

- Estimate the completeness of the organic emissions characterization, in order to evaluate the uncertainty associated with the SSRA process

The first objective is achieved via analysis for specific target analytes. Target analyte lists, by design, address known toxic compounds. Analyses for full, commercially available target analyte lists should generally be completed by all facilities. *A priori* deletion of individual compounds (e.g., because they are

not found in the waste, or because they are not expected to be risk drivers) is not appropriate. Organic stack emissions cannot be predicted with certainty based upon waste characteristics. In addition, analyses for complete target analyte lists, when conducted using standard U.S. Environmental Protection Agency (EPA) methods, do not subject facilities to significant additional costs or burdens during the trial burn process. Therefore, *a priori* deletion of individual compounds is not likely to significantly reduce costs and could jeopardize the chances of identifying the greatest possible percentage of organics. Measurements for non-toxic volatile organics are also highly recommended in order to improve the overall emissions characterization.

The second, equally important objective, can be achieved by performing an organics mass balance for the organic stack emissions. The mass balance endeavors to (1) quantify the TO mass being emitted from the stack, and (2) estimate the quantity of unidentified organics, based on the difference between the TO mass and the total quantity of identified organics. Measurements for TO mass support this second objective. The human health risk assessment (HHRA) guidance (EPA in press) contains a detailed discussion regarding the use of TO for performing the organics mass balance and estimating uncertainty.

This appendix emphasizes methods and standard target analyte lists that are commercially available. Research by Ryan and others (1997a, 1997b), Lemieux and Ryan (1997b, 1998), and Midwest Research Institute (MRI) and AT Kearney, Inc. (1997) provides valuable insight into the limitations of standard methods for identifying and quantifying organics. However, this appendix incorporates virtually the entire repertoire of commercially available methods for stack samples, and alternative options are limited at this time. Some of the more 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) appear promising for further research, but additional method development is needed to support the use of these methods for stack samples on a commercial scale. Thus, it is unreasonable to presume that these innovative methods could be used for typical trial burn applications.

Until further method development can be pursued, organics determinations should rely on the best currently available methods for specific target analytes and tentatively identified compounds (TIC), combined with a TO determination, to clearly communicate the portion of the organic mass that cannot be identified. Research by Ryan, Lemiuex, and MRI highlights the significance of currently available options for optimizing organic emissions characterization. All of their studies relied on comprehensive evaluations

for TICs to expand identifications beyond standard target analyte lists (Lemieux and Ryan 1997b, 1998; MRI 1997). TIC identification also played a key role in full-scale research (Energy and Environmental Research Corporation [EER] 1997). Several of the studies (MRI 1997; EER 1997) emphasize the importance of determining as many volatile compounds as possible, regardless of toxicity. In these studies, screening for C1 through C4 straight-chain alkanes, alkenes, and alkynes was performed using either an on-line gas chromatograph/flame ionization detector (GC/FID), or C1-C4-targeted analyses of Method 0040 bag samples. Methane can comprise a significant percentage of the total stack organics (MRI 1997; Johnson 1996a). Determinations for methane and other aliphatics add little cost to the emissions testing and can potentially alleviate concerns about the percentage of the TO mass that might be toxic. Finally, several of the studies indicate that total hydrocarbon (THC) measurements may not be adequate or appropriate for supporting an organics mass balance (Ryan and others 1997a; MRI 1997). An obvious drawback to THC monitors is that they only measure gas-phase organics. Particulate material, including an indeterminate but sometimes significant fraction of the organic material, is removed by filtration and discarded. This is clearly unacceptable when attempting to measure TOs (Johnson 1996a). In lieu of THC, the TO mass determination has been repeatedly cited as the preferred starting point for the mass balance (Lemieux and Ryan 1997b, 1998; Johnson 1996a; EPA 1996d).

B.1.2   DETECTION LIMITS

In planning the specific sampling and analysis procedures, each facility should carefully consider detection limits that may be required in order to demonstrate risks below target levels. The HHRA guidance (EPA in press) contains a detailed discussion regarding required treatment of reliable detection limits (RDL), estimated detection limits (EDL), and estimated maximum possible concentrations (EMPC) in risk assessments. If detection limits are not low enough to achieve target risk levels, then modifications to the sampling and analytical procedures (e.g., longer sampling times, high resolution analytical techniques, etc.) may need to be considered.

It is highly recommended that a facility evaluate anticipated detection limits in a preliminary risk evaluation to determine whether modifications to the sampling and analytical procedures will be needed. This guidance, as well as the cited references, provide limited information regarding detection limits that can generally be expected from the various sampling train/analytical method combinations. However, detection limits are best determined based upon discussions with the qualified analytical chemist that will oversee the analysis. Detection limits for D/Fs have been found to be critical for the indirect risk pathway.

Other organics that may require particular attention because they could be important contributors to indirect risk include the following:

Polycyclic Aromatic Hydrocarbons (PAH)

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 (PCB)

Total PCBs
13 dioxin-like coplanar PCBs, listed in Table B8-1

Other Chlorinated Organics

Hexachlorobenzene
Pentachlorophenol

Phthalates

Bis(2-ethylhexyl) phthalate
Di(n)octyl phthalate

B.1.3   METHOD SUMMARY

Table B1-1 provides a summary of applicable stack sampling and analysis requirements for the SSRA data needs.   Specific information on each determination is provided in subsequent sections.

The emissions determinations rely on SW-846 methods (EPA 1996a), where available. Method numbers correlate with those in SW-846 unless otherwise specified. The method suffixes correspond to those in the December 1996 update (EPA 1996a). However, SW-846 will continue to be updated, and the latest revision of the recommended methods should be used as guidance. Where SW-846 does not provide a method for a particular determination, alternate sources are referenced. All of the procedures discussed in this appendix have been intentionally limited to methods that are commercially available.

SW-846 methods, as written, are intended as guidance and should be used as starting points for standard operating procedures (SOP) of the methods that will actually be used. SW-846 also provides guidance on individual method modifications. Other methods, not in SW-846, may be used for generating SSRA emissions data, provided that the user can demonstrate and document that the methods meet the data quality objectives (DQO) for the particular application. Even when using SW-846 methods, either as

written or modified, the user will need to demonstrate that the methods generate data that meet the DQOs. Therefore, detailed information regarding the actual methods should be described in detail in the trial burn plan, and the trial burn plan should define DQOs for the particular application. In some cases, additional modifications to standard EPA methods may be appropriate in order to address site-specific circumstances (e.g., sampling port limitations or a need for reduced detection limits). These modifications to standard EPA methods should be described in detail in the trial burn plan and are subject to approval by the regulatory agency.

TABLE B1-1

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-TCDD 2,3,7,8-TCDF Total TCDDs Total TCDFs 2,3,7,8-PeCDD 2,3,7,8-PeCDFs Total PeCDDs Total PeCDFs 2,3,7,8-HxCDD 2,3,7,8-HxCDFs Total HxCDDs Total HxCDFs 2,3,7,8-HpCDD 2,3,7,8-HpCDFs Total HpCDDs Total HpCDFs OCDD OCDF	All facilities	Method 0023A may be modified to allow simultaneous sampling and analysis of PCBs, PAHs, or SVOCs. However, specific approval is required for this modification, and a detailed description of the proposed methodology must be provided.
Non-D/F Organics: Volatile Organics	Tedlar Bag M0040 for Organics with BP < 30 °C	GC/FID GC/ECD	Alkanes, alkenes, alkynes	Optional, but highly recommended	Recommended in order to determine quantities of non-toxic organics to reduce uncertainty. Examples: Methane, ethane, ethene, acetylene, propane, propene, and propyne Analysis by GC/ECD may also be considered in order to determine low concentrations of chlorinated compounds.
		8260B GC/MS	• Volatile target analyte list, per Table B3-1 • 30 TICs, per Section B.5	All facilities	Analyze condensate.
Volatile Organics (continued)	VOST M0030/0031 for Organics with BP 30-100 °C	5041A/8260B GC/MS	• Volatile target analyte list, per Table B3-1 • 30 TICs, per Section B.5	All facilities	Analyze condensate.

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TABLE B1-1

RISK-BASED STACK EMISSION DETERMINATIONS (Continued)

Pollutant Category	Sampling Method [1]	Analysis Method [1]	Constituents To Be Determined	Applicability	Comments
Semivolatile Organics	MM5 M0010 for Organics with BP >100 °C	3542/8270C GC/MS	• Semivolatile target analyte list, per Table B4-1 • 30 TICs, per Section B.5	All facilities	Method 0010 maybe modified to allow simultaneous sampling and analysis of PCBs, PAHs, and D/Fs. However, specific approval is required for this modification, and a detailed description of the proposed methodology must be provided.
Chlorobenzenes/ Chlorophenols	MM5 M0010	GC/MS	• CBs/CPs in Table B6-1	All facilities	Separate analysis of the M0010 extract for CBs/CPs is recommended.
PAHs	MM5 M0010	HRGC/HRMS	• PAHs in Table B7-1	All facilities	Separate cleanup of the MM5 extract and analysis for PAHs by HRGC/HRMS is recommended.
PCBs	M0023A	CARB 428 [2] HRGC/HRMS	Total PCBs, based upon summation of homologue groups listed in Table B8-1	Site-specific determination as discussed in Section B.8	In order to determine PCBs from the M0023A sampling train, the condensate and impinger contents must 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 1668 [3] HRGC/HRMS	Thirteen dioxin-like congeners listed in Table B8-1		
Aldehydes/ Ketones	M0011	8315A HPLC	See M0011 for list, additional compounds can be determined	Site-specific determination as discussed in Section B.10	
Facility-Specific Compounds	Compound-specific, see Section B.11	Compound-specific, see Section B.11	Significant facility-specific compounds may need to be determined as appropriate: • Pesticides per Table B11-1 • Nitroaromatics • Cyanides	Site-specific	These additional compounds may need to be determined as necessary to represent the wastes burned at a particular facility.

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TABLE B1-1

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	All facilities	A separate M0010 train is required for the total organic mass determination.
	MM5 M0010	GC/FID	Total organic mass (μg) for organics boiling between 100-300 °C		
		Gravimetric	Total organic mass (μg) for organics boiling at > 300 °C		
THC/CO	CEMs - 40 CFR Part 266 Appendix IX Section 2.0		THC/CO, corrected to 7% oxygen, dry basis	All facilities	Baseline may be needed for continuous performance assurance.
Metals	M0060/ 0061	6010A/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	All facilities	Tier 1 metals may be excluded (i.e., assumption of no partitioning/ removal).
Particle-Size Distribution	See discussion in Section B.15		Site-specific particle-size distribution	See discussion in Section B.15	
Hydrogen Chloride and Chlorine	M0050/0051	M9057/9056	Hydrogen chloride and chlorine	All facilities	

Notes:

[1]   Unless specified otherwise, all sampling and analysis methods are from "Test Methods for Evaluating Solid Waste," SW-846, 3rd ed., as updated by Updates I, II, IIA, IIB, and III, through December 1996. 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.

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TABLE B1-1

RISK-BASED STACK EMISSION DETERMINATIONS (Continued)

[2]   California Environmental Protection Agency, Air Resources Board, CARB Method 428, Sacramento, CA.

[3]   EPA "Draft Method 1668 Toxic Polychlorinated Biphenyls by Isotope Dilution High Resolution Gas Chromotography/High Resolution Mass Spectrometry," Office of Science and Technology, Office of Water, March 1997.

[4]   "Guidance for Total Organics - Final Report," prepared for EPA by Radian Corporation, EPA/600/R-96/033, March 1996. 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.

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B.2 DIOXINS AND FURANS

All testing for collection of SSRA data is expected to include stack sampling and analysis for D/F compounds. In order to calculate a toxic equivalent factor (TEQ) in accordance with 40 CFR Part 266, Appendix IX, Section 4.0 and EPA (1989), the analysis should have sufficient resolution to quantify each congener with 2, 3, 7, 8 substitutions, as well as total quantities of other remaining congeners for each homologue. As indicated in Table B1-1, Method 0023A is used for stack sampling and sample preparation, followed by analysis in accordance with Method 8290 high resolution gas chromatography/ high resolution mass spectrometry (HRGC/HRMS). Method 0023A may be modified to allow for simultaneous sampling and analysis of other pollutant classes (e.g., PCBs, PAHs, semivolatile organic compounds [SVOC], and chlorobenzenes/chlorophenols [CB/CP]). However, specific approval is required for this modification. Simultaneous determinations from single Modified Method 5 (MM5) samples are discussed further in Section B.9.

Method 0023A supersedes Method 23 for Resource Conservation and Recovery Act (RCRA) testing (EPA 1997a). 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 labeled surrogate standards are spiked onto the XAD-2® sorbent prior to sampling, and onto the filter prior to extraction.

As discussed in Section B.1.2, target detection limits for D/Fs should be considered very carefully. Section 6.2.3 of Method 0023A provides guidance on determining the required sampling time based upon desired D/F detection limits. Desired detection limits for a particular application may be determined by performing a preliminary risk assessment prior to testing.

Sample recovery and preparation steps are reviewed briefly in this section because they are critical to the determination of whether Method 0023A can be modified to provide simultaneous analytical results for PAHs, PCBs, SVOCs, or CB/CPs. Combined determinations are discussed in more detail in Section B.9. After sampling, Method 0023A specifies sequential acetone, methylene chloride, and toluene rinses of the front half and back half portions of the sampling train. Methods 0023A allows all of the solvents to be combined in one container for the front half rinse and another for the back half rinse. However, the toluene has to be stored separately if SVOCs and CB/CPs are also being determined because some of the SVOCs could be lost in subsequent preparation steps. Also, if the sampling train is to be analyzed exclusively for D/Fs, the impinger liquid may be discarded after weight or volume is recorded. However,

if any other determinations are being made, the condensate and impinger liquid need to be retained and analyzed.

In the lab, 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 separately Soxhlet extracted with toluene and concentrated. One half of each fraction is archived, and the other portion is solvent-exchanged to hexane and then subjected to three column chromatographic cleanup steps as described in Method 8290. Finally, after addition of additional standards, the two fractions are analyzed separately by Method 8290 HRGC/HRMS. High resolution gas chromography/low resolution mass spectrometry (HRGC/LRMS) as provided in Method 8280 results in order-of-magnitude higher detection limits, and is not appropriate for collection of SSRA data. The mass of each isomer from the front half train fraction is added to that from the back half fraction to obtain a train total before further calculations. Section 7.4 of Method 0023A provides a suggested approach for this addition when a measured amount of an isomer is found in one fraction, but is below the detection limit in the other. Section 7.9.4 of Method 8290 provides guidelines regarding treatment of detection limits in the summation to determine total homologue concentrations.

Analysis of stack samples for fluorine-, bromine- and sulfur-substituted D/Fs is not anticipated at this time. Few calibration standards exist to accomplish these analyses, and analytical methods are not yet well defined. EPA has conducted preliminary studies of chlorinated, brominated, and mixed bromochloro D/Fs in stack emissions (Lemieux and Ryan 1997a, 1998). However, further research is necessary to better quantify these compounds and to further develop the appropriate sampling and analytical methodologies (EPA 1996b, 1996c). The HHRA guidance (EPA in press) recommends that these compounds be addressed in the uncertainty section of the SSRA.

B.3 VOLATILE ORGANIC COMPOUNDS

Two sampling methods are needed to determine volatile organic compounds (VOC). These include the volatile organic sampling train (VOST) (Method 0030/0031) and Tedlar bag (Method 0040) methods. VOST can typically achieve lower detection limits than the gas bag (i.e., parts per billion [ppb] verses parts per million [ppm] levels). However, it will not reliably capture very volatile compounds (i.e., those boiling below 30 °C). Thus, the bag sample is needed to augment the VOST results for very volatile compounds. Attachment 1 of this appendix provides a memorandum clarifying certain aspects of the Method 0040 Tedlar bag method. The VOST samples are thermally desorbed by Method 5041A. The Tedlar bag samples are introduced into the gas chromatograph through use of a sample loop. The condensate samples from both the VOST and Tedlar bag determinations can be introduced by direct aqueous injection, or by Method 5030 purge and trap. All samples (VOST, Tedlar bag, and condensates) should be analyzed by GC/MS for the Method 8260B volatile target analyte list, summarized in Table B3-1, and TICs as described in Section B.5. If a compound is detected in both the bag and VOST samples, the higher of the two results should be used for the SSRA and in the summation of total identified organics. If a compound is not detected, the lower of the two detection limits should be used.

Individual laboratories are likely to have target analyte lists for volatiles that differ slightly from Method 8260B and Table B3-1. Based upon a review of the lists from several laboratories, the differences are usually limited to a handful of problem compounds. If a laboratory does not include all of the Table B3-1 compounds on their standard volatile target analyte list, the laboratory should identify the excluded compounds and explain the reason for exclusion. The permit writer would likely approve use of the laboratory's standard VOC list in lieu of Table B3-1, after consideration of the laboratory's rationale and a review to ensure that the excluded compounds have not historically been found in stack emissions, based on Appendix A-1 of the HHRA guidance (EPA in press), Lemieux and Ryan (1997b, 1998), MRI (1997), and EER (1997).

Table B1-1 also indicates that Method 0040 bag samples should be analyzed by GC/FID for C1-C4 straight-chain aliphatics (alkanes, alkenes, etc.). As discussed in Section B.1.1, these compounds are generally non-toxic, but can make up a significant portion of the TO mass. The GC/FID evaluation adds little to the cost and is highly recommended in order to reduce uncertainty in the SSRA. Analysis by gas chromatograph/electron capture detector (GC/ECD) may also be considered in order to determine low concentrations of chlorinated compounds.

TABLE B3-1

VOLATILE TARGET COMPOUND LIST - METHOD 8260B ANALYTES

	Volatiles	CAS Number	Boiling Point,°C [1]
1.	Acetone[2]	67-64-1	56
2.	Acrylonitrile	107-13-1	78
3.	Benzene	71-43-2	80
4.	Bromodichloromethane	75-27-4	87
5.	Bromoform[3]	75-25-2	149
6.	Bromomethane	74-83-9	4
7.	2-Butanone[4]	78-93-3	80
8.	Carbon Disulfide	75-15-0	46
9.	Carbon Tetrachloride	56-23-5	77
10.	Chlorobenzene[3]	108-90-7	132
11.	Chlorodibromomethane	124-48-1	119
12.	Chloroethane	75-00-3	12
13.	Chloroform	67-66-3	62
14.	Chloromethane	74-87-3	-24
15.	Dibromomethane	74-95-3	97
16.	Dichlorodifluoromethane[4]	75-71-8	-30
17.	1,1-Dichloroethane	75-34-3	57
18.	1,2-Dichloroethane	107-06-2	83
19.	1,1-Dichloroethene	75-35-4	32
20.	cis-1,2-Dichloroethene	156-59-2	48
21.	trans-1,2-Dichloroethene	156-60-5	48
22.	1,2-Dichloropropane	78-87-5	95
23.	cis-1,3-Dichloropropene	10061-01-5	108
24.	trans-1,3-Dichloropropene	10061-02-6	107
25.	Ethylbenzene [3]	100-41-4	136
26.	Iodomethane	74-88-4	43
27.	Methylene Chloride	75-09-2	40
28.	Styrene [3]	100-42-5	145
29.	1,1,2,2- Tetrachloroethane [3]	79-34-5	146
30.	Tetrachloroethene	127-18-4	121
31.	Toluene	108-88-3	110
32.	1,1,1-Trichloroethane	71-55-6	74
33.	1,1,2-Trichloroethane	79-00-5	114
34.	Trichloroethene	79-01-6	87
35.	Trichlorofluoromethane	75-69-4	24
36.	1,2,3-Trichloropropane [3]	96-18-4	157
37.	Vinyl Chloride	75-01-4	-13
38.	Xylenes (total) [3]	1330-02-7	137

TABLE B3-1

VOLATILE TARGET COMPOUND LIST - METHOD 8260B ANALYTES (Continued)

Notes:

[1]   Existing sampling methods for volatiles are boiling point specific. The appropriate sampling methods should be considered to achieve the required volatile target analyte list. For example, compounds with boiling points less than 30 °C cannot be reliably sampled with 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. Therefore, the results for these compounds should be considered semi-quantitative, at best. However, they have been retained on the target analyte list in the interest of providing the most complete emissions characterization possible using currently available methods.

[3]   These constituents boil at greater than 121 °C. Although they are listed as Method 8260B analytes, they cannot be reliably sampled with VOST and should be added to the SVOC target analyte list (Table B4-1).

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

B.4   SEMIVOLATILE ORGANIC COMPOUNDS

The MM5 sampling train (Method 0010) is used to sample semivolatile organics.   In order to determine SVOCs from the Method 0010 train, the sampling train components are prepared in accordance with Method 3542. Method 3542 involves separate processing and analysis of three fractions: the filter/front-half rinse, the XAD-2® resin/back half rinse, and the condensate/condensate rinse.   Each fraction should be analyzed by GC/MS for the Method 8270C semivolatile target analyte list, summarized in Table B4-1, and TICs as described in Section B.5.

Sample recovery and preparation steps are reviewed briefly in this section because they are critical to the determination of whether Method 0010 can be modified to provide simultaneous results for D/Fs, PAHs, PCBs, SVOCs, and CB/CPs (discussed later in Section B.9). After sampling, Method 0010 specifies that a methanol/methylene chloride solvent be used for the front half and back half rinses. In the lab, isotopically-labeled standards are added to the filter and XAD-2® resin/back half fractions as specified in Method 3542, and these fractions are separately Soxhlet extracted with methylene chloride. The front half rinse is liquid-liquid extracted by separatory funnel to recover the methylene chloride layer, which is added to the filter extract. The condensate/condensate rinse is spiked with standards and is also liquid-liquid extracted to recover the methylene chloride layer. All three methylene chloride extracts, from the filter/front-half rinse, the XAD-2® resin/back half rinse, and the condensate/condensate rinse, are individually concentrated and analyzed by Method 8270C GC/MS. Detection limits for the Table B4-1 compounds vary between analytes, but are generally expected to be in the range of 1 to 10 micrograms per milliliter (μg/mL) of final extract volume. Quantitation limits are on the order of 10 μg/mL.

Individual laboratories are likely to have target analyte lists for semivolatiles that differ slightly from Method 8270C and Table B4-1. Based upon a review of the lists from several laboratories, the differences are more extensive than for the volatiles, and could encompass as many as thirty compounds. If a laboratory does not include all of the Table B4-1 compounds on their standard semivolatile target analyte list, the laboratory should identify the excluded compounds and explain the reason for exclusion. The permit writer would likely approve use of the laboratory's standard list in lieu of Table B4-1, after consideration of the laboratory's rationale and a review to ensure that the excluded compounds have not historically been found in stack emissions based on Appendix A-1 of the HHRA guidance (EPA in press), Lemieux and Ryan (1997b and 1998), MRI (1997), and EER (1997).

TABLE B4-1

SEMIVOLATILE TARGET COMPOUND LIST - METHOD 8270C ANALYTES

	Semivolatiles	CAS Number
1.	Acenaphthene	83-32-9
2.	Acenaphthylene	208-96-8
3.	Acetophenone	98-86-2
4.	4-Aminobiphenyl	92-67-1
5.	Aniline	62-53-3
6.	Anthracene	120-12-7
7.	Benzidine	92-87-5
8.	Benzoic Acid	65-85-0
9.	Benzo(a)anthracene	56-55-3
10.	Benzo(b)fluoranthene	205-99-2
11.	Benzo(k)fluoranthene	207-08-9
12.	Benzo(g,h,i)perylene	191-24-2
13.	Benzo(a)pyrene	50-32-8
14.	Benzyl alcohol	100-51-6
15.	Bis(2-chloroethoxy)methane	111-91-1
16.	Bis-(2-chloroethyl)ether	111-44-4
17.	Bis(2-ethylhexyl)phthalate	117-81-7
18.	4-Bromophenyl-phenyl ether	101-55-3
19.	Butylbenzylphthalate	85-68-7
20.	4-Chloroaniline	106-47-8
21.	4-Chloro-3-methylphenol	59-50-7
22.	1-Chloronaphthalene	90-13-1
23.	2-Chloronaphthalene	91-58-7
24.	2-Chlorophenol	95-57-8
25.	4-Chlorophenyl-phenyl ether	7005-72-3
26.	Chrysene	218-01-9
27.	Dibenz (a,j) acridine	224-42-0
28.	Dibenzo(a,h)-anthracene	53-70-3
29.	Dibenzofuran	132-64-9
30.	Di-n-butylphthalate	84-74-2
31.	1,2-Dichlorobenzene	95-50-1
32.	1,3-Dichlorobenzene	541-73-1
33.	1,4-Dichlorobenzene	106-46-7
34.	3,3'-Dichlorobenzidine	91-94-1
35.	2,4-Dichlorophenol	120-83-2
36.	2,6-Dichlorophenol	87-65-0
37.	Diethyl phthalate	84-66-2
38.	p-Dimethylaminoazobenzene	60-11-7
39.	7,12-Dimethylbenz(a)anthracene	57-97-6
40.	a,a-Dimethylphenethylamine	122-09-8
41.	2,4-Dimethylphenol	105-67-9

TABLE B4-1

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

	Semivolatiles	CAS Number
42.	Dimethylphthalate	131-11-3
43.	4,6-Dinitro-2-methylphenol	534-52-1
44.	2,4-Dinitrophenol	51-28-5
45.	2,4-Dinitrotoluene	121-14-2
46.	2,6-Dinitrotoluene	606-20-2
47.	Di-n-octyl phthalate	117-84-0
48.	Diphenylamine	122-39-4
49.	Ethyl methanesulfonate	62-50-0
50.	Fluoranthene	206-44-0
51.	Fluorene	86-73-7
52.	Hexachlorobenzene	118-74-1
53.	Hexachlorobutadiene	87-68-3
54.	Hexachlorocyclo-pentadiene	77-47-4
55.	Hexachloroethane	67-72-1
56.	Indeno(1,2,3-cd)-pyrene	193-39-5
57.	Isophorone	78-59-1
58.	3-Methylcholanthrene	56-49-5
59.	Methyl methanesulfonate	66-27-3
60.	2-Methylnaphthalene	91-57-6
61.	2-Methylphenol	95-48-7
62.	4-Methylphenol	106-44-5
63.	Naphthalene	91-20-3
64.	1-Naphthylamine	134-32-7
65.	2-Naphthylamine	91-59-8
66.	2-Nitroaniline	88-74-4
67.	3-Nitroaniline	99-09-2
68.	4-Nitroaniline	100-01-6
69.	Nitrobenzene	98-95-3
70.	2-Nitrophenol	88-75-5
71.	4-Nitrophenol	100-02-7
72.	N-Nitroso-di-n-butylamine	924-16-3
73.	N-Nitrosodimethylamine	62-75-9
74.	N-Nitrosodiphenylamine	86-30-6
75.	N-Nitroso-di-n-propylamine	621-64-7
76.	N-Nitrosopiperidine	100-75-4
77.	2,2'-oxybis (1-Chloropropane)[1]	108-60-1
78.	Pentachlorobenzene	608-93-5
79.	Pentachloronitrobenzene	82-68-8
80.	Pentachlorophenol	87-86-5
81.	Phenacetin	62-44-2

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

	Semivolatiles	CAS Number
82.	Phenanthrene	85-01-8
83.	Phenol	108-95-2
84.	2-Picoline	109-06-8
85.	Pronamide	23950-58-5
86.	Pyrene	129-00-0
87.	1,2,4,5-Tetrachlorobenzene	95-94-3
88.	2,3,4,6-Tetrachlorophenol	58-90-2
89.	1,2,4-Trichlorobenzene	120-82-1
90.	2,4,5-Trichlorophenol	95-95-4
91.	2,4,6-Trichlorophenol	88-06-2
Additional Constituents from the Method 8260B Target List:		
92.	Bromoform	75-25-2
93.	Chlorobenzene	108-90-7
94.	Ethylbenzene	100-41-4
95.	Styrene	100-42-5
96.	1,1,2,2-Tetrachloroethane	79-34-5
97.	Toluene[2]	108-88-3
98.	1,2,3-Trichloropropane	96-18-4
99.	Xylenes (total)	1330-02-7

Notes:

[1] Also known by the name bis(2-Chloroisopropyl) ether

[2] Toluene is recommended in order to confirm sampling of constituents down to 100 °C

B.5   TENTATIVELY IDENTIFIED COMPOUNDS

For both the Method 8260B and Method 8270C determinations discussed in Sections B.3 and B.4 (i.e., VOCs by VOST and Tedlar bag, and SVOCs by MM5), analysis for specific target analytes should be accompanied by an evaluation of TICs. Besides target analytes, 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 organics.

The mass spectrum of the non-target compounds can be searched against a library of mass spectra. A forward library search selects the largest mass spectral peaks from the unknown spectrum and looks for library spectra containing those peaks. A reverse search looks for the peaks in the library spectrum that occur in the unknown spectrum. Any components that are identified are referred to as TICs, since there is no reference standard analyzed at the same time as the unknown.

Without a compound-specific calibration, TICs can only be quantified using the nearest internal standard and an assumed relative response factor (RRF) of one (1.0). The resulting concentration is considered "estimated," due to lack of a compound-specific response factor. The error introduced by an assumed RRF of 1.0 is unknown and will vary from compound to compound.

The EPA Contract Laboratory Program provides guidelines regarding TIC determinations (EPA 1994). These are reproduced here as follows:

> A library search should be executed for non-target sample components for the purpose of tentative identification. Up to 30 organic compounds of greatest apparent concentration not listed on the relevant target compound list, and excluding internal standards and surrogates, should be tentatively identified via a forward search of the NIST/EPA/NIH (May 1992 release or later) and/or Wiley (1991 release or later), or equivalent mass spectral library. Computer generated library search routines should not use normalizations which would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are as follows:
>
> - Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
>
> - The relative intensities of the major ions should agree within +/- 20%.
>
> - Molecular ions present in the reference spectrum should be present in the sample spectrum.

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- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

If, in the judgement of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as "unknown". The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown aromatic, unknown hydrocarbon, unknown chlorinated compound). If probable molecular weights can be distinguished, these should also be included.

An estimated concentration for tentatively identified non-target compounds should be determined by the internal standard method. For quantitation, the nearest internal standard free of interferences should be used, using an assumed relative response factor of one (1). The resulting concentration should be qualified as "estimated", due to lack of a compound-specific response factor, and as "presumptive evidence of presence", indicating the quantitative and qualitative uncertainties associated with the non-target component. An estimated concentration should be calculated for all tentatively identified compounds, as well as those identified as unknowns.

Where possible, additional standards containing TICs should be prepared and analyzed to confirm identification. A multiconcentration calibration with the additional standards can be used to establish RRFs specific to each compound, and the semivolatile extracts can be re-analyzed to enhance quantitative accuracy. For volatiles, the RRFs can be used to re-quantify prior analyses to enhance quantitative accuracy.

B.6   CHLOROBENZENES/CHLOROPHENOLS

Some labs offer an expanded GC/MS target analyte list for CB/CPs, similar to Table B6-1. Although there is some overlap with the Table B4-1 SVOC constituents, the CB/CP list is more extensive and is recommended. The CB/CP analysis uses the same extracts prepared for the SVOCs, as discussed in Section B.9. Therefore, dual analysis for both SVOCs and CB/CPs should not adversely impact the detection limits for either determination. If a CB/CP compound is detected in both the SVOC and CB/CP analyses, the higher of the two results should be used for the SSRA and in the summation of total identified organics. If a compound is not detected, the lower of the two detection limits should be used.

TABLE B6-1

CHLOROBENZENES AND CHLOROPHENOLS

Chlorobenzenes	CAS Number	Chlorophenols	CAS Number
1,2-Dichlorobenzene	95-50-1	2-Chlorophenol	95-57-8
1,3-Dichlorobenzene	541-73-1	3-Chlorophenol[2]	108-43-0
1,4-Dichlorobenzene	106-46-7	4-Chlorophenol[2]	106-48-9
1,3,5-Trichlorobenzene	108-70-3	2,4-Dichlorophenol	120-83-2
1,2,4-Trichlorobenzene	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[1]	634-90-2	2,6-Dichlorophenol	87-65-0
1,2,4,5-Tetrachlorobenzene[1]	95-94-3	3,5-Dichlorophenol	591-35-5
1,2,3,4-Tetrachlorobenzene	634-66-2	3,4-Dichlorophenol	95-77-2
Pentachlorobenzene	608-93-5	2,3,5-Trichlorophenol	933-78-8
Hexachlorobenzene	118-74-1	2,4,6-Trichlorophenol	88-06-2
		2,4,5-Trichlorophenol	95-95-4
		2,3,4-Trichlorophenol	15950-66-0
		2,3,6-Trichlorophenol	933-75-5
		2,3,5,6-Tetrachlorophenol[3]	935-95-5
		2,3,4,5-Tetrachlorophenol[3]	490-151-3
		Pentachlorophenol	87-86-5

Note:

[1]   Co-elute, reported as totals

[2]   Co-elute, reported as totals

[3]   Co-elute, reported as totals

B.7 POLYCYCLIC AROMATIC HYDROCARBONS

Although the Method 8270C list (Table B4-1) includes most PAHs, detection limits for PAHs have been found to be critical for the indirect risk pathway. Therefore, it is recommended that PAHs be determined by separate HRGC and either HRMS or LRMS analysis after the application of chromatography cleanup procedures designed to remove interfering organics. If a PAH compound is detected in both the SVOC and PAH analyses, the higher of the two results should be used for the SSRA and in the summation of total identified organics. If a compound is not detected, the lower of the two detection limits should be used.

California Environmental Protection Agency, Air Resources Board (CARB) Method CARB 429 (CARB 1997) provides guidelines for sampling and analysis of the PAHs listed in Table B7-1. Method CARB 429 specifies sample collection with a MM5 sampling train. After sampling, the train components are sequentially rinsed with acetone, hexane, and methylene chloride. The filter, XAD-2® resin, concentrated rinses, and condensate are Soxhlet extracted with methylene chloride, as are the impinger contents/rinses. The methylene chloride extracts are concentrated, solvent exchanged to hexane, and subjected to a silica gel or alumina column clean up.

Following the cleanup, the extracts are analyzed by HRGC, and either isotope dilution HRMS or LRMS. The decision regarding specific procedures will depend on the detection limits which are determined to be necessary for PAHs based upon a preliminary risk evaluation. PAHs can be analyzed by LRMS with usual detection limits ranging from 1 to 5 micrograms (µg) per fraction. PAHs can be analyzed by HRMS with usual detection limits ranging from 10 to 50 nanogram (ng) per fraction. Actual detection limits are limited by the background level of PAHs observed in the XAD-2® resin.

The Method CARB 429 PAH procedures can likely be successfully merged with either the Method 0023A D/F procedures or the Method 0010/3542 SVOC procedures with careful planning. An extract that has been subject to chromatography cleanup procedures for PAHs would not be suitable for any other semivolatile determination. However, absent this final step, the sample preparation and extraction can be designed to achieve multiple semivolatile determinations. This is discussed further in Section B.9.

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TABLE B7-1

POLYCYCLIC AROMATIC HYDROCARBONS

PAH	CAS Number
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Anthracene	120-12-7
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
1-Chloronaphthalene	90-13-1
2-Chloronaphthalene	91-58-7
Chrysene	218-01-9
Dibenz(a,j)acridine	224-42-0
Dibenzo(a,h,)anthracene	53-70-3
Dibenzo(a,e)pyrene	192-65-4
7,12-Dimethylbenz(a)anthracene	57-97-6
Fluoranthene	206-44-0
Fluorene	86-73-7
Indeno(1,2,3-cd)pyrene	193-39-5
3-Methylcholanthrene	56-49-5
2-Methylnaphthalene	91-57-6
Naphthalene	91-20-3
Phenanthrene	85-01-8
Pyrene	129-00-0

B.8 POLYCHLORINATED BIPHENYLS

The need for sampling and analysis of PCBs requires careful consideration and is discussed in detail in the HHRA guidance (EPA in press). Determinations regarding the need for PCB analysis may become more straight forward as additional data are collected and evaluated. However, in the interim, the following general guidelines may be considered in conjunction with site-specific concerns:

- PCBs should automatically be tested at combustion units that burn PCB-contaminated wastes or waste oils

- PCBs should be tested at units that burn highly variable waste streams, such as municipal or commercial wastes, for which PCB contamination is reasonable

- PCBs should be tested at facilities that burn highly chlorinated waste streams

In regards to PCB testing at other hazardous waste combustion facilities, the HHRA guidance (EPA in press) 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." For any facility where uncertainty regarding PCB formation may be cause for concern, a PCB determination can be easily added to the D/F test procedures.

Method CARB 428 (CARB 1990a), which provides guidelines on sampling and recovery procedures for PCB determinations, specifies sampling with a MM5 sampling train followed by Soxhlet extraction with toluene. Since Method 0023A for D/Fs also requires toluene extraction, PCBs and D/Fs may be determined from the same Method 0023A sampling train. However, if both D/Fs and PCBs are to be determined from the same sampling train, it is necessary to split the sample after extraction for different preliminary fractionation and cleanup procedures. PCB cleanups typically involve silica gel or florisil. In addition, the condensate and impinger contents must be retained and analyzed. This is discussed further in Section B.9.

PCBs are often discussed in terms of commercial mixtures, or Arochlors. However, PCBs change in the environment, and their compositions differ from the commercial mixtures. Characterization of combustion emissions in terms of Arochlors, for example by Method 8082, would be both imprecise and inappropriate. EPA's current toxicity approach (1996e) requires data on (1) the total PCB concentration and (2) congener-specific analyses for the 13 toxic dioxin-like coplanar and mono-ortho-substituted PCBs listed in Table B8-1. Dioxin TEQs are applied to the congener-specific concentrations to evaluate dioxin-like toxicity. Risks from the dioxin-like congeners (evaluated using dioxin TEQs) are then added to risks from

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TABLE B8-1

POLYCHLORINATED BIPHENYLS

Dioxin-Like Coplanar PCBs		CAS Number
3,4,3',4'-Tetrachlorobiphenyl	IUPAC 77	32598-13-3
2,3,4,3',4'-Pentachlorobiphenyl	IUPAC 105	32598-14-4
2,3,4,5,4'-Pentachlorobiphenyl	IUPAC 114	74472-37-0
2,4,5,3',4'-Pentachlorobiphenyl	IUPAC 118	31508-00-6
3,4,5,2',4'-Pentachlorobiphenyl	IUPAC 123	65510-44-3
3,4,5,3',4'-Pentachlorobiphenyl	IUPAC 126	57465-28-8
2,3,4,5,3',4'-Hexachlorobiphenyl	IUPAC 156	38380-98-4
2,3,4,3',4',5'-Hexachlorobiphenyl	IUPAC 157	68782-90-7
2,4,5,3',4',5'-Hexachlorobiphenyl	IUPAC 167	52663-72-6
3,4,5,3',4',5'-Hexachlorobiphenyl	IUPAC 169	32774-16-6
2,3,4,5,2',3',4'-Heptachlorobiphenyl	IUPAC 170	35065-30-6
2,3,4,5,2',4',5'-Heptachlorobiphenyl	IUPAC 180	35065-29-3
2,3,4,5,3',4',5'-Heptachlorobiphenyl	IUPAC 189	39635-31-9
Total Homologue Groups (Sum to Determine Total PCBs)		
Monochlorobiphenyls		
Dichlorobiphenyls		
Trichlorobiphenyls		
Tetrachlorobiphenyls		
Pentachlorobiphenyls		
Hexachlorobiphenyls		
Heptachlorobiphenyls		
Octachlorobiphenyls		
Nonachlorobiphenyls		
Decachlorobiphenyls		

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the rest of the mixture (evaluated using slope factors applied to total PCBs reduced by the amount of dioxin-like congeners). The HHRA guidance (EPA in press) provides more information on this issue.

Method CARB 428 provides guidelines for analysis to determine the total homologue group concentrations listed in Table B8-1, which can be summed to provide a total PCB concentration. Knowledge of the PCB distribution by homologue group is necessary in order to determine which toxicity value to apply. Method CARB 428 calls for analysis by HRGC/LRMS, giving target detection limits on the order of 0.1 to 1.0 µg per sample per homologue group when both D/F and PCBs are determined from the same sample.

However, since PCBs have been found to be risk drivers, CARB 428 should be used with HRMS to provide PCB homologue group concentrations at lower detection limits.

Method CARB 428, as written, will not provide information on the 13 co-planar PCBs. However, guidelines on isotope dilution HRGC/HRMS analysis for the thirteen co-planars have been published as Draft Method 1668 (EPA 1997b), and Method 1668 determinations are already being provided at some commercial laboratories with high resolution GC/MS capabilities.

B.9   ANALYSIS OF MM5 SAMPLES FOR MULTIPLE POLLUTANT CLASSES

As discussed in the previous sections, the MM5 sampling train is used to sample several different categories of semivolatile organics:

- Section B.2 - Dioxins/furans
- Section B.4 - Semivolatile organic compounds
- Section B.6 - Chlorobenzenes/chlorophenols
- Section B.7 - Polycyclic aromatic hydrocarbons
- Section B.8 - Polychlorinated biphenyls

The sample recovery and preparation steps associated with the various SVOC, CB/CP, PAH, and PCB determinations significantly influence whether the determinations can be conducted from a single Method 0010 sampling train, or in conjunction with the Method 0023A D/F train. This topic is discussed in more detail in this section.

In some cases (e.g., sampling platform constraints, sample port constraints, to increase sampling efficiency, etc.) it may be necessary to analyze a single MM5 train sample for multiple pollutant classes. This could encompass all of the semivolatile determinations discussed previously, D/Fs, SVOCs, CB/CPs, PAHs, and PCBs. In this situation, all aspects of the sampling and analysis must be considered carefully to ensure that the resulting data will not be invalid for one or more of the compound classes. A separate MM5 train must always be run exclusively for TOs, as discussed later in Section B.12.

Procedures for multiple determinations are subject to approval by the regulatory agency. The facility should provide a detailed description in the trial burn plan of how the sampling analysis for multiple compounds will be performed. Documentation should include detailed information on sampling, recovery, spiking, analysis, quality assurance and quality control (QA/QC) procedures, and anticipated impacts on detection limits.

Potential liabilities associated with combined semivolatile determinations are discussed in detail in Johnson (1995). The following briefly summarizes key information from that paper.

Detection Limits:

Increased detection limits can occur as a result of combining semivolatile determinations. It is often necessary to split the sample for separate processing through two different preparatory procedures. If the sample is split into two equal parts, each may have its detection limit doubled.

Sample Preparation:

The choice of solvents is critical. If methylene chloride is combined with toluene or other higher boiling point solvent, it may become difficult to concentrate the resulting extract without potential loss of the more volatile compounds.

Cleanup procedures are also critical. Many analytical methods include cleanup procedures, such as column chromatography or gel-permeation chromatography, designed to remove interfering organics but to have minimal effect on the target analytes. When combining determinations, it is important to ensure that the target analytes will not be removed with the unwanted compounds. Determinations for D/Fs, PAHs, and PCBs each involve specific cleanup procedures, which make the resulting extract unsuitable for any other determinations.

Standards:

In combining methods, it is important to consider whether internal standards, surrogate standards, or recovery standards could be a source of incompatibility between methods. Assistance should be obtained from a well qualified analytical chemist who understands the methods and calculations involved.

Alternatively, standards can serve a beneficial function when multiple methods are combined because standards can be used to ensure that losses are not incurred. For example, isotopically-labeled D/F, SVOC, PAH, and PCB standards can be used at various stages as follows:

- Standards can be added to the sampling module, to gauge potential losses during sampling
- Standards can be added prior to sample recovery, to gauge losses during extraction, concentration, and cleanup
- Standards can be added immediately prior to analysis, primarily to compensate for instrument response changes

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Although most of the methods already utilize these types of standards, additional standards should be added as needed to address concerns associated with combined methods.

The importance of consulting a qualified analytical chemist on these issues cannot be overstated. However, procedures which have been used by some commercial labs are summarized below in order to highlight some of the basic considerations.

Determinations from One Sampling Train

All determinations (D/F, SVOCs, CBs/CPs, PAHs, and PCBs) can be made from a single Method 0023A sampling train, if necessary. However, the toluene train rinses from the D/F train recovery have to be stored separately, the condensates and impinger contents have to be retained and analyzed, and two Soxhlet extractions are required.

Procedures used by one lab illustrate these points. This lab performs the first Soxhlet extraction with methylene chloride. The resulting extract is split in half, one half for the D/F determination and the other half for everything else. The toluene rinse is added to the remaining Soxhlet extractor contents, and a second extraction occurs with toluene. Half of the resulting toluene extract is combined with the half methylene chloride extract, and the combined extract is subjected to D/F cleanup and analysis (the other half of the toluene extract is not used). From the remaining methylene chloride extract, one portion is subjected to PAH cleanup and analysis, one portion is subjected to PCB cleanup and analysis, and one portion can be analyzed directly for SVOCs and/or CB/CPs.

The D/F detection limit is not compromised by this methodology, because Method 0023A already calls for a 1:1 split of the extract (half is archived). The combined methodology essentially uses part of the archive for the other analyses. The SVOC and CB/CP detection limits are doubled by this methodology (a dilution factor of 2x must be applied, because of the 1:1 methylene chloride extract split). The PAH and PCB detection limits may or may not be affected, depending on the portions removed for clean up and the final concentrated volumes prior to analysis.

Alternatives to this methodology exist. Since Method CARB 428 requires a toluene extraction for PCBs, PCBs would preferably be determined with D/Fs from the combined toluene/methylene chloride extract instead of with SVOCs from the straight methylene chloride extract. One portion would be used for D/F cleanup and analysis, and another portion would be removed for PCB clean up and analysis.

Determination from Two Sampling Trains

If two sampling trains can be used, a reasonable combination would include D/Fs and PCBs from a Method 0023A train, and all other determinations from a second Method 0010 train. The D/F and PCB combination is natural, because both components are amenable to toluene extraction as described in Method CARB 428.

In order to determine PCBs from Method 0023A, it is recommended that at least four isotopically labeled PCB surrogates be spiked onto the XAD-2® resin together with the D/F surrogates prior to sampling. The amount of surrogates and internal standards added to the samples should be adjusted to compensate for the additional analysis (Ryan 1998). The Method 0023A train components would be subject to a single Soxhlet extraction with toluene, and the extract would be split. One portion would be used for D/F clean up and analysis, and another portion would be removed for PCB cleanup and analysis. The D/F detection limit would not be compromised by this methodology, and the PCB detection limit would depend on the portion removed for clean up and the final concentrated volume prior to analysis.

The second MM5 train, Method 0010, would be subject to a single Soxhlet extraction with methylene chloride. One portion would be subjected to PAH cleanup and analysis, and another portion could be analyzed directly for SVOCs and/or CB/CPs. The detection limits for SVOCs and CB/CPs would not be compromised by this methodology. The detection limits for PAHs would depend on the portion removed for cleanup, and the final concentrated volume prior to analysis.

PAHs

With either method, the PAHs could possibly be determined with the D/F extract, because toluene is an acceptable alternative extractant for PAHs (Johnson 1995). Care would have to be taken not to take the extract to dryness, because PAH vapor pressures could cause significant losses with complete evaporation. Also, the sample extract would have to be split for separate D/F cleanup and analysis, PCB cleanup and analysis, and PAH cleanup and analysis.

Clean Up Procedures

Determinations for D/Fs, PAHs, and PCBs each involve specific cleanup procedures. An extract which has been subjected to any of these cleanups should not be analyzed for any other pollutants. However, absent

the final cleanup steps, the extraction and preparation for all three determinations can probably be combined.

Multiple Analysis of Single Extracts

SVOCs and CB/CPs, and perhaps other semivolatiles, can always be determined simultaneously with no compromise in detection limits. This holds true for any determinations that simply involve multiple injections of a single extract, with no splitting during preparation.

B.10   ALDEHYDES/KETONES

The final category of specific organic analytes is aldehydes/ketones (A/K). Some A/Ks are already included on the Table B3-1 and B4-1 constituent lists. These have been retained on Tables B3-1 and B4-1 because the VOST, Tedlar bag, and MM5 methods often provide information on A/K concentrations. However, in order to reliably determine A/Ks, specific sampling and analytical procedures are required. Reliable A/K determinations require a Method 0011 sampling train. The stack gases are sampled isokinetically and collected in aqueous acidic 2,4-dinitrophenylhydrazine solution. A dinitrophenyl-hydrazone derivative is formed, which is then extracted, solvent-exchanged, concentrated, and analyzed by high performance liquid chromatography (HPLC) according to Method 8315. This methodology can determine concentrations of the following A/Ks, although many laboratories have extended the method to other aldehydes and ketones:

- Formaldehyde
- Acetaldehyde
- Acetophenone
- Isophorone
- Propionaldehyde

The need for Method 0011 A/K sampling should be considered carefully. Stack sampling port and platform restrictions will likely limit the number of isokinetic sampling trains that can be run at one time. Unless a facility burns large quantities of A/K wastes, the 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. Also, as stated previously, the VOST, Tedlar bag, and MM5 methods are likely to provide some A/K information, although the data would not be of the same quality as that from Methods 0011/8315.

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B.11   FACILITY-SPECIFIC COMPOUNDS

The previous sections identified target analyte lists that are generally applicable to all facilities. However, it may be necessary for individual facilities to sample and analyze for additional compounds based upon the wastes that they burn. Potential candidates for additional facility-specific determinations include any highly toxic, persistent, or bioaccumulative constituents burned in large quantities. These could encompass compounds such as pesticides, nitroaromatics, and cyanides.   These constituents would be in addition to, and not substitutes for, the target analyte lists described previously in this appendix. Table B11-1 lists organochlorine pesticides which can be determined by Method 8081A GC/ECD, together with the waste codes which might contain these compounds.

Other facility-specific considerations might include D017 waste (2,4,5-TP [Silvex]), D016 and U240 waste (2,4-D), K025 waste (1,3-Dinitrobenzene), and cyanide wastes (F007-F012, F019, K007, K011, K013, K027, K060, K088, and U246). Method 8151A provides analytical procedures for chlorinated herbicides. Method 8270C can provide data on nitroaromatics. Method CARB 426 (CARB 1991) can be used for determination of cyanide emissions.

TABLE B11-1

ORGANOCHLORINE PESTICIDES - METHOD 8081A ANALYTES

Compound	CAS Number	Waste Codes
Aldrin	309-00-2	P004
α-BHC	319-84-6	D013, U129
β-BHC	319-85-7	D013, U129
γ-BHC (Lindane)	58-89-9	D013, U129
δ-BHC	319-86-8	D013, U129
Chlorobenzilate	510-15-6	U038
α-Chlordane	5103-71-9	D020, K097, U036
γ-Chlordane	5103-74-2	D020, K097, U036
Chlordane - mixed isomers	57-74-9	D020, K097, U036
1,2-dibromo-3-chloropropane	96-12-8	U066
4,4'-DDD	72-54-8	U060, U061
4,4'-DDE	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	76-44-8	D031, K097, P059
Heptachlor epoxide	1024-57-3	D031, K097, P059
Hexachlorobenzene	118-74-1	D032
Hexachlorocyclopentadiene	77-47-4	U130
Isodrin	465-73-6	P060
Methoxychlor	72-43-5	D014, U247
Toxaphene	8001-35-2	D015, K041, K098, P123

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B.12   TOTAL ORGANICS

The importance of determining the TO mass being emitted from the stack has been discussed previously in Section B.1.1. Procedures for determining TO mass are outlined in a final EPA (1996d) report dated March 1996. Although other methods for measuring TOs are often proposed, a discussion regarding why these other methods, including THC monitoring, are inappropriate for the TOs determination is found in Johnson (1996a).

TOs, as determined by the published methodology, means the total amount of organic material which is recoverable by means of solvent extraction or other preparatory steps used in the survey analysis. The results are reported as "µg total organic per m³." This result can be compared directly to the summed mass of all of the identified constituents. It is not necessary, or actually appropriate, to convert the TO result to another basis, such as ppm carbon or ppm propane.

In order to determine the unidentified organic mass, the masses of specific quantified toxic compounds are subtracted from the results of the TO determination. This would include compounds such as D/Fs, PAHs, PCBs, SVOCs, VOCs, and A/Ks. The mass of organic material remaining after correction for identified compounds is referred to as the "unspeciated (or unidentified) organic mass." The HHRA guidance (EPA in press) provides more detail regarding the use of this information in the SSRA.

The TO procedure is based on the determination of organics in three boiling point ranges (1) the volatile, field gas chromatography (FGC) fraction (boiling point less than 100 °C), (2) the semivolatile, total chromatographable organics (TCO) fraction (boiling point between 100 and 300 °C), and (3) the nonvolatile, gravimetric (GRAV) fraction (boiling point greater than 300 °C). The sum of the constituent concentrations in the three fractions represents the estimated TOs.

The TO procedure involves two separate sampling procedures. The FGC fraction is collected using a Tedlar bag as described in Method 0040. The TCO and GRAV fractions are collected during the same sampling period as the FGC fraction by using a separate Method 0010 sampling train. The operation of the Method 0010 train for TO will be the same as that used for the SVOCs. However, a separate Method 0010 train must be run exclusively for TO. The MM5 trains used for sampling specific semivolatile constituents (D/F, SVOCs, etc.) *cannot* be used for the TOs determination, because the addition of standards to those trains would register as TOs and would complicate interpretation of results.

Each fraction is discussed in more detail below.

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Field Gas Chromatography Fraction (boiling points < 100 °C)

The FGC fraction is collected using a Tedlar bag, Method 0040. The analysis procedures are normally performed in the field to minimize sample loss due to storage and shipping. The analysis is by GC/FID, and results are reported in Table B12-1 as seven subcategories according to boiling point range.

Total FGC organics are determined by summing the peak areas, converted to concentration values in micrograms per cubic meter ($\mu g/m^3$), in each retention time window. It is strongly recommended that methane be determined as an individual compound during the FGC analysis. Methane can be a major component of the volatile organic emissions, and it is beneficial to have its mass in the assigned side of the organics material balance rather than as part of the unidentified component (Johnson 1996a).

The condensate fraction from the Method 0040 sampling is normally transferred to a zero-headspace vial and shipped to the laboratory for analysis. The condensate is analyzed by purge and trap GC/FID, based on calibration with a C5-C7 mixture. Results can be reported as C5, C6, and C7 fractions.

Total Chromatographable Organics Fraction (boiling points 100-300 °C)

The TCO and GRAV fractions are both collected using a single MM5 sampling train, SW-846 Method 0010. Organics are recovered from the various components of the sampling train according to Method 3542. After recovery, the three resulting methylene chloride extracts are combined before analysis for TCO and GRAV.

TCO analysis is a form of low-resolution GC/FID, where the area under the response curve is integrated between boiling points 100-300 °C (e.g., by summing peak areas in the C7-C17 range). For purposes of comparison, "hot" THC continuous emission monitor (CEM) samples are only required to be maintained above 150 °C, and do not involve filter analysis.

Gravimetric Mass Fraction (boiling points > 300 °C)

The GRAV fraction is the only fraction for which the mass is determined directly. The GRAV procedure is carried out by analysis of an aliquot of the same methylene chloride extract as was used for the TCO determination. The aliquot is placed in a weighing pan, allowed to dry, and weighed. The mass (in μg) is recorded as the GRAV value. When divided by the sample volume, the result in $\mu g/m^3$ can be added to the FGC and TCO values for the TOs determination.

Because high field blank results for the gravimetric portion have been reported, trouble-shooting measures have been identified to minimize potential sources of contamination (EPA 1997c). This section provides a summary of these "lessons learned" for the gravimetric determination. In order to obtain the most accurate results possible for the nonvolatile portion of the TO emissions, it is important to ensure that the XAD-2® resins used in the gravimetric analysis are clean. Field results have shown high blank results that were attributed to old and dirty XAD-2® resins. It is recommended that only XAD-2® resins that have been recently cleaned (preferably no longer than 14 days prior to sample analysis) be used to analyze trial burn samples for the purpose of generating data for an SSRA. The following gravimetric laboratory procedures are recommended for minimizing sources of contamination:

- Assure all glassware and 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 pan that composite extracts are transferred to for drying, by building a tent with aluminum foil, shiny side out

- Run a control pan

- Check calibration on balance prior to each weighing

- Use a balance precise to 10 μg

- Take extra care in handling XAD-2® resin (make sure that the resin does not float out of the extraction thimble)

- Run three non-filtered and filtered extracts through gravimetric measurements (using filters specified in Method 0010) and compare the results to determine if a carry through problem may exist; as a rule of thumb, if the XAD-2® resin and condensate/back-half rinse extract exceeds the criteria for clean XAD-2® in Method 0010, Appendix A, the resin is the likely source of the problem

- Confirm that the clean XAD-2® resin used in the laboratory and in the field meets Method 0010, Appendix A requirements

- Reconstitute the gravimetric sample from the extract composite and run it on the GC/MS for rhombic sulfur; also, run TO extract prior to performing the procedure for rhombic sulfur on the GC/MS (This should only be applied to actual samples, not blanks, where there can be significant sources of sulfur in the fuels or wastes.)

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TABLE B12-1

TOTAL ORGANICS FGC ANALYSIS

Compound	Boiling Point °C	Reporting Range °C	Report As	Comparisons
Methane	-161	-160 to -100	C1	Cold THC CEM: Boiling point < 0°C
Ethane	-88	-100 to -50	C2	
Propane	-42	-50 to 0	C3	
Butane	0	0 to 30	C4	
Pentane	36	30 to 60	C5	VOST: Boiling Point 30-100 °C
Hexane	69	60 to 90	C6	
Heptane	98	90 to 98	C7	

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Attempts to more specifically characterize the GRAV fraction have met with mixed results. The GRAV fraction may include organic and/or inorganic mass not directly attributable to organic incinerator emissions. These artifacts may be composed of inorganic salts, super-fine particulate, fractured XAD-2® resin, or some other unknown (Lemiuex and Ryan 1998).

The TO measurement is an estimate. For both the FGC and TCO fractions, the estimated mass is calculated based on detector responses to specific compounds that are presumed to be representative of the specific fraction. However, the TO measurements are strongly believed to be the best currently available procedure for generating a TOs analysis for the purpose of indicating uncertainty due to the fraction of organics that have not been quantified. TO measurements may be very conservative measurements of uncertainty because the GRAV fraction may contain inorganic species.

It is recommended that the individual boiling point category and subcategory data from the various components of a TO determination be reported, since this information may be very useful during later interpretation. For example, the unidentified mass in the GRAV range cannot be due to vinyl chloride, just as the unidentified material in the FGC analysis cannot be dioxin or PAH compounds (Johnson 1996a).

Estimates of compounds that are potentially associated with the three TO fractions are summarized from MRI (1997). The FGC fraction would be expected to contain lighter hydrocarbons and halogenated alkanes and alkenes. This could include compounds such as methane and halogenated ethanes, ethenes, and propanes. The TCO fraction will contain a wide range of semivolatile compounds that could include compounds such as D/Fs, phthalates, phenols, halogenated aromatics, and nitrogenated and sulfonated compounds. The GRAV portion is extremely difficult to analyze. However, it would be expected to contain high molecular weight organics of C17 or greater, D/Fs, many PAHs, and high molecular weight organic acids and salts. Potential contaminants in the GRAV fraction include salts. One attempt to characterize the gravimetric fraction of reaction products from D/Fs sorbed on a calcium-based sorbent involved thin-layer chromatography separation followed by multiple analytical techniques (Gullett and others 1997). This showed the gravimetric portion from that particular research to be higher molecular weight, chlorinated compounds with both aromatic and aliphatic components. The author noted that these higher molecular weight products would not likely be detected by conventional GC/MS analysis.

Lemieux and Ryan (1997b, 1998) have suggested a number of techniques which may be explored to identify more of the TOs, with particular emphasis on the semivolatile and non-volatile (TCO and GRAV) fractions. Each sample would be segregated or fractionated based on polar characteristics using HPLC.

Then, each fraction could be analyzed by GC/MS as well as MDGC/MS. These recommendations involve innovative techniques and would first need to be demonstrated at lab-scale test facilities prior to field use.

B.13 TOTAL HYDROCARBON AND CARBON MONOXIDE CONTINUOUS EMISSIONS MONITORS (CEM)

Even if THC monitoring is not required by current regulations at a facility, it should be performed in conjunction with the organic emissions determinations during risk testing. This can be accomplished by having a temporary monitor brought in during the testing, if necessary. Performance specifications for THC monitoring are provided at in 40 CFR Part 266, Appendix IX, Section 2.2.

Although THC monitoring is not adequate for determining TO mass, as discussed in Section B.1.1, it may prove to be a useful tool for continuous performance assurance. Both THC and carbon monoxide (CO) can be indicators of whether good combustion practice is being maintained, and whether organics emissions may have changed from the baseline determined during the risk testing.

B.14   METALS

As indicated in Table B1-1, the additional metals which will be evaluated in SSRAs (i.e., aluminum, cobalt, copper, manganese, nickel, selenium, vanadium, and zinc) can all be collected in the Method 0060 multiple metals train with the 10 traditional metals. Thus, there are no new sampling considerations related to total metals.

Although total metals determinations are not substantially impacted by SSRAs, metals chemical speciation data, especially for mercury, represents a new data need. The HHRA guidance (EPA in press) provides default assumptions for ratios of divalent particulate mercury, divalent mercury vapor, and elemental mercury vapor. However, these default assumptions could be replaced by site-specific data if mercury speciation sampling were performed.

Based on a preliminary review of mercury partitioning data from the Method 0060 train components, it would appear that the HHRA (EPA in press) default assumptions probably over-estimate particulate mercury for most hazardous waste combustion sources, and underestimate elemental mercury vapor for cement kilns. If this is the case, then speciated mercury data could potentially reduce the estimated risk for cement kilns by reducing the local deposition of divalent mercury. The impact for other facilities would be more difficult to predict, but it is likely that local deposition rates would decrease if speciated mercury data showed less divalent particulate and more divalent vapor.

A modified mercury speciation sampling train has recently been developed under direction of the National Exposure Research Laboratory (Giglio 1997). This train, the alkaline mercury speciation (AMS) method, uses dilute sodium hydroxide impingers for capturing divalent mercury, followed by an empty impinger to stop carryover and two acidified potassium permanganate impingers for capturing elemental mercury. AMS has been shown in bench-scale testing to be highly effective at collecting both divalent and elemental mercury, with fewer interferences from both sulfur dioxide and chlorine than observed in previous speciation methods. However, further method development is needed. At the present time, this method has not been subject to 40 CFR Part 63, Appendix A, Method 301 field validation.

B.15   PARTICLE-SIZE DISTRIBUTION

Particle size distribution may be determined using cascade impactors, or by analysis of particulates deposited on filters using scanning electron microscopy (SEM). Unfortunately, preliminary data collected and analyzed using these methods indicates a large amount of uncertainty, especially for particle sizes less than 1 micron.

Method CARB 501 (CARB 1990b) specifies procedures for collection of particle-size data using cascade impactors. Method CARB 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 (HWC) 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. In addition, HWC facilities with wet stacks may experience a problem with particle agglomeration.

For SEM, 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. Again, particle agglomeration can be a problem. A disadvantage of SEM is that it only provides physical particle size, whereas the impactors give aerodynamic size.

EPA (1997d) recognizes the inherent problems associated with measuring very low masses of particulates and recommends modified Method 5 (Method 5I) to improve accuracy, precision, and representativeness by significantly reducing variability and potential errors. Although Method 5I was not written specifically for particle-size determinations, it is possible that some of the procedures recommended in Method 5I could also be used in conjunction with cascade impactor or SEM measurements to improve performance.

Since there are no default particle-size distribution assumptions for HWC facilities with no air pollution control devices (APCD), these facilities will generally need to attempt a particle-size distribution measurement using currently available procedures. The permit writer should be cognizant of the inherent problems associated with these procedures, and should work with the facility to obtain the best data possible under the circumstances. HWC facilities equipped with wet APCD systems or APCD components other than electrostatic precipitators (ESP) or fabric filters (such as dry scrubber systems or high efficiency particulate air [HEPA] filters) will either need to attempt a particle-size distribution measurement, or may be able to obtain particle-size data from the APCD vendor.

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For facilities equipped with ESPs or fabric filters, the HHRA guidance provides a nine-category particle-size default assumption. However, since the default assumption may be overly biased towards larger particles, a particle-size distribution measurement is highly recommended. If the majority of the particle mass is very small (less than 1 or 2 microns), it will generally not be necessary to achieve high resolution in cut sizes for the small particles. A sensitivity analysis (The Air Group 1997) concluded that as few as three size categories could be used in the model with little impact (less than 10 percent) on concentration, dry and wet deposition. Also, the sensitivity analysis noted that small particles in the range of 1 micron have very low terminal velocities and effectively are suspended in air. This generally translates to reduced potential for risk, because indirect risks tend to be driven by deposition.

For facilities equipped with ESPs and fabric filters, it may also be possible to demonstrate via preliminary air dispersion and deposition modeling that the HHRA guidance default assumptions are conservative (in that they will result in higher potential for risk), and that site-specific measurements are therefore unnecessary. The sensitivity analysis (The Air Group 1997) clearly showed that deposition rates will be substantially higher for distributions which are skewed towards larger particles for most downwind distances up to 9-15 kilometers. Based on recent measurements, the default assumptions appear to be biased towards larger particles. If site-specific modeling (using the default assumptions, versus an assumption of smaller particle sizes in the 1 to 2 micron range) confirmed that deposition would be higher for key receptor locations using the default assumptions, then particle-size measurements could be avoided.

A final consideration is that particles from cement kilns may have a higher density (2 grams per cubic centimeter [gm/cm^3]) than the density default assumption (1 gm/cm^3) in the HHRA guidance. This can result in up to 50 percent greater dry deposition near the source.

B.16   HYDROGEN CHLORIDE AND CHLORINE

Since potential risks from hydrogen chloride and chlorine are limited to the inhalation pathway, the multi-pathway SSRA is not expected to impact the current regulatory approach with respect to hydrogen chloride and chlorine for boiler and industrial furnace (BIF) facilities. However, hazardous waste incinerators (HWI) will now be expected to characterize their stack emissions for both hydrogen chloride and chlorine, and the 40 CFR Part 264.343 technology-based limits may be superseded by risk-based limits, if the risk limits are more stringent. Sampling procedures are specified in Methods 0050/0051, and the collected samples are analyzed for hydrogen chloride and chlorine using Method 9057. For analytical determination of additional halides, Method 9056 may be used instead of Method 9057.

Johnson (1996b) provides a convenient summary of research evaluating the use of Methods 0050/0051 for hydrogen chloride and chlorine determinations. This summary discusses areas of potential concern, and highlights special considerations, which can help to ensure the quality of the final results.

One area of concern repeatedly noted by cement kiln representatives is that hydrogen chloride determinations from Methods 0050/0051 could be biased high because volatile particulate chloride salts, such as ammonium chloride, could penetrate the filter and be converted to hydrogen chloride within the sampling train (Gossman 1997). Industry has proposed correcting the hydrogen chloride results based upon analysis of the impinger solutions for cations including $Na+$, $Ca+$, $K+$, and NH_4+.

EPA has considered this issue and does not believe that salts will significantly bias the results (Johnson, 1996b, EPA 1996f). Johnson (1996b) emphasizes that correction of the hydrogen chloride results is not appropriate, because it is not possible to determine how and in what form the ionic material entered the impingers. The prescribed filter will not pass significant quantities of solid halide salts such as sodium chloride ($NaCl$), calcium chloride ($CaCl_2$), or potassium chloride (KCl). Therefore, the presence of $Na+$, $Ca+$ or $K+$ in the impingers could reflect contamination during handling, a broken filter, or operation with a wet filter. These problems can be addressed by use of a cyclone and adequate heating in the sampling train, and careful handling of the train components with special concern for minimization of contamination.

There is some evidence that it may be possible for ammonium chloride to penetrate the filter as a vapor. If ammonium chloride is believed to be causing a significant bias, then an infrared spectroscopy-based CEM monitor for hydrogen chloride could be considered. However, potential inaccuracies relative to Methods

0050/0051 which could bias hydrogen chloride high are not expected to significantly impact the SSRA process, because excess risks due to hydrogen chloride have not historically been an issue.

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B.17 PROCESS SAMPLES

Trial burn protocols for collection of SSRA data will also need to address analysis procedures for completely characterizing the trial burn wastes, fuels, raw materials, and spike materials. Data equivalent to the following should be generated:

- 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

- 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 organic halogens, and elemental composition

- Survey analysis or a comparable evaluation for (1) TO content, (2) organic compound class types, and (3) major organic components, including analysis for VOCs, SVOCs, PCBs, and PAHs using standard analytical methods

These data define a facility's baseline with respect to long-term impacts and potential effects on human health and the environment. Any significant changes to the facility's baseline can necessitate additional risk-based data collection or risk analyses.

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ATTACHMENT 1

METHOD 0040 CLARIFICATIONS
(3 pages)

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.

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