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Municipal Waste Combustion Study

Sampling and Analysis of Municipal Waste Combustors



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FOREWORD

This document is intended to serve as a resource document outlining recommended sampling, analysis and monitoring procedures for municipal solid waste combustion facilities. The effort reported here has focused on gathering information on probable measurement requirements and on available methods that may meet those requirements. Critical evaluations of alternative methods and recommendations to fill gaps in available methodology were outside of the scope of this assignment.

The Arthur D. Little, Inc. effort is part of a major program to develop an EPA report to Congress on Municipal Waste Combustion. The overall effort is being directed by Radian Corporation (G. Wilkins, Project Manager). The Arthur D. Little contribution is being performed under EPA subcontract with Dynamic Corporation (C. Matkovich, work assignment director). L. D. Johnson is the EPA work assignment director for the Arthur D. Little effort. Key Arthur D. Little staff involved in this work are J. C. Harris (to whom comments should be addressed), D. L. Cerundolo, and K. E. Thrun. The Arthur D. Little reference numbers for this work are 55464 and 55465.

I. INTRODUCTION

A. OVERVIEW

This report is an assessment of sampling and analysis methods for municipal waste combustors. The information presented in this report was developed during a comprehensive, integrated study of municipal waste combustion. An overview of the findings of this study may be found in the Report to Congress on Municipal Waste Combustion (EPA/530-SW-87-021A). The Technical volumes issued as part of the Municipal Waste Combustion Study include:

Municipal Waste Combustion Study:
 Report to Congress
 EPA/530-SW-87-021A

EPA/530-SW-87-021B

EPA/530-SW-87-021C

- Municipal Waste Combustion Study:
 Emissions Data Base for Municipal
 Waste Combustors
- Municipal Waste Combustion Study:
 Combustion Control of Organic
 Emissions
- Municipal Waste Combustion Study:
 Flue Gas Cleaning Technology
 EPA/530-SW-87-021D
- Municipal Waste Combustion Study: Costs of Flue Gas Cleaning Technologies
 EPA/530-SW-87-021E
- Municipal Waste Combustion Study: Sampling and Analysis
 EPA/530-Sw-87-021F
- Municipal Waste Combustion Study: Assessment of Health Risks Associated with Exposure to Municipal Waste Combustion Emissions
 EPA/530-SW-87-021G

- Municipal Waste Combustion Study: Characterization of the Municipal Waste Combustion Industry
 EPA/530-SW-87-021H
- Municipal Waste Combustion Study: Recycling of Solid Waste
 EPA/530-SW-87-0211

B. PURPOSE OF THIS DOCUMENT

The purpose of this document is to provide guidance on sampling and analysis methods to assist federal, state, and local environmental authorities in reviewing plans for operations and testing of MSW combustors. The sampling and analysis procedures outlined here are intended to represent state-of-the-art methods that may be useful in determining the regulatory compliance status of MSW incineration facilities and in assessing their environmental impacts. These same methods may be useful in research and development programs related to MSW combustion technology, standard setting, etc.

C. SCOPE

This document provides an overview of available state-of-the-art methods for sampling and analysis to address testing and monitoring of MSW combustors. For purposes of this report, testing and monitoring are defined as follows:

"testing" means performing periodic sampling and analysis by EPA-approved or recommended methods to: confirm compliance with any limits that have been imposed by regulatory agencies as permit conditions; generate data that may be used as inputs to environmental risk assessments; and/or support research and development in municipal waste combustion.

"monitoring" means obtaining continuous instrumental measurements of key process parameters and selected pollutants in the emissions to verify that the facility continues to operate "in control".

The testing can be expected to focus on several categories of potential pollutants:

Criteria pollutants: particulates, CO, SO₂, NO₂,

Acid gases: HCl, HF

Trace metals: Cr(III), Cr(VI), Cd, As, Hg, Pb, Be, etc.

Organic pollutants: chlorina dibenzo-p-dioxins, chlorinated dibenzofurans, and other trace level species that may be indicators of potential environmental impacts

The parameters for which continuous monitoring may be required during routine operation or requested as part of special purpose programs include:

temperature
opacity
carbon monoxide
carbon dioxide
oxygen
nitrogen oxides
sulfur oxides
hydrochloric acid
"total hydrocarbon"
performance "indicator" species (e.g., CO)

Procedures for measuring the above parameters in ultimate effluents from MSW combustion facilities (stack gas, solid residues such as bottom- and fly-ash, and liquid effluents such as scrubber water) are described in this report. Two other aspects of MSW combustor sampling and analysis--measurements on the MSW feed and measurements on flue gases upstream of air pollution control devices--are also addressed, but procedures appropriate for these media are

less well developed or defined. In both cases, the principal difficulty is in obtaining a representative sample. MSW is highly heterogeneous and some individual items present are so large or bulky as to preclude effective use of compositing procedures. (See Section IIIE for further discussion). Flue gas sampling (discussed in Section IIIC) is complicated by uneven flow conditions and by components (e.g., high particulate material and acid gas loadings) that clog or corrode conventional sampling equipment.

This document speaks only to issues of MSW combustor source sampling and analysis. Procedures for assessing ambient air impacts, either by dispersion modelling or by direct ambient air sampling and analysis in the vicinity of the facility, are not described. Sampling and analysis of fugitive emissions (e.g., from transfer or storage operations) are not covered in this document.

D. USE OF REPORT

It is anticipated that this report will serve as a useful reference point for MSW combustor owner/operators and for federal, state and local authorities involved in facility permitting process. The sampling and analysis methods described and/or recommended here are not to be construed as representing unique or mandatory requirements for emissions testing or continuous monitoring at MSW combustion facilities. Inclusion in this report does not mean that a sampling or analysis method is an official EPA method. The procedures described here should be reviewed against those in the current Code of Federal Regulations and in official methods manuals, such as "Test Methods for Evaluating Solid Waste" (SW-846)⁽¹⁾, before any MSW combustor test program is finalized.

II. SAMPLING AND ANALYSIS STRATEGIES

A. _ PURPOSE OF DATA COLLECTION

The principal purpose of generating data from MSW combustor sampling and analysis is to determine the effects of emissions from a facility on health and the environment. These data can be used to determine compliance with applicable criteria or to perform an assessment of the health risk associated with the emissions. In some cases, the purpose of the sampling and analysis may be primarily to support research and development in MSW combustion technology. In those instances, there may be a requirement for some types of measurements (e.g., characterization of waste feed or in-furnace measurements) that are more extensive than those needed for compliance testing or risk assessment.

Table 1 indicates some examples of the types of compounds for which measurements have been made in various test programs. Most of these are not regulated pollutants in stack gas emissions, and inclusion in the Table is not meant to imply that measurement of these potential pollutants should be required. However, this document presents methods that would be applicable to the sampling and analysis of these types of pollutants if such measurement were determined to be necessary or useful.

In every case, it is essential that critical decision limits for each parameter be established in specific quantitative terms prior to selection of sampling and analysis methods. This may require, in many cases, that a preliminary air quality modelling run be performed in order to calculate what stack gas concentration corresponds to a specific ambient air quality criterion. This exercise allows calculation of the sampling and analysis method detection limit that will be necessary to meet the project objectives.

The precision and accuracy criteria for the measurement method will also depend on the specific uses to be made of the data. It is important to establish whether it is <u>each</u> of n measurements, or the <u>mean</u> of n measurements,

TABLE 1

EXAMPLES OF POLLUTANTS THAT HAVE BEEN OF INTEREST IN RESEARCH AND DEVELOPMENT OR OTHER SPECIAL PURPOSE PROGRAMS

Selenium

Metals: Arsenic Volatiles: Benzene Carbon Tetrachloride Beryllium Chloroform Cadmium Formaldehyde Chromium Perchloroethylene Copper Toluene Lead Manganese Mercury Nickel

Semivolatiles: Benzo(a)pyrene Others: Hydrogen Chloride Chlorobenzenes Hydrogen Fluoride Chlorodibenzodioxins Sulfur Dioxide Chlorodibenzofurans Chlorophenols Naphthalene Phenol Polychlorinated Biphenyls Pyrene

Source: Arthur D. Little, Inc., conversations with regulatory authorities.

Arthur D. Little, Inc.

or the <u>95% confidence limit</u> around the mean that is to be compared with the critical decision limit.

The general purposes of collecting data by testing and monitoring of MSW combustors are discussed below. The specific purposes (and thus the critical decision limits) must be established on a case-by-case basis.

<u>Criteria Pollutants</u>. The criteria pollutants (particulate material, carbon monoxide, nitrogen oxides, ozone, and sulfur dioxide) are those species for which EPA has established primary and/or secondary National Ambient Air Quality Standards (NAAQS). As the name implies, these standards apply to the cumulative impact from all sources, not the source-by-source emissions, on ambient air concentrations. However, it may be necessary to measure emissions of criteria pollutants from an MSW combustor in order to assess its incremental contribution to the total ambient level. This is especially likely in the case of new MSW facilities in areas where current levels are close to or exceed the NAAQS. The criteria pollutants are also of concern with regard to Prevention of Significant Deterioration (PSD) determinations.

Acid Gases. In addition to SO_{χ} (discussed above), hydrochloric acid and a lesser quantity of hydrogen fluoride are acid gases that can be expected to be present in MSW combustor off-gases. Although there are not federal EPA standards relating to HCl emissions from facilities other than hazardous waste incinerators, many state environmental agencies (e.g., Maine, Massachusetts, New Jersey, California) consider that acid gas removal from MSW incinerator effluents represents Best Available Control Technology (BACT). Testing of stack emissions of HCl and HF may be required to demonstrate that a degree of acid gas control consistent with BACT has been achieved.

<u>Trace Metals</u>. Trace metal species, in addition to lead, that may need to be measured in MSW incinerator effluents include: arsenic, beryllium, cadmium, chromium, and mercury. In general, air emissions of trace metals from MSW sources are not currently addressed in EPA regulations, but may be of concern with regard to potential health effects. In some cases, it may be necessary to differentiate Cr (III) from Cr (VI) in order to assess the magnitude of health

effects. The metals content of MSW incinerator aqueous effluents (e.g., scrubber or quench water) and of solid residues (e.g., bottom ash, fly ash) may need to be ascertained in order to determine disposal status vis-a-vis NPDES or RCRA regulations, respectively.

Organic Pollutants. Data on chlorinated dibenzo-p-dioxins and dibenzofurans in stack gas effluents may be required as inputs to air quality models in order to estimate whether the risk of exposure to these chemicals from this source is within the range of acceptability. Permitting authorities may request data on other trace organic such as polynuclear aromatic hydrocarbons or phenols, in order to perform similar risk calculations. Again, NPDES or RCRA regulations may require the determination of specific organic chemicals in aqueous effluents or solid residues, depending on the disposal or treatment alternatives that are to be applied to these streams. Selected organics may also be measured during MSW combustion research and development as indicators of the efficiency of the combustion process and/or pollution control devices.

Monitoring. Continuous monitoring of MSW combustor emissions provides a mechanism for tracking the performance of the system in real time. The parameters that can be monitored continuously are generally those (e.g., temperature, oxygen, carbon monoxide) that indicate the overall combustion efficiency or those (e.g., opacity, SO_{y}) that indicate air pollution control device (APCD) performance. These measurements are important for confirming that a facility is continuing to operate under controlled, steady-state conditions and is in compliance with specific emissions limitations written into its operating permits. In addition, the on-line monitor data can serve as an "early warning system" to detect combustor/APCD system upsets due to mechanical failures and/or gross changes in waste composition (e.g., very wet waste). Thus, even if an on-line monitor is not sufficiently accurate or precise for determining compliance with emissions limitations (e.g., commercially available opacity meters do not reliably determine particulate matter emissions below 0.03 gr/dscf), data from such an instrument is nevertheless useful as an indicator of potential upset conditions.

B. SELECTION OF SAMPLING AND ANALYSIS METHODS

Once the uses of the data have been defined and the consequent data quality objectives have been established, it is possible to make an informed selection among alternative sampling and analysis (S/A) methods.

The principal criteria to be used in making this selection are the following:

- <u>regulatory status</u>. Is the S/A method chosen approved by EPA for this measurement purpose?
- <u>sensitivity</u>. Has the method been proven to have a detection limit that is sufficiently low to allow accurate quantification of the pollutant of interest at concentrations corresponding to the critical decision limit?
- <u>selectivity</u>. Will other species that are likely to be present in MSW combustor effluents interfere in the determination?
- <u>reliability</u>. Is the method sufficiently rugged to be applicable in the hostile invironment represented by MSW incineration?

It is important to emphasize that these criteria must be applied to the overall sampling--sample preparation--analysis <u>system</u>, not just to the analysis method <u>per se</u>.

C. QA AND QC OVERVIEW

Quality Assurance (QA) and quality control (QC) are vitally important components of any sampling and analysis program. QC procedures, including the analysis of standards, blanks, replicate samples, and spikes, provide on-going confirmation that the sampling and analysis methods are "in control" and that

the data generated are valid for the intended purpose. QA procedures ensure that all data, including QC data, are reviewed and that any necessary corrective actions are instituted in a timely fashion.

In order to ensure the effective implementation of QA/QC functions, it is necessary that <u>specific</u> quantitative Data Quality Objectives (DQOs) be established for each measurement. Guidance in developing a QA/QC plan for MSW combustion testing/monitoring is discussed further in Section VII of this report and in the EPA report, "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans."⁽²⁾

III. SAMPLING

A. OVERVIEW

Sampling of MSW combustion facilities for purposes of determining compliance with regulatory limitations or of assessing potential environmental risks is usually focused primarily on air emissions (stack gas). Solid residues (bottom ash and fly ash) are also commonly sampled. Some facilities may also have aqueous effluents from wet scrubbing or ash quenching operations.

Figure 1 shows a generalized schematic of the MSW combustion process, with sampling points indicated generically, Figures 2, 3, and 4 present, respectively, schematics of a mass burn, refuse-derived-fuel (RDF), and starved air MSW incinerator, again with generic identification of sampling locations. Exact sampling points must be specified on a case-by-case basis for each facility, taking into account accessibility, temperature and flow conditions, and operational modes (e.g., batch or continuous discharge of residue).

The critical considerations in selection of a sampling method are: (1) the representativeness of the sample and (2) compatibility of the sampling procedure with the intended analytical finish.

To ensure representativeness, emissions samples are usually integrated over time. A 1-4 hour time-integrated sample is usually taken to smooth out the perturbations that occur due to the inherent variability of MSW. In the case of stack sampling, it is often possible to accomplish this directly by adjusting the sampling rate to cover the desired time period. In the case of liquid or solid residues from MSW combustors, the time integration is usually accomplished by preparing a composite sample, combining equal-sized aliquots collected at intervals over the duration of a test. Sampling of solid waste, if requested in a particular facility test, is usually done by compositing of subsamples, in accordance with procedures described in SW-846. In all cases, the representativeness of the sampling method can be checked, but not proven, by acquiring duplicate samples representing the same time period of facility operation.



FIGURE 1 GENERALIZED MUNICIPAL SOLID WASTE INCINERATION PROCESS SCHEMATIC

(Adapted from original by S-Cubed, a Division of Maxwell Laboratories, Inc.)

*In many facilities, fly ash and bottom ash are collected in a single hopper.



FIGURE 2 SIMPLIFIED SCHEMATIC OF A MASS BURN MSW COMBUSTOR. SHOWING SAMPLE LOCATIONS (Adapted from original by C. R. Brunner, "Incineration Systems Seminar," (1982))

*In many facilities. fly ach and hottom ach and collocated the to the



FIGURE 3 SIMPLIFIED SCHEMATIC OF AN RDF MSW COMBUSTOR, SHOWING SAMPLE LOCATIONS

(Adapted from original by C. R. Brunner, "Incineration



FIGURE 4 SIMPLIFIED SCHEMATIC OF A STARVED-AIR MSW COMBUSTOR, SHOWING SAMPLING LOCATIONS (Adapted from original by C. R. Brunner, "Incineration Systems Seminar," (1982))



Compatibility is a complex issue. Most analytical methods (e.g., GC/MS for trace organics, AAS for trace metals) cannot be applied directly to the sample but require extensive sample preparation. Even methods that are inherently "on-line" procedures (e.g., continuous instrumental monitoring of CO or SO_X) may require sample clean-up to remove particulate material, water vapor, etc. or other forms of sample conditioning prior to analysis. It is important that the QAPP (quality assurance project plan) for any MSW combustion sampling and analysis program contain procedures to assure that no unacceptable losses are introduced by whatever procedures are required to ensure compatibility.

B. SAMPLING METHODS FOR STACK GAS EMISSIONS

Table 2 lists EPA-approved and/or recommended state-of-the-art stack sampling methods for various pollutants and/or categories of pollutants. (Note: Table 2 includes only extractive sampling methods. Continuous monitoring methods are discussed in Section VI.) Most of these procedures have been subjected to extensive method development, validation and/or round-robin collaborative testing. Although they may not all have been validated at MSW combustion facilities specifically, there is every reason to believe that they will be directly applicable for the purpose of sampling MSW stack emissions.

In fact, a number of these methods have been employed in recent MSW combustion sampling and analysis programs^(3,4) and appear to provide reliable data. For example, Table 3 shows the results obtained in a series of 6 replicate stack gas emission tests for polychlorinated dioxins and furans at one MSW combustor using the ASTM sampling and analysis protocol⁽⁵⁾ (see below and Appendix B for description).(6) These data show the precision (relative standard deviation (RSD)) that can be achieved when sampling and analysis is carried out according to the recommended methods by experienced personnel (in this case, Radian Corporation for sampling and Triangle Laboratories for analysis). The RSD values in the table reflect the combined effects of actual variations in emissions, sampling variance, and sample preparation/analysis variability for this test series. RSD's could be expected to be somewhat higher at lower PCDD/PCDF emission levels. However, the data indicate that the state-of-the-art sampling and analysis methods are workable in experienced hands. It should be

TABLE 2

STACK SAMPLING METHODS

<u>Pollutant</u>	Principle	Comment	<u>Reference</u>
<u>Criteria and Conven</u> tional Parameters	<u>-</u>		
Particulate	Isokinetic collection of a l hr. sample on glass fiber filter at 120 <u>+</u> 14°C. Train includes: T-controlled probe,	Designed to meet 0.08 gr/SCF standard. Probably adequate down to 0.01 gr/SCF, especially if sampling period is increased to 2 hrs.	EPA Meth. 5
	optional cyclones, heated filter, impingers, flow control and gas volume metering system.		
	Visual determination of opacity		EPA Meth. 9
	Instrumental measurement of opacity (optical density)	Not reliable for quantifica- tion at 0.03 gr/SCF or below.	-
Sulfur Oxides	Collection in isopropanol (SO ₃) and hydrogen peroxide (SO ₂) impingers of M5-type train.	Low ppm to percent	EPA Meth. 6,8
Carbon Monoxíde	Integrated gas bag or direct interface via air-cooled condenser.	Water vapor, carbon dioxide are interferences; need silica gel, ascarite traps to remove. 20-1000 ppm	EPA Meth. 10
Nitrogen Oxides	Collection in evacuated flask containing sulfuric acid and hydrogen peroxide.	Grab sample (not time-integrated) ppm levels Does not differentiate NO from NO ₂	EPA Meth. 7,7A

TABLE 2 (cont.)

STACK (FLUE GAS) SAMPLING METHODS

<u>Pollutant</u>	Principle	Comment	<u>Reference</u>
Hydrochloric Acid	Collection in aqueous NaOH impingers in M5-type train.	ppm to percent range.	(18)
Hydrogen Fluoride	Collection on paper or membrane <u>(not</u> glass fiber) filter and aqueous impingers in M5-type train.	Low ppm range.	EPA Meth. 13B
<u>Trace Metals</u>			
General	M5 or SASS train, glass fiber filter and nitric acid or ammonium persulfate impingers	ppb to ppm levels if is ^ 0.75 M of stack gas	(18)
Lead	Collection on glass fiber filter and nitric acid impingers in M5-type train.		EPA Meth. 12
Mercury	Collection in iodine monochloride or acidic permanganate impingers in M5-type train.	Probe must be glass- or quartz-lined. ppm levels. Other reagents also possible	EPA Meth. 101
Arsenic	Collection on glass fiber filter and aqueous impingers in M5-type train.		EPA Meth. 108
Beryllium	Collection on millipore AA filter and aqueous impingers in M5-type train.	Probe must be glass or quartz-lined.	EPA Meth. 104

•

TABLE 2 (cont.)

STACK (FLUE GAS) SAMPLING METHODS

<u>Pollutant</u>	Principle	Comment	Reference
<u>Trace_Organics</u>			
Specific Volatile organics	Collection on Tenax-GC and charcoal at 1 LPM for 20 minutes.	ppb-ppm levels;multiple species	VOST
Semi-volatile organics, including dioxins, furans	M5 train modified to include XAD-2 trap for organic collection between filter and impingers.	ppb-ppm levels; multiple species	MM 5
	5-fold scale up of MM5 system.	sub-ppb levels for dioxins/furans if dedicated sample	SASS
Vinyl chloride*	Integrated gas bag	0.1-50 ppm	EPA Meth. 106
Formaldehyde	Collection on DNPH-coated sorbent or in aqueous DNPH impingers.	ppm levels	(18)
Gaseous Hydro- carbons, total	Integrated bag sample or direct interface	ppm levels	EPA Meth. 18
Gaseous Hydro- carbons, total	Evacuated stainless steel or aluminum tank behind chilled condensate trap.		EPA Meth. 25

* VOST can also be used for vinyl chloride, but collection and recovery efficiency may be low.

TABLE 3

	Avg conc	(n = 6 MM5)	runs)
	ng/dscm	sd	rsd
DIOXINS	_		
2,3,7,8	1.73	0.65	38
tetras	32	12	38
pentas	35	12	54
nexas	20	10	20
neptas	30	12	20
UCLA	16	20	00
Subtotal	169	49	29
monos			
dis	1	1	60
tris	12	, 5	37
Total	1 83	51	28
FURANS			
2.3.7.8	23	5	23
tetras	182	49	27
pentas	106	31	29
hexas	69	20	29
heptas	36	14	38
octa	18	25	139
Subtatal		101	25
SUDIDIAL	411	101	23
monos	1	1	95
dis	31	8	25
tris	136	26	19
lotal	279	126	22
GRAND TO	TALS, DIO	(INS + FURA	NS
CI4-CI8	580	145	25
CL1-CL8	762	169	22

Data from 1986 Test as Saugus Resource Recovery Plant

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STACK GAS (Corrected to 12% CO2)

recognized that these procedures require an exceptionally high level of quality control to ensure that adequate recoveries and detection limits have been achieved in each instance.

The Method 5 (M5) type train represents the principal method for sampling of criteria pollutants, acid gases, metals, and semi-volatile organics. The basic Method 5 train, shown schematically in Figure 5, includes a <u>probe</u> with buttonhook nozzle and pitot tube, a <u>filter</u> section, an <u>impinger</u> train and a <u>metering</u> system. The probe and filter sections are maintained at a temperature of 250° F; material recovered from these train components and dried to constant weight is defined as particulate material. For quantification or chemical analysis of particulate material, the sampling must be done <u>isokinetically</u> (i.e., gas velocity into the probe equals the gas velocity within the stack).

As noted in Table 2, the M5 train is used with minor modifications to determine many inorganic species, such as sulfur oxides or trace metals. These modifications do not involve substantial changes in train geometry but relate to the use of: glass- or quartz probe liners; special filter media; or selective reagents in the M5 impingers. For example, use of a glass lined probe, glass fiber filter and 0.1 N nitric acid in the impingers of a standard M5 train provides good collection efficiency for most trace metals. To quantify heavy metals in the stack emissions, the probe catch, filter and/or impinger solutions are digested as described in Section IV G and analyzed as described in Section V D.

For sampling of semivolatile organics in stack emissions, a more significant modification of the standard M5 train is required. The Modified Method 5 (MM5) train (SW-846 method 0010), shown in Figure 6, incorporates a condenser/cooler section and a module filled with a solid adsorbent between the exit of the filter and the entrance to the first impinger. The adsorbent recommended is Amberlite XAD-2, which has been shown $(^{7,8})$ to give good collection efficiency for vapor phase organic compounds with boiling points above about 100° C. This category, "semivolatile" organics, includes many species that are of potential interest for risk assessment (Table 1), including chlorobenzenes, chlorophenols, polycyclic aromatic hydrocarbons, and chlorinated



FIGURE 5 SCHEMATIC OF STANDARD EPA METHOD 5 TRAIN.

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FIGURE 6 MM5 TRAIN SCHEMATIC DIAGRAM

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dibenzodioxins/furans. The MM5 train is recommended for sampling of dioxins/furans in MSW combustion effluents in the joint ASME/EPA Environmental Standards Workshop draft Protocol.⁽⁵⁾ (See Appendix B.) The MM5 approach has also been used by other agencies involved in sampling for dioxins/furans, including the New York State Department of Environmental Conservation (9) and Environment Canada (10). There are some differences in configuration between the MM5 train designs currently in use; these may produce somewhat different distribution of collected pollutants across the train components (i.e., different fractional collection on filter vs. sorbent vs. condensate). However, all contain the same basic components and should provide comparable overall collection efficiencies.

The MM5 train, like the M5 train, is used to sample isokinetically. Also, as with the M5, a variety of impinger reagents can be used for selective collection of species such as trace metals (Table 2).

The Source Assessment Sampling System (SASS) (SW-846 method 0020) is an alternative to the MM5 train. The SASS, shown schematically in Figure 7, is essentially a fivefold scale-up of the MM5 system. Use of SASS is recommended when calculations indicate that the sampling flow rate of the M5/MM5 train (0.75-1.0 cu. ft. per min.) would not collect a sufficient quantity of pollutant in a reasonable time period to meet data quality objectives for detection limits. Note that the design criteria for the SASS train cyclones are based on a constant sampling rate, not on a variable rate as used in true isokinetic sampling. The SASS may therefore be most suitable for sampling semi-volatile organics and trace metals that are present in the stack as vapor phase materials. The variation from isokineticity may introduce errors when the SASS is used to collect particulate material; however, the variations and any resultant errors are generally small compared to other sources of variance in an MSW combustor sampling and analysis program.

The operation of both the MM5 and the SASS train is described in reference 11. Note that each of these stack sampling trains generates multiple components for subsequent sample preparation and analysis (Sections IV and V). Note also that, while the M5-type approach can be modified to meet a number of sampling



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Source: IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition), EPA-600/7-78-201

objectives (particulate material, trace metals, semi-volatile organics, acid gases), it is generally recommended that one not attempt to meet more than one (or two) of these goals with a single stack sample. In theory, for example, one could run a MM5 train, dry the probe wash and filter to constant weight for weighing of particulate material, then split the particulate catch--digesting one-half for trace metal determination and extracting the other half for semi-volatile organic analysis. In practice, such an approach is likely to result in sample losses and in unnecessarily high limits of detection for particular pollutants.

The Volatile Organic Sampling Train (VOST) was developed $^{(12)}$ to sample organic vapors that are too volatile for efficient collection in the MM5 or SASS. This includes most organics with boiling points of about 100° C or lower. This includes a number of species that may be of interest such as carbon tetrachloride, benzene and vinyl chloride. A schematic of the VOST is shown in Figure 8. As shown, the VOST system includes a probe, glass wool roughing filter, a gas cooling/condensing section, and two solid adsorbent tubes in series. The first tube contains 1.6g of Tenax-GC[®] sorbent and the second contains 1.0g of Tenax backed up by 1.0g of charcoal. The VOST is used to collect a series of 20L stack gas samples at a flow rate of 1 LPM through 5 successive pairs of fresh traps. After sampling, the tubes are sealed and returned to the laboratory for thermal desorption and analysis of volatiles by GC/MS (Section V). A protocol for use of VOST has been published by EPA⁽¹³⁾ and is also available in SW-846 as method 0030⁽¹⁾.

The VOST system has been extensively validated in the laboratory $^{(12)}$ and applied successfully in the field $^{(14)}$. In addition, EPA has sponsored the development and testing of a series of VOST audit cylinders, containing known mixtures of volatile organics, that are available to regulatory agencies as checks on overall VOST sampling and analysis performance by users of the system

C. SAMPLING METHODS FOR FLUE GAS

The methods described in Section B, above, are also applicable to sampling of flue gases upstream of air pollution control devices (APCDs). However, flue



FIGURE 8 SCHEMATIC OF VOLATILE ORGANIC SAMPLING TRAIN (VOST)

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gas is typically hotter, wetter, dirtier (higher particulate loadings, higher levels of condensable organics) and more corrosive than stack gas. Thus modifications are frequently required to adapt stack gas methods to flue gas sampling. For example:

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- When the flue gas temperature is in excess of about 500°C, a water-cooled jacket must be placed around the outside of the heated probe.
- The flow conditions wit. the flue and difficulty in accessing sampling points may preclude isokinetic sampling and/or traversing of the duct. A preliminary velocity traverse will usually allow selection of a fixed sampling point of "average" velocity that is away from the walls of the flue. The probe can then be located at this position and the sampling rate adjusted to be as close to isokinetic as practical.
- High loadings of particulate material and/or condensable organics may cause frequent interruptions of sampling for replacement of filters to avoid excessive pressure drops across the train. Use of a roughing filter (in-flue) or insertion of a cyclone component upstream of the M5-type filter may be necessary to allow reasonably convenient continuity of sampling.
- Glass, quartz, or Teflon liners may be required to protect all stainless steel surfaces from corrosion.

The principal reason for sampling the flue upstream of the APCD is to allow assessment of control device removal efficiency. An alternative approach is to sample and analyze the material collected in the device, rather than the flue gas challenge concentration, and compare this to the quantity emitted in the stack gas. The efficiency can then be estimated as:

$$E(\mathbf{\hat{x}}) = \frac{\begin{array}{c} Q \\ collected \end{array}}{\begin{array}{c} collected \\ Q \\ collected \end{array}} + \begin{array}{c} Q \\ emitted \end{array}} x 100$$
where Q collected - concentration in fly ash x rate of fly ash collection in APCD

Q = concentration in stack gas x volume flow rate of stack
gas

This "mass balance" is probably comparable in uncertainty to that based on direct flue gas measurements for "major" pollutants in MSW combustion, such as particulate material or acid gases. It cannot be recommended for trace level pollutants such as individual metals or organics.

D. SAMPLING METHODS FOR SOLID AND LIQUID EFFLUENTS

The methods specified in SW-846⁽¹⁾ and in "Sampling and Analysis for Hazardous Waste Combustion (First Edition)"⁽¹⁵⁾ are generally directly applicable to MSW combustor solid and liquid effluents. Table 4 summarizes the relevant methods. In addition, EPA is currently in the process of developing specific recommendations for sampling MSW combustor ash.

For both liquid and solid effluents, the sampling strategy will depend on whether the stream is generated continuously (as in once-through scrubber water) or in a batch process (as in a fabric filter). In the former case, composite samples are generated by collecting equal-sized aliquots at regular time intervals over the course of the test run (e.g., from a tap on a discharge line (liquid) or from a conveyor (solid).) In the latter case, composite samples are prepared from subsamples from statistically selected points that represent the horizontal (area) and vertical (depth) extent of the batch.

Particular problems may be encountered in sampling MSW combustor bottom ash, which may include bulky items such as metal containers. This issue should be specifically addressed in the sampling and analysis plan for each test. It must be recognized that any decision to "sample around" such bulky objects could compromise the overall validity of the data collected, unless it could be established that they are negligible sources of the compounds to be determined.

SAMPLING METHODS FOR SOLID AND LIQUID EFFLUENTS*

<u>Stream</u>	Principle	Method
Liquids in pipelines.	Attach TFE line to tap. Flush container with fresh sample, then fill.	Тар
Liquids in sumps, tanks, or open drain.	Glass or TFE beaker on rod.	Dipper
Wet or dry ash on conveyors or in bins.	Stainless steel trowel or lab scoop. Obtain random sample below surface level.	Scoop
Dry fine ash on conveyors, in bins or piles.	Tube within a tube, rotated to align slots for sampling.	Thief
Wet ash in bins or piles.	Section of tube cut in half lengthwise. Insert into waste and withdraw.	Trier

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*Reference 1

E. SAMPLING METHODS FOR WASTE FEED

This stream is grossly inhomogeneous. None of the sampling techniques promulgated for hazardous waste sampling $(SW-846)^{(1)}$ is directly applicable to MSW as-received at a mass-burn combustion facility. (Some refuse-derived-fuel (RDF) processes may produce a waste stream that is sufficiently homogeneous and finely divided to be amenable to scoop or trier/thief sampling.)

Researchers have chosen one of two approaches towards sampling MSW: stratified random sampling at the source (socio-economic demography)⁽¹⁶⁾ or by subjectively-modified random sampling at the repository, be it an incinerator or a landfill^(17,18,19). For purposes of evaluating the performance of an MSW combustor, or of understanding the relationship between emissions and waste feed characteristics, the latter is the preferred approach.

Procedures used for sampling and testing of refuse, and the resulting variability in measurements of properties of MSW, have been summarized by Hasselriis (20). Based on this review, it is recommended that 3 to 10 samples of MSW should be collected over at least a 2 week sampling period. The smallest sample should be 1 "unit" of MSW (i.e., one trash bag or barrel of domestic waste at the source; one truck hopper load or crane bucket load at an MSW combustor plant. Cone and quarter procedures can be applied to reduce the unit to a manageable sample size (80-130 kg); this sample can then be shredded to achieve a reasonably homogeneous material for analysis. As an example, the MSW sample processing protocol reported by Bell⁽¹⁶⁾ is included in Appendix A. If any element of subjective sampling is imposed (e.g., exclusion of bulky items or hospital wastes) this must, at a minimum, be explicitly noted and an estimate of the quantity of rejected material be provided.

The EPA, Department of Energy(DOE), and American Society for Testing of Materials (ASTM) have been collaborating in the development of protocols for RDF sampling, including sampling accuracy, bias, and reproducibility estimates. A draft procedure has been approved by an ASTM subcommittee and is awaiting ballot approval by the main E-38 Committee on Resource Recovery. This protocol should be a useful resource for designing waste sampling plans for MSW combustors in general.

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IV. SAMPLE PREPARATION PROCEDURES

A. OVERVIEW

The sample preparation procedures for use on MSW combustor samples involve a number of steps. In the field, the collected samples must be transferred to appropriate, clean containers (generally glass or TFE for organic analysis and high-density linear polyethylene for inorganic analysis) and appropriately preserved and stored. In the laboratory, the sample must be converted (via digestion, extraction, etc.) into a matrix which is compatible with the final analysis methods needed. Table 5 presents a summary of the sample preparation procedures that will commonly be required for MSW combustor samples. This table indicates how samples collected by procedures in Section III are converted to forms amenable to analysis by procedures in Section V.

In some cases (e.g., analysis of chloride in caustic impinger solutions) the sample preparation may be minimal (e.g., diluting an aliquot to a known volume). In other cases (e.g., analysis of dioxins/furans in an MM5 stack gas sample) the procedures may be complex, requiring extraction of multiple components, concentration and clean-up of extracts.

The use of surrogate or standard addition methods is strongly recommended as a QC check on any losses in the sample preparation steps. For this purpose, the additions should be made to the sample prior to any sample preparation.

B. REPRESENTATIVE ALIQUOT FROM FIELD SAMPLES

Combination and preparation of representative aliquots of collected samples is appropriate for all MSW combustor solid and liquid effluent samples. The collected sample is homogenized prior to withdrawal of aliquots for analysis. Individual aliquots are composited to form a single sample (or replicate QC samples) for subsequent preparation and analysis procedures. Table 6 summarizes these procedures.

SUMMARY OF SAMPLE PREPARATION METHODS

				C1	coss Referenc	<u>es</u>
MSW Combustor Stream	Sample <u>Type</u>	For Analysis Of	Preparation Procedure	Sampling	Prep	Analysis
Stack Gas	M5, MM5 or SASS	,				
	- probe wash - filter	Particulate	Dry to constant weight	III B	-	-
	 probe wash filter impinger solutions 	Metals	Standard addition to split samples. Digest in acidic oxidizing medium	III B	IV G	VD
	- probe wash - filter - sorbent module	Semivolatile organics	Add surrogate. Soxhlet extract with CH ₂ Cl ₂ . Concentrate. Clean-up as necessary	III B	IV C-F	VD
	- condensate	Semivolatile organics	Add surrogate Liquid-liquid extract at pH 2 and pH 11 with CH ₂ C1 ₂ . Concentrate. Clean-up as necessary	III B	IV C-F	VD
	VOST - sorbent cartridges	Volatile organics	Spike with internal standard. Thermally desorb onto analytical trap. Desorb this tray into GC/MS.	III B		VD
	- condensate	Volatile organics	Spike with internal standard. Purge onto analytical trap. Deso into GC/MS.	III B rb		VD

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SUMMARY OF SAMPLE PREPARATION METHODS (cont.)

				C	<u>ross Referenc</u>	es Î
MSW Combustor Stream	Sample <u>Type</u>	For Analysis Of	Preparation Procedure	<u>Sampling</u>	Prep	<u>Analysis</u>
Flue Gas	M5, MM5, SASS	(same as for stack	gas)	III C		
	VOST					
Bottom Ash and Fly Ash	Composite Grab	Metals	Standard addition to split samples. Digest in acidic medium in Parr bomb.	III D	IV G	VD
		Semi-volatile organics	Add surrogate. Soxhler extract with CH ₂ Cl ₂ . Concentrate. Clean-up as necessary.	t III D	IV C-F	VD
Liquid Effluents	Composite Grab	Metals	Standard addition to split samples. Digest in acidic, oxidizing medium.	III D	IV G	VD
		Volatile Organics	Spike with internal standard. Purge onto analytical trap. Desor into GC/MS.	III D	IV G	VD
		Semivolatile Organics	Add surrogate. Liquid liquid extract at pH 2 and pH 11 with CH ₂ Cl ₂ . Concentrate. Clean-up necessary.	III D as	IV C-F	VD

SUMMARY OF	SAMPLE	PREPARATION	METHODS	(cont.))
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					Cross Referen	ces
MSW Combustor <u>Stream</u>	Sample Type	For Analysis Of	Preparation Procedure	<u>Sampling</u>	Prep	<u>Analysis</u>
Waste Feed	Composite Grab		Grind or mill to reduce particle size. Take subsamples.	III E		
		Metals			IV G	VD
			Same as for ash			
		Semivolatile Organics	samples.		IV C-F	VD
		Volatile ^{**} Organics	Spike with internal standard. Dilute in reagent water or poly-			VD .
			ethylene glycol in pur cell. Purge, trap and desorb into GC/MS.	ge		

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*Cross references are to sections of this document.

** Reference: Miller, N.C., R.W. James and W.R. Dick n, "Evaulated Methodology for the Analysis of Residual Waste," Report prepared under EPA Contract No. 68-02-1685 (December 1980). Also see SW-846 method 8240.

SUMMARY OF PROCEDURES FOR COMPOSITING SAMPLES

Physical <u>Form</u>	Homogenizing	Compositing	Minimum Quantity <u>of Composited Sample</u>
Aqueous	Shake well and pour aliquot	Combine aliquots in clean container and shake to mix well.	l L (semi-volatile organics) l L (metals)
	NOTE: For volatiles analysis, by adding aliquots from cell.	composite just prior to analysis multiple VOA bottles to purge	5 mL (volatile organics)
Sludges/ Slurries	Stir or shake well; use dipper to take > 3 portions.	Combine aliquots in clean container and stir or shake to mix.	100 mL (semi-vol organics) 100 g (metals)
Solids	Grind, if necessary, to reduce particle size (20 mesh screen) using agate or alumina equipment; riffle through steel or aluminum riffler.	Combine aliquots, cone-blend three times, roll-blend, cone and quarter.	50 g (organics) 100 g (metals)

Samples of stack (flue) gas collected with an extractive sampling train (M5, MM5, SASS or VOST) already represent time-averaged sample collections. In effect, the sampling approach has composited the gas on a time-weighted basis. It is generally inappropriate to further composite such samples. However, in some cases where ultra-low levels of detection are required (e.g., dioxin/furan analysis), it may be necessary to pool the entire extracts from multiple sampling runs.

C. RECOVERY METHODS

The specific sampling methods listed in Table 2 contain explicit procedures for the physical recovery of samples from the train. However, they do not necessarily specify procedures for monitoring the chemical recovery achieved in the sample preparation process. There are two basic approaches that can be used for this purpose: (1) addition to each sample of surrogate compounds, which are chemically similar to the species of interest but not expected to be present in the sample (e.g., for GC/MS analyses, stable isotope-labelled analogs of the target compounds); or (2) standard addition (spiking) of the target species themselves to selected split samples.

The spiking levels used in each instance are selected after consideration of the target detection level for each analyte and the expected concentration of the species in the sample. For MSW incinerator effluent samples, it is generally desirable to select spiking levels that correspond to 2 to 10 times the target detection limit or to 2 to 4 times the critical decision limit. The level chosen should be explicitly stated in the QAPP for each test program.

For example, assume that the critical decision limit for a semi-volatile organic pollutant (e.g., 2, 3, 7, 8-teterachlorodibenzodioxin, TCDD) is 1 ng/m^3 in stack gas, and a 5 m³ sample of stack gas is to be collected using the MM5 train. An appropriate level of surrogate (e.g., ${}^{13}C_{12}$ -2, 3, 7, 8-TCDD) to be spiked into the MM5 train components prior to extraction can be calculated as:

 $4 \times 1 \text{ ng/m}^3 \times 5 \text{ m}^3 = 20 \text{ ng surrogate}$

Assuming that the organic extract is concentrated to a final volume of 1.0 ml, and that 5 μ L are injected into the GC/MS system, this spiking level would yield 100 pg of surrogate on-column if recovery through the sample preparation steps were 100%, and 50-pg on column if recovery were only 50%. It must be confirmed by analysis of calibration solutions that these levels are within the analytical detection limit of the GC/MS system. Recovery of 60% or higher can be expected⁽²¹⁾ if the laboratory procedures are under control.

D. EXTRACTION METHODS

Solvent extraction with methylene chloride is the procedure most broadly used to prepare samples for organic analysis. In the case of stack sampling trains, several separate extractions (of probe wash and filter, sorbent trap, and of condensate) will be required. It is general practice to combine these extracts prior to analysis so that a single value is obtained for the stack gas concentration of each species. This approach allows lower detection limits to be achieved. Further, there is no intrinsic advantage to differentiating between material collected in the "particulate" (front half) vs "vapor" (back half) portions of the train, since these catches do not necessarily indicate the particulate/vapor distribution present in the stack^(4,22,23).

Liquid-liquid extraction, using a manual, separatory funnel method or a continuous extractor, applies to: (1) spent scrubber water or other waste water effluent from the MSW combustor and (2) aqueous condensate collected from the stack gas effluent in the MM5 or SASS trains. The volumes of sample/extracting solvent and any necessary pH adjustment of the sample should be as specified in EPA Method 625 if the purpose of data collection is NPDES compliance determination. In the case of stack gas condensate, these parameters can be scaled down to accommodate the actual quantity of sample collected.

Soxhlet extraction applies to: (1) solid effluents from the MSW combustor and (2) probe wash, filter and sorbent components of the MM5 or SASS trains. Quantities of sample and extraction solvent should be as specified in Method PO24 b (Sampling and Analysis for Hazardous Waste Combustion)⁽¹⁵⁾ or Method 3540 (SW-846).⁽¹⁾

Some very wet ash samples or sludges may require alternative extraction procedures (e.g., homogenization, Methods PO22 a,b or PO24 a,c). ⁽¹⁵⁾ Also, solid or slurry samples that are not suitable for direct introduction to the purge cell of a purge-and-trap apparatus may require a micro-extraction (e.g., Methods PO22b, PO24c) ⁽¹⁵⁾ prior to determination of volatiles.

If the MSW combustor test program includes evaluation of solid residues vis-a-vis the RCRA hazardous waste characteristics, a separate sample of the solid material must be extracted by the EP (Method 1310, SW-846) or the new TCLP (Fed. Reg. Vol. 51, No. 114, June 13, 1986), when promulgated as a final method.

E. DRYING AND CONCENTRATING OF EXTRACTS

Unless an alternative procedure is specified in a particular analytical procedure, solvent extracts should be passed through a short column of anhydrous sodium sulfate into a Kuderna-Danish evaporative concentrator apparatus. In most cases, rapid concentration to a final extract volume of 1-10 mL will provide adequate detection limits without unacceptable losses of semi-volatile organic species.

F. SAMPLE CLEAN-UP

For some samples, the level of interfering compounds is sufficiently high to preclude successful analysis for the species of interest. For such samples, one or more clean-up steps must be included in the sample preparation procedures Because of the wide variation in sample matrices and in the physical/chemical properties of the species that may be sought, no single method or set of methods can be recommended for MSW combustor samples. This is one of the reasons why use of surrogate spiking of MSW combustor samples is strongly recommended (Section IV C). If it can be demonstrated that recovery and detectability of the surrogate are adequate, then no clean-up steps are necessary. However, if interferences overload the analytical column or detector and the surrogate is not detectable, clean-up will be required. This must be established empirically for each project. The QAPP should specify the criteria for acceptable surrogate recovery/detectability and corrective actions to be taken if the criteria are not met.

Some analysis methods (e.g., Methods 8010-8250, SW-846⁽¹⁾) specify that silica gel, Florisil or alumina column clean-up be applied. In some cases three or more sequential clean-up steps may be required. For example, the ASME methodology for analysis of dioxins and furans⁽⁵⁾ specifies sequential passage of the concentrated sample extract through 1) a combination column containing silica gel and acid and base-modified silica gel, 2) a basic alumina column, 3) a PX21 carbon/celite 545 column and 4) a silica/diol column. Such an extensive clean-up is usually not necessary unless the critical decision limit is in the ng/mg³ range. However, using at least one column clean-up step (silica gel, alumina) may significantly improve detection limits when critical concentrations are in the μ g/m³ range.

G. DIGESTION

The preparation method for all samples requiring metals analysis includes a digestion step. Its purpose is to convert all of the metal-containing species into inorganic form.

For most sample types, an acidic, oxidizing medium is specified for digestion. Solid samples can be digested using HF and HNO₃ in a Parr bomb. Solutions can be digested using HNO₃ and $H_2O_2^{(24)}$. In some instances, repeated digestion using HNO₃ alone⁽¹⁾ may give adequate recovery. For mercury in solid materials, Method 105 (40 CFR Part 61) calls for aqua regia digestion followed by potassium permanganate oxidation.

A relatively new development is the use of microwave energy, rather than a conventional hot plate, for acid digestions. This reduces the time and acid quantity required for complete digestion (24).

V. ANALYSIS PROCEDURES

A. OVERVIEW

The overall strategy for analyzing samples from MSW combustion must reflect the multiple possible purposes of data collection discussed in Section II A.

When the purpose of the data collection is to determine compliance with a specific regulation concerning air, water, or solid effluents (or their disposal) it is essential that the analysis method used be one recognized by the appropriate agency. These include, but are not necessarily limited to:

EPA	NSPS Methods 1-5	40	CFR	Part	60
EPA	NESHAPS Methods 101-108	40	CFR	Part	61
EPA (601-6 200.7	Clean Water Act Methods 512; 624, 625; 1624, 1625; 7	40	CFR	Part	136
EPA F	CRA Methods	SW-	846		

7040-7951; 8010-8310

One exception to the above generalization relates to measurement of criteria pollutants in combustor effluents. The EPA NAAQS methods for criteria pollutants are ambient air monitoring methods that are suitable for source monitoring only with modifications (gas conditioning; dilution). However, there are NSPS methods applicable to direct measurement of criteria pollutants in combustion sources.

Even when the purpose of data collection is to provide input for more general environmental assessment, or risk assessment, rather than regulatory compliance, the above EPA-approved methods are frequently useful. In particular, the nearly-identical GC/MS-based methods designed for determination of priority pollutants (624, 625; 1624, 1625) or Hazardous Substance List (HSL) compounds (RCRA 8240, 8250, 8270) have wide applicability for organic analysis. The corresponding procedures for metals analysis by atomic absorbtion spectroscopy (AAS) or inductively coupled plasma spectroscopy (ICP) are also directly applicable to MSW combustor samples.

For some assessment purposes, official federal EPA methods may be inappropriate or unavailable. In these cases, methods promulgated by ASTM and ASME should be used if available. For example, there is at present no official method for determination of dioxin/furan congeners that applies specifically to MSW stack emission sample analysis. However, a procedure developed to support a joint ASME-EPA project on MSW combination is recommended ⁽⁵⁾. In addition, SW-846 method 8280 may be used for homolog-specific analysis.

Similarly, there are presently no official methods suitable for screening MSW combustor samples to identify and/or quantify other pollutants that may be present as a result of incomplete combustion. Research in this area is underway as well. The selection of appropriate analysis methods for such pollutants must be established on a case-by-case. Part C of this section provides some preliminary suggestions.

Potentially useful methods for direct analysis of selected species in MSW combustor effluents using continuous instrumental monitors will be discussed in Section VI of the report.

B. PROXIMATE ANALYSIS

"Proximate analysis" is a term used in "Sampling and Analysis for Hazardous Waste Combustion (First Edition)"⁽¹⁵⁾ to describe procedures for determining the approximate (gross) composition of hazardous waste. The methods recommended for that purpose include:

% moisture, solid and ash determination elemental analysis (%C, N, S, P, F, Cl, Br, I) total organic carbon total organic halogen heating value viscosity

These methods are applicable to MSW.

C. SCREENING ANALYSIS

As noted above, screening analysis is intended to identify and/or quantify species that are present in a sample and are of potential concern with regard to effects on health and/or environment but were not specifically pre-selected for analysis (see Section D, Directed Analysis). There are no official procedures for screening analysis. In practice, the approach that has most commonly been used in research and development programs involving waste combustion has been as follows.

For organic species, perform full-mass range scanning (e.g., 40-500 amu) under appropriate GC/MS conditions (usually capillary column and El ionization). In most cases, the GC/MS conditions specified in EPA methods 624/1624/8240 for volatiles and in EPA methods 625/1625/8250/8270 for semivolatiles will be applicable to screening analysis of MSW combustor samples. In addition to providing data for directed analysis, the results of these analyses can be used to identify unknown or unexpected compounds by comparison to a library of reference spectra or by spectral interpretation. A typical criterion for screening analysis is to attempt to identify the 20 most intense unknown peaks or those peaks whose intensity exceeds 10% of the internal standard intensity (whichever is the lesser number of unknowns).

For inorganic species, ICP analysis can be used to screen for about 20-23 metals that are known or suspected to be of environmental concern. Alternative approaches sometimes recommended to address a broader range of elements include: X-ray fluorescence, neutron activation analysis, particle-induced X-ray emission, and spark source mass spectrometry. All of these are multielement methods and require minimal sample preparation. However, the instrumentation required is expensive and not widely available. Also, the methods are more

amenable to qualitative screening than to quantification unless standards and samples are carefully matched to eliminate sample matrix effects.

It is probable that screening analysis is more likely to be requested for MSW combustor air emission samples than for liquid or solid effluents. These methods can be applied to samples of MSW combustor stack gas collected with the MM5, SASS or VOST (volatile organics only) after suitable sample preparation techniques have been applied. They should also apply to liquid or solid effluent samples after sample preparation.

D. DIRECTED ANALYSIS

As noted in the overview to this Section, analysis methods are available for most species that are likely to be pre-selected as targets for analysis in MSW incineration. Table 6 lists suitable analysis methods for organics and metals that may be of concern. Specific methods for distinguishing between species such as Cr (VI) and Cr (III), suitable for use with combustion effluent samples, based on selective extraction of Cr (VI) by an alkaline reagent, are under development and in the process of validation by EPA's Emission Measurement Branch at Research Triangle Park, North Carolina⁽²⁵⁾. In addition, SW-846 lists methods both for Cr(VI) and for total chrome; these methods are potentially applicable to MSW combustor samples providing that suitable procedures for solubilization of the chromium are applied.

Note that, for organic analysis, Table 7 lists only the GC/MS alternatives. Methods that use GC or HPLC with detection principals less specific than MS (e.g., flame ionization (FID) or electron capture (ECD) detection for GC, ultraviolet (UV) or refractive index (RI) for HPLC) are less likely to be useful for MSW combustion samples, because of the variety and quantity of potentially interfering substances likely to be present.

ANALYSIS METHODS FOR TRACE ORGANICS AND TRACE METALS, . APPLICABLE TO MSW COMBUSTOR SAMPLES

<u>Species</u>	Method	Reference
Volatile Organics	Packed column GC/MS; full mass range scanning 20-260 amu.	1, 15
Semivolatile Organics	Capillary column GC/MS; full mass range scanning 40-500 amu.	1, 15
Dioxins/Furans	Capillary column GC/MS; selected ion monitoring.	1, 5
Metals	Flame (high levels) or furnace (low levels) AAS.	1, 24
	Inductively coupled plasma spectroscopy (not for mercury, lead, arsenic)	1, 24

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VI. CONTINUOUS MONITORING METHODS

A. OVERVIEW

Continuous monitoring systems include <u>in situ</u> measurements, in which a sensor is mounted directly in a stack or flue, and <u>extractive</u> methods, in which a sample of stack or flue gas is pumped through an interface to the measuring device. <u>In situ</u> monitoring offers the advantage that no alteration in flue gas composition is introduced by the svetem. Conversely, however, an <u>in situ</u> sensor must be physically resistant to st. conditions (temperature, moisture, particulate matter) and be chemically selective (blind to potential interferents). An extractive approach is amenable to gas sample conditioning to remove substances that might interfere with the desired measurement or damage the instrument. It also allows instruments to be placed in a sheltered location where maintenance and calibration are more convenient. However, this approach provides opportunity for loss of target species in transfer lines and in components of the gas conditioning system.

Many continuous monitors are based on rather sophisticated chemical analysis principles. Manufacturers have made considerable efforts to "ruggedize" the commercially available systems so that they are capable of unattended operation for periods of days to weeks and can be maintained/calibrated by plant operating personnel. Despite these advances, it is vital that a rigorous QA/QC program be established for continuous monitors to ensure that misleading data are not recorded and that operating problems are not overlooked.

B. SAMPLE CONDITIONING

An extractive sampling system interface typically includes the following components:

- probe
- coarse filter
- transfer lines

- pump
- moisture removal system
- fine filter

The probe must be located at a point in the stack or flue that allows a representative sample to be withdrawn. A multi-port probe may be useful in this regard. Depending on stack or flue temperature and corrosivity, materials of construction may be stainless steel or ceramic. The coarse filter, usually located in-stack to minimize effects of condensation, is typically sintered metal or ceramic, depending on temperature. Ceramic is more resistant to high temperature corrosion effects but also more susceptible to cracking. Plugging of the probe and/or coarse filter can be a severe problem, especially when _ ...mpling flue gas upstream of particulate control devices. Backflushing the system regularly with clean carrier gas may help but frequent replacement of the in-stack filter will probably still be required.

The transfer lines must be constructed of inert materials that are resistant to corrosion and do not absorb the species to be measured; ceramic (probe) and Teflon[®] are materials of choice for most applications. Stainless steel would be an alternative if the stack or flue gas is not highly corrosive. The pump must also be constructed of, or coated with, inert material such as Teflon[®]. Especially when samples are to be monitored for organics, any potential contamination of the sample with lubricants must be avoided. Diaphragm or bellows pumps can meet this constraint.

Moisture removal can be accomplished in several ways: adsorption (e.g., silica gel); condensation; dilution to below dew point; membrane permeation system. Issues that must be addressed in selection of the drier component include: adequate capacity for water removal given the moisture content of the stack or flue gas; and minimal coincident losses of target species along with the water. A condensation approach, for example, may lead to unacceptable losses of acid gases such as HCl and SO.

The fine particulate filter is usually located close to the analyzer inlet. It usually must achieve virtually complete removal of all particles larger than

1 micron. When sampling flue gases, these filters require replacement whenever the pressure drop across the filter approaches the limit of pumping capacity.

C. MONITORS FOR INORGANICS

The following is based on information provided by instrument suppliers and by references 26 and 27.

Continuous temperature measurements in combustor flue or stack gases are generally accomplished by using type J, K, or RT thermocouples. The thermocouples must be shielded from radiation and protected against mechanical damage and corrosion by shielding inside a ceramic or metal protection tube or in a thermowell.

Continuous monitoring of particulate material is generally accomplished using an <u>in situ</u> opacity meter. Typically, these devices measure changes in optical density, OD (percent transmittance), due to scattering and/or adsorption of light by particles in the stock. The OD reading obtained depends not only on the mass loading of particulates that are present, but also on their size distribution, the particle shape, particle composition, the system's temperature, the presence or absence of water droplets and the configuration of the stack. The lack of measurement specificity may render opacity monitors less reliable at MSW combustors than at other stationary sources, as waste feeds at MSW locations are highly variable, probably causing emission levels and compositions to vary over time as well. Also, commercially available opacity meters for stack monitoring may be uncertain by a factor of two or more at particulate loadings below 0.03 gr/SCF.

Extractive sampling, rather than <u>in situ</u> monitoring, is most commonly used for inorganic gases, although <u>in situ</u> monitors are available for CO, CO₂, O₂, NO_x, and SO_x. Typically, the detection of pollutant species of concern is accomplished using one of the detection principles identified in the descriptive information presented below. There is relatively little history of application of these instruments to MSW combuster stack gas and, especially, flue gas.



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for continuous monitoring at other types of

ietection principle used by continuous analyzers is Amenable for use in the determination of CO, y NDIR is based on the principle that each of ers, will absorb specific signature wavelengths of rating matched beams at the correct signature h a clean "reference" cell while the other is r. sample gas, and determining the difference in beams, it becomes possible to measure the amount les that is present.

complished using devices such as a thermistor, a device.

f NDIR based instrumentation is the fact that it i that the technology is applicable to a wide Also, instruments are relatively rugged and have been in use in field monitoring situations ire associated with this detection principle are recies that will absorb similar signature nd the fact that optical systems needed to he generated infrared light may degrade due to

NDUV) analyzers employ much the same philosophy as up the analyzers based on NDIR absorbtion, only in this instance, the light source emits in the ultraviolet or visible regions of the spectrum and a reference cell is generally not used. Typically, a reference wavelength in a

region where the pollutant species of interest has minimal absorptive capacity is generated and quantitation is completed by differential analysis.

An important advantage of the NDUV analyzers is that water vapor is not an interference, as water does not absorb light in the ultraviolet region of the spectrum. As is the case with most extractive monitoring techniques, however, particulates which will absorb or scatter generated light must be removed from the sampled gas stream.

Polerographic Analyzers

Numerous pollutant species of potential interest at MSW combustors may be measured continuously using polarographic analyzers. Polarographic analyzers operate on the principle of selective diffusion and chemical reaction of a pollutant species of interest which induces a current flow that is measured electronically. The sensing device intrinsic to the operation of all polarographic analyzers is commonly called the electrochemical transducer.

In operation, the pollutant species of interest enters the transducer through a selective, semi-permeable membrane. Once in the transducer, the pollutant is oxidized or reduced by reaction with an electrolyte solution which induces a current flow. The induced current flow is proportional to the concentration of the pollutant species in the gas stream. The selectivity of electochemical transducers is dependent upon the selection of membrane materials, electrolyte, and sensing electrode chemistry or composition.

The polarographic analyzers offer several advantages over other analyzers, including multi-pollutant capability by switching transducer, fast response and simplicity of operation. Principle disadvantages of this technique are that transducers must be replaced or rejuvenated periodically, and the instrument must be frequently calibrated because the response of the transducer does deteriorate as the electrolyte solution is consumed.

Electrocatalytic Analyzers

Electrocatalytic analyzers are currently available for oxygen determination. This type of instrumental determination is based on the principle that current flow is induced when two solutions containing similar materials at differing concentrations are brought into contact. Thus, by having two cells, one a reference and the other the unknown, separated by a porous zirconium oxide barrier (acting as both an electrolyte and catalyst), an electron current flow can be promoted, measured, and related directly to oxygen content.

Paramagnetic Oxygen Analyzers

Oxygen content may also be determined using a paramagnetic analyzer. Detection in a paramagnetic analyzer utilizes the fact that oxygen molecules (and the molecules of a few other compounds) are attracted by a magnetic field.

Two different philosophies of paramagnetic detection are commonly used in instrumentation. One, called thermomagnetic or magnetic wind instruments are based on the principle that the magnetic attraction of oxygen decreases as temperature increases. The second, called magneto-dynamac, uses the paramagnetic attraction of oxygen to swing a specialty torsion balance.

Chemiluminescence

Certain inorganic pollutants, most notably nitrous oxide and ozone, may also be detected using analyzers based on chemiluminescence. Within this type of instrumentation, the pollutant species of interest is mixed with a second reactant to generate light. Ideally, the generated spectrum of light produced is specific only to the pollutant of interest, but more commonly, optical means are used to isolate and quantitate the intensity of specific wavelength. By measuring the intensity of the generated light, a direct estimate of the concentration of pollutant species present in the gas sample may be obtained.

Information of currently available instrumentation for inorganic pollutant species in MSW combuster exhausts are presented in Tables 8 through 14.

Continuous Analyzers for Carbon Monoxide

Detection Principle	Ranges	Interferences	Comments	Examples
Nondispersive	0-50 PPM	Water Vapor and	In-situ or remote;	Anarad, Inc.
Infrared	0-100 PPM	Particulates; other	Water Vapor and	Dynatron
1	0-200 PPM	species with similar	Particulates should	Horiba
1	0-1000 PPM	infrared absorbance	be removed; corro-	Infrared Ind.
1	0-5000 PPM	(characteristics	sive gases may etch	Rosemont (Beckman)
1	0-1 %	1	loptics	Servomex
1	0-5 %		1	Siemens
			}	
Polarographic	0-50 PPM	Unsaturated Hydro-	Requires sample	Energetics Science
(Electrochemical)	0-100 PPM	carbons and ammonia	conditioning to	Interscan
1	0-250 PPM		remove particulate	Neotronics
	0-500 PPM		and reduce tempera-	Sensidyne
1	0-999 PPM	(ture	1
1	0-4 8	1	1	1
1	l	ł	1	1
1	1	8	1	1
1	1		1	1
1	1	ł	1	1 1

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Continuous Analyzers for Carbon Dioxide

Detection Principle	Ranges	Interferences	Comments	Examples
Nondispersive	0-10 PPM	Water Vapor and	In-situ or remote;	Anarad, Inc.
Infrared	0-100 PPM	Particulates; other	Water Vapor and	Dynatron
•	0-500 PPM	species with similar	Particulates should	Horiba
	0-2500	infrared absorbance	be removed; corro-	Infrared Ind.
1	0-5000 PPM	characteristics	sive gases may etch	Rosemont (Beckman)
1	0-0.5 %	1	optics	Servomex
Ì	0-2.5 %	Ì	1	Siemens
1	0-5 %			Syconex Corp.
1	0-20 %	1	ĺ.	1
ļ	0-100 %			1
 Polarographic	0-50 PPM	Unsaturated Hydro-	Requires sample	 Sensidyne
(Electrochemical)	0-100 PPM	carbons and ammonia	conditioning to	
1	0-250 PPM	Ì	remove particulate	i
4	0-500 PPM	Ì	and reduce tempera-	i i
j	0-999 PPM	Ì	ture	i i
1	0-4 %	1	ĺ	Í
1	1	1	1	1
1			1	1
1	1	1	1	1
1		1	1	1 i

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Continuous Analyzers for Oxygen

Detection				
Principle	Ranges	Interferences	Comments	Examples
Polarographic (Electrochemical)	0-1 % 0-5 %		Gas must be cooled and particulate re-	Horiba MSA
	0-10 % 0-25 % 0-35 % 0-100 %		moved	Neutronics Servomex
Electrocatalytic	0-10 % 0-22 %		Good for high tem- perature application	Anarad, Inc. Dynatron Lynn Products MSA Servomex Westinghouse
Paramagnetic	0-1 % 0-5 % 0-2.5 % 0-10 % 0-25 % 0-50 % 0-100 %			Horiba Rosemont (Beckman) Siemens

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Continuous Analyzers for Sulfur Dioxide

Detection				
Principle	Ranges	Interferences	Comments	Examples
Nondispersive Infrared	0-500 PPM 0-2000 PPM 0-10000 PPM 0-1 % 0-5 % 0-10 % 0-30 % 0-100 %	Water Vapor and Particulates; other species with similar infrared absorbance characteristics	In-situ or remote; Water Vapor and Particulates should be removed; corro- sive gases may etch optics; Generally selected for percent applications	Anarad, Inc. Dynatron Infrared Ind. Rosemont (Beckman) Siemens Syconex Corp.
 Nondispersive Ultraviolet 	0-50 PPM 0-100 PPM 0-500 PPM 0-1000 PPM 0-5000 PPM			 Anarad, Inc. Teco
 Polarographic (Electrochemical) 	0-5 PPM 0-10 PPM 0-50 PPM 0-100 PPM	Methyl and Ethyl Mercaptans, Hydrogen Sulfide, Ammonia		 Interscan

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Continuous Analyzers for Nitrogen Oxides

Ranges	Interferences	Comments	Examples
0-500 PPM 0-2000 PPM 0-10000 PPM 0-2 % 0-10 %	Water Vapor and Particulates; other species with similar infrared absorbance characteristics	Water Vapor and Particulates should be removed; corro- sive gases may etch optics	Horiba Rosemont (Beckman) Siemens Syconex Corp.
0-50 PPM	 		Anarad Inc
0-25 PPM 0-50 PPM 0-250 PPM	Methyl Mercaptan, Ammonia, Nitrogen Dioxide, Sulfur Dioxide	Requires sample conditioning to remove particulate and reduce tempera- ture	Energetics Science
0-2.5 PPM 0-10 PPM 0-25 PPM 0-100 PPM 0-1000 PPM 0-2500 PPM 0-10000 PPM	Possible Ammonia, Carbon Dioxide, and Water	Need to dry and remove particulates from sample	Monitor Labs Rosemont (Beckman) Thermo Electron
	Ranges 0-500 PPM 0-2000 PPM 0-10000 PPM 0-2 % 0-10 % 0-50 PPM 0-50 PPM 0-50 PPM 0-50 PPM 0-250 PPM 0-250 PPM 0-100 PPM 0-100 PPM 0-1000 PPM 0-1000 PPM	RangesInterferences0-500 PPM 0-2000 PPM 0-10000 PPM 0-2 %Water Vapor and Particulates; other species with similar infrared absorbance characteristics0-2 % 0-10 %Infrared absorbance Icharacteristics0-50 PPM 0-50 PPMMethyl Mercaptan, Ammonia, Nitrogen Dioxide, Sulfur Dioxide0-25 PPM 0-250 PPMPossible Ammonia, Carbon Dioxide, and Water0-2.5 PPM 0-1000 PPM 0-1000 PPM 0-1000 PPMPossible Ammonia, Icarbon Dioxide, and Water	Ranges Interferences Comments 0-500 PPM Water Vapor and Particulates; other Water Vapor and Particulates should 0-10000 PPM species with similar infrared absorbance characteristics Water Vapor and Particulates should 0-10 % infrared absorbance characteristics sive gases may etch optics 0-50 PPM Methyl Mercaptan, Ammonia, Nitrogen Dioxide, Sulfur Requires sample conditioning to remove particulate and reduce tempera- ture 0-2.5 PPM Possible Ammonia, Carbon Dioxide, and 0-25 PPM Need to dry and remove particulates from sample 0-25 PPM Water Interferences

Continuous Analyzers for Hydrochloric Acid

Detection Principle	Ranges	Interferences	Comments	Examples
Nondispersive Infrared 		Water Vapor and Particulates; other species with similar infrared absorbance characteristics	In-situ or remote; Water Vapor and Particulates should be removed; corro- sive gases may etch optics	Flakt Syconex Corp Teco
Polarographic (Electrochemical)	0-5 PPM 0-10 PPM 0-20 PPM 0-50 PPM 0-200 PPM	Chlorine gas, Methyl and Ethyl mercaptan, Hydrogen Sulfide, Ammonia, Nitric Ox- ide, Hydrogen Cyan- ide, and Sulfur Di- loxide	Requires sample conditioning to remove particulate and reduce tempera- ture	Interscan

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Continuous Analyzers for Hydrogen Cyanide

Polarographic 0-5 PPM Chlorine gas, Methyl Requires sample Interscan(Electrochemical) 0-10 PPM and Ethyl mercaptan, conditioning to 0-20 PPM Hydrogen Sulfide, remove particulate 0-50 PPM ArmonicNitrie Over lend veduce termove	
(Electrochemical) (0-10 PPM [and Ethyl mercaptan, conditioning to [10-20 PPM [Hydrogen Sulfide,]remove particulate [10-50 PPM [Hydrogen Sulfide,]remove particulate [1
0-20 PPM Hydrogen Sulfide, remove particulate	Í
10.50 PDW Ammonia Nitria Or Land reduce termsus	i
() JO FFM AMMONIA, NICIC UX- Jand reduce tempera-	Í
ide, Hydrochloric ture	i
acid, and Sulfur Di-	i
oxide	i
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D. _ MONITORS FOR ORGANICS

Total hydrocarbons (or total non-methane hydrocarbons) at ppm to percent levels in stack gases can be monitored continuously with a flame ionization detector (FID) or infrared (IR) detector. These detectors are relatively rugged and are quite sensitive to hydrocarbons. The response factor is generally lower for organics that incorporate functional groups such as hauides, hydroxyl, carbonyl, carboxylate.

The photoionization detector (PID) is applicable to many of these organic categories, but experience with this detector as a continuous monitor is more limited. There is some evidence that maintenance is more of an issue with PID than with FID or IR instruments.

The electron capture detector (ECD), which has high sensitivity and selectivity for halogenated organics under laboratory conditions, is not rugged enough for routine continuous monitoring in the field. Also, because these detectors contain radioactive materials, NRC permitting regulations govern their installation and use. The Hall detector, also specific for halogenated species, has been used at hazardous waste incineration sites, but with difficulty.

Catalytic combustion (hot wire) and thermal conductivity detectors are also used for continuous monitoring of organics. However, most commercially available instruments based on these principles are generally designed for percent level concentrations corresponding to explosive limits of combustible gases and vapors. A few low-level instruments suitable for MSW combustion monitoring are available, however,

Monitoring of specific organic compounds, rather than total organics, requires that chromatographic separation be accomplished prior to detection, Instrumental monitors that interface a gas chromatograph to an FID or PID are commercially available. These operate in a semi-continuous basis, since the chromatographic separation imposes a cycle time of (typically) 5-30 minutes between measurements.. The GC/FID or GC/PID analyzers are vulnerable to false positive interferences because the retention time is an imperfect means of compound identification.

Instruments based on more selective detection principles (e.g., GC/MS or GC/FTIR) are beyond the present state-of-the-art for stack monitoring, except in research installations. Instruments using these detectors may be sufficiently expensive to install and demanding to operate that they are not suitable for routine continuous monitoring. Most require, for example, more stringent control of temperature, humidity and power supply than is likely to be practical at an operating MSW plant.

E. INDICATOR OR SURROGATE MONITORING

A conceptual ideal for continuous monitoring of MSW combustors would be a inexpensive, rugged, and simple instrument that provides continuous measurement of a surrogate parameter indicative of total system performance. Identification of a suitable surrogate parameter, which can be reliably correlated with emissions of any and all pollutants of potential concern, is one of the objectives of on-going research in MSW combustion technology. At the present time, the carbon monoxide level in the air emissions is generally regarded as the best available surrogate for chemically-based monitoring of overall combustion efficiency. Monitoring of combustion temperature is also relied on as an indicator that the process is in control. Methods for monitoring these indicator parameters are discussed in Section VI C.

F. SPECIAL QA/QC CONSIDERATIONS

All of the general provisions that will be discussed in Section VII apply to continuous monitoring. A few special considerations are worth noting, however.

First, calibration with zero and span gases should be performed on the system as a whole, not just on the analyzer/detector itself. This may, however, be literally impossible for <u>in situ</u> monitors; generating a stack or flue full of calibration gas of known composition is not a realistic approach. In the case

of extractive monitoring systems, provision should be made to allow introduction of calibration gas at, or just behind, the probe. This approach to "total system" calibration has been incorporated into all of the federally referenced continuous monitoring methodologies that are currently applicable to stationary sources.

The EPA has also established guidelines for instrumentation that is used to continuously monitor sulfur dioxide, nitrogen oxides, carbon dioxide, oxygen, and carbon monoxide emissions from stationary sources. These guidelines fall into two categories including both strumental design criteria and performance specifications.

Instrumental design criteria establish minimum acceptable levels for items such as instrumental response time, interference rejection ratios and ranges. Performance specifications are established to assure that the developed data is accurate and precise. Specifications for calibration drift and the relative accuracy of calibration, as well as requirements for duration of unattended operation are established. Specific criteria applicable to monitors used to measure CO, CO_2 , O_2 , NO_x , and SO_x are provided in Title 40 Code of Federal Regulations, Part 60.13 and Appendix A and B.

Second, QA/QC procedures for continuous monitoring methods must take into account the fact that operating personnel may have had minimal training and experience with chemical measurements and analytical instrumentation. The procedures must, therefore, place minimum reliance on operator judgment and be as explicit and simple as possible concerning QC criteria and corrective actions.

Third, the question of data reduction and data maintenance for continuous monitor output deserves special consideration. A continuous monitor, in one sense, generates an infinite number of data points on pollutant concentration vs. time. It must be determined in advance whether daily, weekly, monthly, etc. data are to be archived and/or reported. Are running averages desired? Commercially available data loggers are able to conduct these functions once decisions are made with respect to these parameters. How should/must short-term excursions from average values be recorded/reported?

G. POTENTIAL FOR PROCESS CONTROL

The acquisition of continuous monitoring data affords opportunities for process control, either by operator intervention or by use of automatic feedback loops. In current MSW combustion practice operator intervention is the more common response mode, but newer facilities are moving toward more automated systems.

Catastrophic failure of the system (e.g., plugging of nozzles in a dry scrubber or breakage of a fabric filter) is generally readily detectable by operators even in the absence of continuous monitoring data. Temperature and, secondarily, oxygen data from continuous monitors can be (and are) used to adjust process operating parameters such as MSW feed rate or over/underfire air supply to the incinerator.

Use of chemical monitoring data for process control is more complicated, both in theory and in practice. In general, the relationship of MSW combustion operating conditions to the emission rates of pollutants, especially trace organics, is not well enough understood to allow systematic process control in response to monitoring data.

VII, QUALITY ASSURANCE AND QUALITY CONTROL

A. OVERVIEW

A vital part of any sampling and analysis program is the provision for procedures which maintain the quality of the data obtained throughout the sampling and analysis exercise. These procedures, termed quality assurance and quality control (QA/QC), serve to (a) document the quality (i.e., accuracy, precision, completeness, representativeness and comparability) of generated data; (b) maintain the quality of data within predetermined control limits for specific sampling and analysis procedures; and (c) provide guidelines for corrective actions if QC data indicate that a particular procedure is out of control.

The following definitions, which represent interdependent activities, serve to differentiate between the complementary activities of quality assurance and quality control.

- <u>Quality Assurance (QA)</u> activities addresses the delegation of program responsibilities to appropriate individuals, documentation, data review, and audits. The objective of the QA procedures is to allow an assessment of the reliability of the data.
- <u>Quality Control (QC)</u> activities address the maintenance of facilities, equipment, personnel training, sample integrity, chemical analysis methods, and production and review of QC data. QC procedures are used continuously during a sampling and analysis program to maintain the quality of data within control limits. QC data should be evaluated immediately by the analysts; if the QC data fall outside a set of specified control limits, corrective actions, as specified in the work plan, must be taken.

In this section, specific QA/QC procedures are described. For an individual sampling and analysis program, these procedures and/or others may be selected to reach the goal of obtaining high-quality data. At a minimum, the procedures
which are selected must be consistent with the standard operating procedures and/or good laboratory practices of the sampling crew and analytical laboratory involved.

The following discussion of QA/QC procedures is based upon a guidelines document⁽²⁾ issued by the Office of Monitoring Systems and Quality Assurance of the EPA Office of Research and Development. This document, QAMS 005/80, entitled "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans," and the references cited therein provide an extensive resource in selecting appropriate QA/QC procedures for sampling and analysis efforts. The QAMS-005/80 document identifies sixteen essential elements of a QA Project Plan (QAPP). These elements are listed in Table 15 and described briefly in the following discussion. A QAPP of some kind would generally be required for most sampling and analysis efforts.

B. TITLE PAGE AND TABLE OF CONTENTS

These elements are self-explanatory. The title page should indicate individuals with QA responsibility for the sampling and analysis efforts. Approval signatures should be required prior to the start of the sampling and analysis efforts. The Table of Contents should include a distribution list for the QAPP.

C. PROJECT DESCRIPTION

A general description of the project, including the experimental design, and intended use of data should be provided. The description may be brief but should have sufficient detail to allow the individuals responsible for review and approval, of the QAPP to perform their task. Flow diagrams, tables and charts should be included, as appropriate. A schedule, with anticipated start and completion dates, should also be specified.

TABLE 15

ESSENTIAL ELEMENTS OF A QA PROJECT PLAN

- 1. Title Page
- 2. Table of Cont nts
- 3. Project Description
- 4. Project Organization and Responsibility
- 5. QA Objectives
- 6. Sampling Procedures
- 7. Sample Custody
- 8. Calibration Procedures and Frequency
- 9. Analytical Procedures
- 10. Data Reduction, Validation, and Reporting
- 11. Internal Quality Control Checks
- 12. Performance and System Audits
- 13. Preventive Maintenance
- 14. Specific Routine Procedures Used to Asses Data Precision, Accuracy and Completeness
- 15. Corrective Action
- 16. Quality Assurance Reports to Management

Source: U.S. Environmental Protection Agency/Office of Monitoring Systems and Quality Assurance, Office of Research and Development, Washington, D.C., "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans," QAMS-005/80 (December 29, 1980)

D. PROJECT ORGANIZATION AND RESPONSIBILITY

A table or chart which shows the project organization and line authority should be included. An example project organization chart is shown in Figure 9. Key individuals who are responsible for ensuring the collection of valid measurement data and the routine assessment of measurement systems for precision and accuracy should be identified; the responsibilities of each individual should also be delineated. It should be noted that the QA coordinator should be organizationally independent of the project organization so that the risk of conflict of interest may be minim.

E. QUALITY ASSURANCE OBJECTIVES

For each major measurement system, numerical QA objectives for accuracy, precision and completeness should be established. These objectives may be generally based on previous experience in applying comparable procedures to similar sample matrices as well as on the requirements of the program. The QA objectives for precision, accuracy and completeness should be summarized in a table or chart; an example of a summary table is shown in Table 16.

All measurements should be made such that results are representative of the media (e.g., waste feed, stack emissions) and conditions being measured. Any factors considered within the experimental design to ensure representativeness should be described.

All data should be calculated and reported in units consistent with other organizations reporting similar data to allow for comparability of data bases among organizations. Units for all measurement parameters should be specified.

F. SAMPLING PROCEDURES

A detailed description of all sampling procedures to be used is an integral part of any QAPP. Where applicable, the following information should be included:

• Description of techniques or guidelines used to select sampling sites.



FIGURE 9 EXAMPLE OF PROJECT ORGANIZATION AND RESPONSIBILITY

TABLE 16

SUMMARY OF ESTIMATED PRECISION, ACCURACY, AND COMPLETENESS OBJECTIVES^a

Parameter	<u>Precision</u> ^b	Accuracy ^b	<u>Completeness</u> ^C
Flue gas dioxin/furans (Modified Method 5)	±	50-100	100
Ash dioxins/furans	±	50-100	100
Velocity/volumetric flow rate (EPA Method 1 & 2)	<u>+</u>	<u>+</u> 20	100
Fixed gases/molecular weight (Modified EPA Method 3)	\pm 10 ^f	<u>+</u> 20 ^e	100
Moisture (EPA Method 4)	<u>+</u> 20 ^d	$\pm 10^{d}$	100
Flue gas SO ₂ (continuous monitor)	$\pm 20^{f}$	<u>+</u> 20 ^e	100
Flue gas temperature (thermocouple)	<u>+</u> 10°F	<u>+</u> 20°F	100
Ash (NAA)	ND	ND	100
Particulate Mass	<u>+</u> 10	<u>+</u> 12	100
Flue gas HCl (IC Analysis)	<u>+</u> 10	<u>+</u> 10	100
Flue Gas Lead/Cadmium (AA/AAF, NAA)	ND	ND	100
Flue Gas Chromium/Nickel (AA/AAF, NAA, Colorimetry)	<u>+</u> 10	± 10	100

^aAll objectives are expressed in terms of percent (%). ^bPrecision and accuracy estimiated based on results of EPA collaborative tests. ^cValid data percentage of total tests conducted. ^dRelative error (%) derived from audit analyses, where

Percent - Measured Value - Actual Value x 100% Actual Value

^eCoefficient of variation (CV) determined from daily analysis of a control sample where

 $CV = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$ %

 $f_{Percent}$ difference for duplicate analyses, where

Percent = $\frac{\text{First Value - Second Value}}{0.5 (\text{First + Second Values})} \times 100\%$

ND - not determined for this method

Source: "Revised Sampling and Analytical Plan for the Marion County Solid Waste-to-Energy Facility Boiler Outlet Salem Oregon," EPA Contract No. 68-02-4338, DCN: 86-222-124-02-05, September 16, 1986.

- Specific sampling procedures to be used (by reference in the case of standard procedures and by actual description of the entire procedure in the case of nonstandard procedures).
- Charts, flow diagrams, or tables delineating sampling program operations.
- A description of containers, procedures, reagents, etc., used for sample collection, preservation, transport, and storage.
- Special conditions for the preparation of sampling equipment and containers to avoid sample contamination (e.g., containers for organics should be solvent-rinsed; containers for trace metals should be acid-rinsed).
- Sample preservation methods and holding times.
- Time considerations for shipping samples promptly to the laboratory.
- Sample preparation (e.g., concentration, dilution, cleanup techniques).
- Forms, notebooks, and procedures to be used to record sample history, sampling conditions, and analysis to be performed.

G. SAMPLE CUSTODY

It is essential that adequate chain-of-custody procedures be established for each project. The following sample custody procedures should be addressed in the QA Project Plans: Field Sampling Operations:

- Documentation of procedures for preparation of reagents or supplies which become an integral part of the sample (e.g., filters and absorbing reagents).
- Procedures and forms for recording the exact location and specific consideration associated with sample acquisition.
- Documentation of specific sample preservation method
- Pre-prepared sample labels containing all information necessary for effective sample tracking.
- Standardized field tracking reporting forms to establish sample custody in the field prior to shipment.

Laboratory Operations:

- Identification of the person responsible to act as sample custodian at the laboratory facility who is authorized to sign for incoming field samples, obtain documents of shipment (e.g., bill of lading number of mail receipt), and verify the data entered into the sample custody records.
- Provision for a laboratory sample custody log consisting of serially numbered standard lab-tracking report sheets.
- Specification of laboratory sample custody procedures for sample handling, storage, and dispersement for analysis.

H. CALIBRATION PROCEDURES AND FREQUENCY

For each critical measurement parameter, including all critical pollutant measurement systems, the following information should be included:

- Calibration procedures and information.
- Applicable standard operating procedure (SOP) or written description of the calibration procedure(s) to be used.
- Frequency planned for recalibration.
- Calibration standards to be used and their source(s), including traceability procedures and verification of purity procedures.

I. ANALYTICAL PROCEDURES

For each critical measurement parameter, the applicable standard operating procedure (SOP) should be referenced or a written description of the analytical procedure(s) to be used provided. Officially approved EPA procedures should be used when available and if applicable.

J. DATA REDUCTION, VALIDATION, AND REPORTING

For each critical measurement parameter, the following items should be briefly addressed:

- The data reduction scheme planned on collected data.
- All equations used to calculate the concentration or value of the measured parameter and the reporting units.
- The principal procedures that will be used to validate data integrity during collecting, transferring (if applicable), and reporting of data.
- The methods used to identify and treat outliers.
- The data flow or reporting scheme from collection of raw data through storage and validation of results. A flowchart will usually be needed.

• Key individuals who will handle the data in this reporting scheme. (If this has already been described under project organization and responsibilities, it need not be repeated here.)

K. INTERNAL QUALITY CONTROL CHECKS

This section presents guidelines for the number and frequency of replicate and spiked QC samples and calibration standards to be used, including concentration of surrogate or spike compounds to be added to designated QC samples. The QA plan should document the objectives for number, type, and frequency of QC samples.

Quality control samples are analyzed in the same way as field samples and interspersed with the field samples for analysis. The results of analyzing the QC samples are used to document the validity of data and to control the quality of data within predetermined tolerance limits. QC samples include blank samples, analytical replicates, and spiked samples.

Blank Samples

These samples are analyzed to assess possible contamination from the field and/or laboratory, so that corrective measures may be taken, if necessary. Blank samples include:

- <u>Field Blanks</u>--These blank samples are exposed to field and sampling conditions and analyzed to assess possible contamination from the field (a minimum of one for each type of sample to be collected and analyzed).
- <u>Method Blanks</u>--These blank samples are prepared in the laboratory and are analyzed to assess possible laboratory contamination (a minimum of one for each lot of samples analyzed).

• <u>Reagent and Solvent Blanks</u>--These blanks are prepared in the laboratory and analyzed to determine the background of each of the reagents or solvents used in an analysis (a minimum of one for each new lot number of solvent or reagent used).

Replicate Samples

These samples are analyzed in order to establish control and assess the precision of the analytical methodology. Replicate samples include:

- Field Replicates These samples are collected in the field and analyzed in order to assess the reproducibility of the sampling program (a minimum of one for each sampling event per sample type and measurement parameter).
- Laboratory Replicates These replicate samples are prepared in the laboratory in order to assess the reproducibility of the laboratory procedures used (a minimum of one for each lot of samples analyzed).

In addition, replicate analyses of specific samples may be undertaken by the analyst to check on the validity of any anomalous results. Such results could be the result of instrument or data system malfunction, operator error, laboratory contamination, etc. Repeat analyses of the sample in question and a previous "normal" sample will serve to indicate which of the possible problems is, in fact, present.

Spiked Samples

Samples may be spiked with one or more selected surrogate compounds prior to extraction and analysis. "Surrogate" compounds are defined as species that are chemically similar to the compounds being determined but that are not expected to be present in the samples (e.g., when GC/MS is the analytical method to be used, stable-isotope labelled analogs of the compounds sought are excellent surrogates). The data on surrogate concentrations are used to calculate surrogate compound recovery from each sample as one measure of the accuracy (bias) of the sample preparation and analysis procedures. To the extent that an analytical method (e.g., GC/MS) is consistent with use of surrogates, this procedure allows recovery to be estimated for <u>every</u> sample at trivial incremental cost to the testing. In some cases, e.g., trace metals, GC/ECD analyses, it may be difficult to select an appropriate surrogate compound that will mimic the behavior of the species sought but not lead to positive interferences in the analysis.

In addition to use of surrogate spiking (if possible), selected samples should be spiked with target analytes at a predetermined concentration level(s). This requires that each of the selected samples be carried through the entire sample preparation and analysis procedure twice, once unspiked and once spiked. Also, spiked blank samples for each measurement parameter should be analyzed in order to assess the inherent accuracy (bias) of the analytical method. To ensure that the per cent recovery of the spike can be determined with a reasonable degree of confidence, the spiking level should be at least 2-3 times the critical decision level (see Section II.A) and at least as high as the level expected in the unspiked sample. Depending on the concentration of analyte in the unspiked sample, these data may provide an estimate of the recovery of the species of interest from the sample matrix.For difficult sample matrices, multiple spiking levels may be used (method of standard additions).

L. PERFORMANCE AND SYSTEM AUDITS

Each QAPP should describe the internal performance evaluation and technical systems audits which are planned to monitor the capability and performance of the system(s) to be used for obtaining critical measurements.

The technical systems audit consists of an evaluation of all components of the critical measurement systems to determine their proper selection and use. This audit includes a careful evaluation of both field and laboratory quality control procedures. Systems audits are normally performed before or shortly after systems are operational; however, such audits should be performed on a

regularly scheduled basis during the lifetime of the project of continuing operation. The on-site technical systems audit may be a requirement for formal laboratory certification programs.

After systems are operational and generating data, performance evaluation audits are conducted periodically, as appropriate, to determine the bias of the critical measurement system (s) or component parts thereof. The plan should include a schedule for conducting performance audits for each critical measurement parameter, including a performance audit for all measurement systems, should the nature of the work require that a performance audit be done. As part of the performance audit process, laboratories may be required to participate in the analysis of performance evaluation samples.

M. PREVENTIVE MAINTENANCE

The QA project plan for a trial burn should itemize the procedures for . preventive maintenance that are relevant to the sampling analysis and efforts required in the project. For example, the following types of preventive maintenance items should be considered and addressed in the QA Project Plan:

- A schedule of important preventive maintenance tasks that must be carried out to minimize downtime of the critical measurement systems.
- A list of any critical spare parts that should be on hand to minimize downtime.

N. SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS

The data quality indicators (e.g., precision, bias, completeness, and method detection limit (MDL)) should be routinely assessed for all critical measurement parameters. Specific procedures to assess precision, bias, completeness, and MDL on a routine basis should be described in each QA Project Plan, as applicable to the measurement parameter and the system being measured. The QA Project Plan should also contain and discuss any statistical or mathematical methods used to evaluate the measurement data.

O. CORRECTIVE ACTION

Corrective action procedures include the following elements and must be described for each project:

- The predetermined limits for data acceptability beyond which corrective action is required.
- Procedures for corrective action.
- For each critical measurement system, identify the individual responsible for initiating the corrective action and also the individual responsible for approving the corrective action, if necessary.

Corrective actions may also be initiated as a result of other QA activities, including:

- Performance evaluation audits.
- Technical systems audits.
- Laboratory/interfield comparison studies.

A formal corrective action program is difficult to define for these QA activities in advance and may be defined as the need arises.

If long-term corrective action is necessary to eliminate the cause of nonconformance, the following closed-loop corrective action system may be used. As appropriate, the sample coordinator, analysis coordinator or the program manager, ensures that each of these steps is followed:

- 1. The problem is defined.
- 2. Responsibility for investigating the problem is assigned.

- 3. The cause of the problem is investigated and determined.
- 4. A corrective action to eliminate the problem is determined.
- 5. Responsibility for implementing the corrective action is assigned and accepted.
- 6. The effectiveness of the corrective action is established and the correction implemented.
- 7. The fact that the corrective action has eliminated the problem is verified and documented.

P. QUALITY ASSURANCE REPORTS TO MANAGEMENT

QA Project Plans should provide a mechanism for periodic reporting to Management on the performance of critical measurement systems and data quality. As a minimum, these reports should include:

- Changes to the QA Project Plan, if any.
- Limitations or constraints on the use or applicability of the data, if any.
- Quality programs, quality accomplishments, and status of corrective actions.
- Results of QA systems and/or performance evaluation audits.
- Assessments of data quality in terms of precision, bias, completeness, representativeness, and comparability.
- Quality-related training.

The final report for each project must include a separate QA section that documents the QA/QC activities that lend support to the credence of the data and the validity of the conclusions.

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APPENDIX A

Equipment and Procedures Used in Milwaukee Sampling Program^{*}

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<u>Overview</u>

During the twelve-month period beginning August 3, 1959, one collection a week was made from each sample area. The material picked up included all garbage, ashes, combustible and noncombustible rubbish produced by the respectence of the sample area.

A special City crew collected the material and separated it during collection into three categories: ashes, combustibles, and noncombustibles. Total weight, volume, density and moisture content determinations were made on each of the three categories. The percent that each component contributed to the total sample was then calculated. In addition to these physical tests, certain chemical analyses were made on the combustible and ash portions. The chemical tests included analyses for hydrogen, nitrogen, carbon, lipids, potassium, and phosphorus. Subsequent calculations for percent liquid content and C/N were also made. All tests were performed on each individual sample.

Equipment:

 A dump truck was outfitted with a specially constructed bed to provide separate compartments for the ash, noncombustibles, and combustibles portions of the combined refuse. An Allis-Chalmers forage harvester (shredder) complete with necessary appurtenances including a loading platform, a 25 horsepower electric motor, a discharge spout, and all required safety devices was used.

^{*}Adapted from Reference 16.

- 2. Six 1 1/2 cubic yard steel bins complete with castors and a removable end.
- 3. A battery-operated fork lift.
- A 1000 pound net-capacity platform scale rebuilt to provide an accuracy of 0.1 pounds.
- 6. Three 55 gallon drums.
- 7. A gram laboratory scale.
- .8. A forced air drying oven.
- 9. A Wiley Mill.
- 10. A sand splitter.
- 11. Eleven drying pans.
- 12. A hand tamp.
- 13. A Parr oxygen-bomb calorimeter.
- 14. Air-tight sample cans.

Sampling Procedure:

- Collected refuse from appropriate sampling area. Separated material during collection into three separate components, ashes, noncombustibles, and combustibles.
- 2. Trucked material to central testing point. A corner of one of the cities incinerator buildings was used as this location.

- 3. Broke open the combustible packages and removed the unburnable items. All combustible material was placed in the proper movable bin and all non-combustibles were thrown into their respective truck compartment.
- 4. Processing of combustibles.
 - All movable bins containing combustible refuse were weighed and volume measurements were taken prior to running the material through the shredder.
 - b. The material was processed through the shredder four times. Two movable bins were placed under the discharge spout to halve the material each time it went through the machine. By halving the refuse four times the samples was reduced to one-sixteenth of its original size.
 - c. The remaining material was quartered by a shovel, retaining about enough to fill a gallon container.
 - d. Weight measurements were taken of all the combustible refuse prior to disposal to determine the moisture lost during the shredding operation.
 - e. The sample was transferred from the gallon container to a drying pan and placed in the oven.
 - f. Weight measurements pertinent to moisture content calculations were recorded.
 - g. A sand splitter was used to quarter the sample after it was processed through a Wiley Mill where it was reduced to a maximum size of one millimeter. The size of the final quarter was about 100 grams.
 - h. Fifty grams of this were sent for certain chemical analyses and the other 50 grams were returned to the drying oven. It was necessary to

redry the material to eliminate moisture added during the grinding process.

- i. The calorimeter test was performed and the information recorded.
- 5. Processing of Noncombustibles
 - a. Noncombustibles were placed in the proper metal bins, weighed, and the volume determined.
 - b. This material was stored in an empty bin and separated periodically into three separate components - cans, bottles. and miscellaneous noncombustibles. Data were recorded to enable calculation of the percent of total weight and volume represented by each component. The material was then thrown away.
 - c. Once a week a grab sample was taken from the material produced by one classification. This sample was taken from a different area each week, thereby each area was tested once every 10 weeks.
 - d. This sample was placed in a drying pan and then put into the oven.
 - e. Weight measurements pertinent to moisture content calculations were recorded.
- 6. Processing of Ashes
 - a. Ashes were placed in the proper bin, weighed and volume measurements were taken.
 - The ashes were quartered by shovel, retaining approximately a pint of material.
 - c. The pint sample was placed in an air-tight container and stored until all such ash samples for the week were placed therein.

- d. At the end of the week the sample container was emptied and the lumps were reduced with a hand tamp.
- e. The material was quartered with the sand splitter, retaining about 2 pounds.
- f. A moisture content was made by use of the drying oven and the pertinent weight measurements were recorded.
- g. The dried ash was reduced to a weight of about 400 grams with the sand splitter.
- h. Half of this was sent to Purdue for further analyses and half was returned to the drying oven.
- i. After a second drying period, a calorimeter test was performed.

APPENDIX B

ASME-EPA DRAFT ENVIRONMENTAL STANDARDS PROTOCOLS FOR SAMPLING AND ANALYSIS OF PCDD/PCDF _____SW COMBUSTOR EFFLUENTS

BRAFT

STANDARD PROTOCOL FOR RECORDING FURNACE OPERATING DATA DURING SAMPLING FOR TRACE EMISSIONS OF CHLORINATED ORGANIC CONFORMS IN REMART FROM SOLID MARTE COMPOSITION PLANTS

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The information on furnace operation which should be gathered during to for trace emissions of chlorinated organic compounds is summarized in following data form. It will be noted that actual values while sampling underway in the form of copies of actual strip charts is the preferable m of reporting operating information.

Where design information is requested, it should be characteristic of mal operation at the time of year when sampling is actually being done. parison between the expected and actual values during sampling is a guide to whether the system was operating normally while it use being sampled. the comparison suggests the system may not have been operating normally ing sampling, it may be difficult to utilized the data.

It will also be noted that some of the required information is to be ilected as nearly continuously as possible during sampling. This is so as permit detection of changes, intended and inedvertent, which may have curred during sampling. The occurrence or absence of any such changes is a iter in interpreting the results of the sampling.

Recording the essential information shall begin at least three hours fore sampling is begun and be continued for at least an hour after sampling terminated.

The following form is intended to accompany reports on source sampling refuse-to-energy facilities.

CKCROUND INFORMATION

- . None and address of the facility:
- ". Name and telephone number of plant general manager or other person to contact regarding emission sampling program:
 - _____
-). Name and telephone number of emission sampling team manager:

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- . Name and talephone number of person responsible for laboratory analysis of samplas:
- 5. Name and telephone number of meteorological monitoring station servicing the locality of the plant:

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- 6. Designation of the combustion train actually sampled:
- 7. Date of emission sampling:
 - Time when compling started:
 - Time when sampling terminated:

FACILITY DESCRIPTION

- B. Type of refuse processing system (e.g., mass-burn, refuse derived fuel):
- 9. Describe refuse preparation method, if appropriate:
- 10. Type of furnace (a.g., waterwall, refractory-wall, hybrid);

Is suxiliary fuel regularly fired? If so, what fuel?

- 11. Design heat release rate (MBtu/hr):
- 12, Basign steam production rate and conditions: _____ lbs/hr @
 - "F, _____ polg, and (if saturated) _____ I quality.
- 13. Feed properties for which unit was designed:
 - Range of heating values _____ to ____ Btu/1b
 - Range of moleture contents _____ to _____ wt I
 - Lange of ash contents _____ to _____ wt I
- 14. Please provide a cross-sectional diagram of the facility, preferably to scale, showing the spatial relationship between the major elements of the

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and residue removal system; shape of the furnace; primary and secondary combustion air ports; the boiler and its flue gas passages; soot blowers; major heat transfer surfaces; aconomizer; sir preheater (if appropriate); air pollution control system; induced draft fan; and stack. Indicate locations of temperature and pressure detectors also.

- 5. Description of the grate system:
 - Supplier:
 - Type (e.g., reciprocating, roller, traveling, rotary):
 - Number of step sections (if appropriate):
 - Grote area (ft²) (or equivalent):
- 6. Description of the boller:
 - Supplier:
 - Furnace volume (ft³):
 - Firebox dimensions (ft): L_____W
 - Kind of soot blowers:
 - Soot blowing schedule (approximate times):
- 17. Type of combustion (e.g., excess sir, starved sir):
- 18. Overfire and underfire air distribution:
 - Describe design and type of all air ports:
 - Describe how total combustion six and six distribution is controlled
 - Verify that air distribution systems are operating as designed:

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Type of draft:		
Now is draft regulated:		
Description of solid waste feeding and stoking system:		
- New is feeding take controlled?		
- Frequency and length of feed ran strake:		
Describe the overall plant control system logic (e.g., what measurements are used as the basis for controlling firing rate?):		
Stock height (ft):		
Stack diameter at top (ft):		
Type of sir pollution control system:		
If electrostatic precipitator:		
- Specific collection area (ft ² /1000 ACPM):		
- Design temperature at inlet (*7):		
- Number of independent hus sections:		
- Which independent bus sections were in service during emission		
esepling?		
- Design particulate loading at inlat: grains/docf		
et outlet: graine/docf		
Rapping frequency:		
If fabric filters		
- Fabric type Weight Weave Finish		
- Bag closning method and frequency:		

- Air-to-cloth ratio (ACFH/ft²):
- Besign pressure drop scross bags (in., W.G.):
- Design gas temperature at inlet ("F):
- Total number of bags:

- 3 -

- 4 -

DKAI			DRAFT		
- Actual number of bags in service at time of sampling:					Construction debris
Which flue gas co monitor:	eponente are regula	arly measured?	Indicate location of	125	
	last rumnt <u>Hodel</u>	Location	Unit Served by This Honitor	ы .	Barometric pressure at start of test (in. Hg):
Oxygen				33.	Relative humidity at start of tests
Carbon Monoxide			<u> </u>	34.	Temperature of combustion air after any air heaters ("F):
Nydrocs rbons			•		Underfire Overfire
Other (Specify)			······	35.	Temestatures of combustion sir at inlate to forced draft fam (*F):
Le flue gas opac	ity regularly monito	orod1			
Description of ex	xisting temperature	monitors:			
Locations:				36.	Combustion air flow rates (ACPH preferable) or pressure if flow is not available — include strip chart record if available or record masure— ments on indicators at 13 minute intervals at a minimum:
Type of temperate	ure detector(s): _				Nadarfira (Partira
Henufacturer and	model mumber:				
Date of most recent calibration:		37.	Solid usste fifing rate over test period (attach strip chart record if available; if not available, give total quantity of waste fired over sampling period and maximum and minimum firing rates):		
Time constants o	f in-plant measurin	g devices (pres	ture gauges, rive gas		
monitors, thermo	couples):				indicate method of determining fiting rate fload cell, cross count, ran
What is the volu	ntery shutdown sche	dule for routim	e maintenance of the		cycle, other (specify)):
process train be	ing sampled?				<u> </u>
Dates of the most recent shutdown for routine maintenance and type of		38.	Auxiliary fuel firing rate over test period (attach strip chart record if available; if not available, give total quantity of weste fired over		
maintenance peri	lormd?	<u></u>			sampling period and maximum and minimum firing rates):
Types of refuse of this information	normally accepted ((108):	at the facility	(please indicate source	19.	If anot blowing occurs during sampling pariod, give times and duration:
		Approximat	e Percentage		
Residentia	1	· · · · · · · · · · · · · · · · ·		40.	furnace temperatures:
Connercial	/institutional				- Design temperatures and locations:F,
Industrial					the second state for the second se

Attach summary record of furnace temperature measurements during -

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- Attach strip chart record of temperature at top of furnace, in front of across tubes - over the sampling period (if records are available for more than one in-plant thermocouple, include them and specify their locations)
- 41. Flue gas analysis:

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- Actach strip chart records for concentrations of the following flue gas constituents, measured over the sampling period: carbon monomide, carbon diomide, enygon, mitrogen emide, sulfur diomide, total hydrocarbons, water waper, and flue gas flow
- Attach strip chart record for in-stack opacity over the sampling
- 42. Include a copy of the operator's log for the period of the test.

SAMPLING FOR THE DETERMINATION OF CHLORINATED Deganic conpounds in Stack emissions

PRINCIPLE AND APPLICABILITY

- 1.1 <u>Frinciple</u>: Stack gamma that may contain chlorinated organic compounds are withdrawn from the stack using a sampling train. The analyte is collected in the sampling train. The compounds of interest are determined by solvent extraction followed by gam chromatography/mass apectroscopy (GC/MS).
- 1.2 Applicability: This method is applicable for the detereinstion of chlorinsted ergenic compounds in stack enissions. The sampling train is as designed that only the total amount of each chlorinated erganic compound in the stack entesions may be determined. To date, so studies have been performed to demonstrate that the particulate and/or gassous chlorinated organic compounds collected in asperate parts of the sampling train accurately describes the actual partition of each in the stack emissions. If separate parts of the sampling train are saalyzed separscaly, the data should be included and so noted as in Section 2 below. The sampling shall be conducted by computent personnel experienced with this test procedure and cognizant of intricacies of the operation of the prescribed sampling train and constraints of the analytical techniques for chlorinated organic cospounds, especially PCDDs and PCDFs.

Note: This method assumes that all of the compounds of interest are collected either on the RAD-2 resis or in upstream sampling train components. Since the method at the present time has not been validated in the presence of all the other components present (BCl, high organic load) in the stock emission, it is recommended that appropriate quality control (QC) stops be coplayed until such validation has been completed. These QC stops may include the use of a backup resin trap or the addition of a representative labeled standard (distinguishable from the internal standard used for quantitation) to the filter and/or the RAD-2 in the field prior to the start of sampling. These stage will provide information on possible breakthrough of the compounds of interest.

. REPORTABILITY

Recognizing that modification of the method may be required for specific applications, the final report of a test where changes are made shall include: (i) the exact modification; (2) the rationale for the modification; and (3) an estimate of the effect the modification will produce on the data-

3. RANGE OF MINIMUM DETECTABLE STACE CAS CONCENTRATION

The range of the analytical method may be expanded considerably through concentration and/or dilution. The total method consitivity is also highly dependent on the volume of stack gas compled and the detection limit of the analytical finish. The user shall determine for their system the minimum detectable stack gas concentration for the chlorinated organic compounds of interest. The minimum detectable stack gas concentration should generally be in the ag/m² (nanogram/cubic meter) or lower range.

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4. INTERFERENCES

Organic compounds other than the compounds of interast may interfore with the analysis. Appropriate sample class-up stops shall be performed. Through all stages of sample handling and analysis, care should be taken to avoid contact of samples and extracts with synthetic organic meterials other than polytetrafluerathylane (TFE®). Adhesives should not be used to hold TFE® liners on 31ds (but, 1f necessary, appropriate blanks must be run) and lubricating and saming grasses must not be used on the sampling train.

5. PRECISION AND ACCURACT

Precision and accuracy measurements have not yet been made on PCDD and PCDP using this method. These measurements are meeded. Revever, recovery efficiencies for source semples spiked with compounds have ranged from 70 to 1202.¹,³

6. SAMPLING RUNS, TIME, AND VOLUME

6.1 <u>Sampling Runs</u>: The number of sampling runs must be sufficient to provide sinimal statistical data and in no case shall be leas than three (3).

6.2 <u>Sampling Time:</u> The sampling time must be of sufficient length to provide coverage of the sverage operating conditions of the source. Novever, this shall not be less than three hours (3).

6.3 <u>Sample Volume</u>: The sampling volume must be sufficient to provide the required amount of analyte to meet both the MDL of the analytical finish and the allowable stack emissions. It may be calculated using the following formula:

Sample Volume ~ A
$$\frac{100}{B} \times \frac{100}{C} \times \frac{1}{D}$$

- A The analytical MDL in ng
- B = Percent (X) of the sample required per analytical finish run



 $DRAFT = The sample recovery (X) DRAFT = The allovable stack emissions (ng/m³) = The allovable stack emissions (ng/m³) = Example: A = 0.050 ng; B = 10X; C = 50X; and D = 1 ng/m³ = 8V = 0.05 x \frac{100}{10} x \frac{100}{50} x \frac{1}{1} = 1m³$

7. APPARATUS

Sampling Train: The train consists of mottle, probe, heated particulate filter, and perbeat module followed by four impingers (fig. 1). Provision is made for the addition of (1) a cyclone in the heated filter box when testing sources emitting high concentrations of particulate matter, (2) a large water trap between the heated filter and the corbent module for stock gases with high moisture content, and (3) additional impingers following the sorbent module. If one of the options is utilized, the option used shall be detailed in the teport. The train may be constructad by adaption of an EPA Method 3 train. Becriptions of the sampling train components are contained in the following dections.

7.1.1 Mozzle

The norrie shall be made to the specifications of EPA Hethod 5. The norrie may be made of mickel plated stainless steel, quarts, or borosilicate glass.

7.1.2 Troba

The probe shall be lined or usde of TPE®, berosilicate, or quarts glass. The liner or probe extends past the retaining sut into the stack. A temperature controlled jacket provides protection of the liner or probe. The liner or probe shall be equipped with a connecting fitting that is capable of forming a lask-free, vacuum-tight connection without scaling grasses.

7.1.3 Sample Transfer Lines (optional)

The sample transfer lines, if needed, shall be heat traced, heavy walled TFE® (1.3 cm (1/2 in.) 0.D. x 0.3 cm (1/8 in.) well) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using scaling greases. The line should be as short as possible and must be maintained at 120°C.

7.1.4 Filter Holder

Borosilicate glass, with a glass frit filter support and a glass-to-glass each or TFE[®] gasket. A rubber gasket shall not be used. The holder design shall provide a positive seal against leskage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).



Impingers are of the Medified Greenberg-Smith Type

Impingers 1 and 2 Centain 100 ml Water 🐾

Impinger 3 Empty

Impinger 4 Contains 200-300 Grama Silics Gel

Impinger 1 is the Henne-Aineed Back-Up to the Reein Cartridge

(T) - Thermecouple lecation

Fig. 1. Modified EPA Method 5 Train for Organics Sampling Source: Methods Hanual Sampling and Analysis Procedures for Assessing Organics Emissi for Source: Assessing Organics Sources in Exposure Evaluation Division Studies,

7.1.5 Cyclone in Filter Box (optional)

The cyclone shall be constructed of bereallicate glass with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases.

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7.1.6 Pilter Meating System

The heating system must be capable of maintaining a temperature around the filter holder (and c; ...one, if used) during sampling of 120±14°C (248±25°F). A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed as that the temperature around the filter holder can be regulated and menicored during sampling.

7.1.7 Bolid Sorbent Hodule

Amberlite $XAD-2^{\circ}$ rasin (XAD-2), confined in a trap, shall be used as the serbent. The serbent module shall be made of glass with connecting fittings that are able to form losk-free, vacuumtight seals without use of sealent groodes (Figs. 2 and 3). The IAD-2 trap must be in a vertical position. It is preceded by a cofi-type condenser, also oriented vertically, with circulating cold water. Gas entering the serbent module must be maintained at $(20^{\circ}C \ (68^{\circ}P)$. Gas temperature shall be senitored by a thermocouple placed either at the inlet or axis of the serbent trap. The serbent bed must be firmly packed and secured in place to prevent settling or channeling during seeple collection. Ground glass cops (or equivalent) must be provided to seal the serbent modules must be maintained in the vertical position during sempling.

7.1.8 lapingers

Four or more impingers with connecting fittings able to form look-free, vacuum-tight scale without scalant greases when conmected together, shall be used. All impingers are of the Greenburg-Smith design modified by replacing the tip with 1.3 cm (1/2 in.) ID glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flack.

7.1.9 Hetering System

The metering system shall consist of a vacuum gauge, a leskfree pump, thermometers capable of measuring temperature to within 3°C (-5°F), a dry gas meter with 2 percent accuracy at the required compling rate, and related equipment, or equivalent.

7.1.10 Barometer

Mercury, ameroid, or other barometers capable of measuring atmospheric pressure to within 2.5 Mg (0.1 in. Mg) shall be used. :





Direction

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7.2 Sample Recovery, Supplies, and Equipment

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7.2.1 Ground Glass Cape or Mexane Rinsed Aluminum Poll

To cap off adsorbant tube and the other papple-exposed portions of the train. If TPR® acrow connections are used, then TPR® acrew caps shall be used.

7.2.2 Tefles FEP® Wash Bottle

Three 500 ml, Malgune No. 0023A59, or equivalent.

7.2.3 Probe and Transfer Line Brunh

Inert bristle brush with stainless steel rod-handle of sufficient length that is compatible with the liner or probe and treasfer line.

7.2.4 Filter Storage Containers

Sealed filter holder or procleaned, wide-mouth amber glass containers with TPE®-lined screw cape or wrapped in boxane tineed aluminum foil.

7.2.5 Balance

Triple beam, Ohaus model 7505, or equivalent.

7.2.6 Aluminum Fell

Reavy duty, hezono-rinoed.

7.2.7 Procleaned Netal Can

To recover used silics gel.

7.2.8 Precleaned Graduated Cylinder, s.g., 250 ml

250 ml, with 2 ml graduations, berosilicate glass.

7.2.9 Liquid Sample Storage Containers

Precleaned amber glass bottles or clear glass bottles wrappe. in apaqua material, I L, with IFE®-lised ocrew caps.

- 8. REAGENTS
- 6.1 Seapling
- 8.1.1 Filter -- Fiberglass Reave-Angel 934 AB or Equivalent

Prior to use in the field, each lot of filters shall be sublected to precleaning and a quality control (QC) contacination check to confirm that there are no contaminants present that will

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terfore with the endlysis of analyte at the target detection mits.

If performed, filter precisening shall consist of Somhlet traction, in batches not to exceed 50 filters, with the solint(s) to be applied to the field samples. As a QC check, the itracting solvent(s) shall be subjected to the same concentraon, cleanup and analysis procedures to be used for the field imples. The background or blank value observed shall be coninted to a per filter basis and shall be corrected for any ifferences in concentration factor between the QC check (GF_{QC}) id the actual sample analysis procedure (GF_{ac}).

Blank value per filter - Apparent up of analyte x
$$\frac{CP_{a}}{CP_{aC}}$$

where:

C7 - Initial volume of extracting solvent Final Volume of concentrated extract

The quantitative criterion for acceptable filter quality will epend on the detection limit criteria established for the field ampling and analysis program. Filters that give a background or lank signal per filter greater than or equal to the target detecion limit for the analyta(s) of concern shall be rejected for ield use. Note that acceptance criteris for filter cleanliness apands not only on the inherent detection limit of the analysis withod but also on the expected field sample volume and on the isoired limit of detection in the sampled stream.

If the filters do not pass the QC check, they shall be reintracted and the solvent extracts re-analyzed until an acceptably low background level is schleved.

1.1.2 Amberlite XAD-2 Resin

The cleanup procedure may be carried out in a giant Somblet SELENCTOF, which will contain enough Amberlite XAD-2[®] reain (XAD-2) for several sampling traps. An all glass thinkle 35-90 mm DD x 150 mm deep (top to frit) containing an extra coarse frit is used for extraction of XAD-2. The frit is receased 10-15 mm above is cronslated ring at the bottom of the thinkle to facilitate drainage. The IAD-2 must be carefully retained in the extractor cup with a glass wool plug and stainless steal acrean since ft floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Frocedute
---------	-----------

initial rinse with I L H₂O for I cycle,

Water	Extract with N ₂ 0 for 8 hr
Nothyl sleohol	Estract for 22 hr
Nothylana chlorida	Extract for 22 hr
Hezana	Estract for 22 br

The IAD-2 must be dried by one of the following techniques.

(a) After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proven to be the fastest and most reliable drying method.

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A simple column with suitable retainers as shown in Fig. 4 will serve as a satisfactory column. A 10.2 cm (4 in.) diameter Pyrem pipe 0.6 m (2 ft. long) will hold all of the IAD-2 from the Somhlet extractor, with sufficient space for fluidining the bad while generating a minimum IAD-2 load at the exit of the column.

The gas used to remove the solvent is the key to preserving the classifiers of the XAD-2. Liquid sitrogen from a regular connercial liquid mitrogen cylinder has routinely proven to be a reliable source of large volumes of gas free from organic contamimants. The liquid mitrogen cylinder is connected to the column by a length of preclassed 0.95 cm (3/8 is.) copper tubing, coiled to pass through a best source. As mitrogen is bled from the cylinder, it is veperised in the hest source and passes through the column. A convenient best source is a water bath basted from a steam line. The final mitrogen temperature should only be warm to the touch and not over 40°C. Experience has shown that about 500 g of XAD-2 may be dried evernight consuming a full 160°L cylinder of liquid mitrogen.

As a second choice, high purity tank mitrogen may be used to dry the XAD-2. The high purity mitrogen must first be passed through a bod of activated charcosl approximately 150 mL is volume. With either type of drying method, the rate of flow should gently sgitate the bod. Excensive fluidation may cause the particles to break up.

(b) As an alternate, if the nitrogen process is not available, the RAD-2 may be dried in a vacuum oven, if the temperature never exceeds 20°C.

The IAD-2, even if purchased clean, must be checked for both methylung chloride and hazane residues, plus normal blanks before use.

(c) Storage of Clean XAD-2: XAD-2 cleaned and dried as prescribed above is suitable for immediate use in the field, provided it passes the QC contamination check described in (d), below. Nowover. precisioned dry XAD-2 may develop unacceptable levels of

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Fig. 4 XAD-2 Fluidized-Bod Drying Apparatus

If precisened XAD-2 is not to be used innediately, it shall be stored under distilled-in-glass methanol. No more than two wacks prior to initiation of field sampling, the excess methanol shall be decented; the XAD-2 shall be washed with a small volume of methylene chloride and dried with clean sitragen as described in (b) above. An aliquet shall then be taken for the QC contamination check described in (d), below.

If the stored IAD-2 fails the QC check, it may be reclammed by repeating the final two steps of the extraction sequence above: sequential methylams chloride and herene extraction. The QC contamination check shall be repeated after the IAD-2 is reclamad and dried.

(d) QC Contamination Check: The IAD-2, whether purchased, "precleased", or cleased as described above, shall be subjected to a QC check to confirm the absence of any contaminants that might cause interferences in the subsequent analysis of field samples. An aliquet of IAD-2, equivalent in size to one field sampling tube charge, shall be taken to characterize a single batch of IAD-2.

The IAD-2 aliquet shall be subjected to the same extraction, concentration, cleanup, and analytical procedure(a) as is (are) to be applied to the field samples. The quantitative criteris for acceptable IAD-2 quality '11 depend on the detection limit criteris established for the field sampling and analysis program. IAD-2 which yields a background or blank signal greater than or equal to that corresponding to one-half the MDL for the analyte(s) of concern shall be rejected for field use. Mote that the acceptence limit for IAD-2 cleanliness depends not only on the inherent detection limit of the analytical method but also on the expected field ample volume and on the desired limit of detection in the sampled stream.

8.1.3 Glass Neel

Cleaned by therough rinsing, 1.e., sequential innersion in three aliquets of hexane, dried in a 110°C oven, and stored in a became-washed glass jar with TPE⁰-lined acrew cap.

8.1.4 Mater

Defenized, then glass-distilled, and stored is hexane-rinsed glass contoiners with TPE®-lined screw caps.

8.1.5 Silica Gel

Indicating type, 6-16 mesh. If previously used, dry at 175450 for 2 hr. New silica gel may be used as received.

8.1.6 Crushed Ice

Place crushed ice in the water both around the impingers during sampling.

SAMPLE RECOVERY REAGENTS

Acetess

Pasticide quality, Burdick and Jackson "Distilled in Glass" or ivalant, stored in original containers. A blank must be eand by the analytical detection method.

Hezene

Peeticide quality, Burdick and Jackson "Distilled in Glass" or livelest, stored in original containers. A blank must be 'sened by the analytical detection method.

, PROCEDURE

Caution: Sections 10.1.1.2 and 10.1.1.3 shall be done in the laboratory.

.1 Sampling

.1.1 Pretest Preparation

All train components shall be usintsined and calibrated cording to the procedure described in APTD-0576 unless otherwise scified borein.

Weigh several 200 to 300 g portions of silics gel in air-tight ntainers to the nestest 0.5 g. Becord the total weight of the lice gel plus container, on each container. As an alternative, a silice gel may be weighed directly in its impinger or sampling lder just prior to train assembly.

Check filters visually spainst light for irregularities and ave or pinholo looks. Pack the filters flat in a precisioned uses container or wrapped became-rinsed sluminum foll.

1.1.1.1 Preliminary Determinations

Select the sampling site and the minimum number of sampling bints according to EPA Hathod 1. Determine the stack pressure, imperature, and the range of velocity boads using EPA Method 2; t is recommended that a leak-check of the pitot lines (see EPA sthod 2, Sec. 3.1) be performed. Determine the molature content sing EPA Approximation Method 4 or its alternatives for the urpose of making isokimetic sampling rate-settings. Determine he stack gas dry molecular weight, as described in EPA Method 2, ec. 3.6; if integrated EPA Method 3 sampling is used for molecuar weight determination, the integrated bag sample shall be taken isultaneously with, and for the same total length of time as, the PA Method 4 sampling.



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Select a norrie size based on the range of velocity heads, such that it is not necessary to change the nerrie size in order to maintain isokinetic sampling rates. Buring the run, do not change the nerrie size. Bnoure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of EPA Method 2).

Select a suitable probe length such that all traverse points can be employ. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probas.

Solect 4 total compling time greater than or equal to the minimum total compling time specified in the test procedures for the specific industry such that (1) the compling time per point is not lass than 2 min., and (2) the comple volume taken (corrected to standard conditions) will exceed the required minimum total gas comple volume determined in Section 6.3. The latter is based on an approximate average compling rate.

It is recommended that the number of minutes campled at each point be an integer of an integer plus one-half minute, in order to avoid time-keeping errors.

10.1.1.2 <u>Cleaning Classware</u>

All glass parts of the train upstress of and including the sorbest module and the first impinger should be closed as described in Section 3A of the 1980 issue of "Henuel of Analytical Methode for the Analysis of Pesticides in Busans and Environmental Samples." Special care should be devoted to the removal of restdual silicone grasse scalasts on ground glass connections of used glassware. These grasse residues should be removed by seeking everal hours is a chronic acid closening solution prior to routine classing as described above.

10.1.1.3 Auberlite XAD-2 Rosin Trap

Use a sufficient smount (at least 30 gas or 5 gas/m³ of stack gas to be sampled) of cleaned RAD-2 to fill completely the glass extent trap which has been thoroughly cleaned as prescribed and rinsed with bexame. Follow the RAD-2 with bexame-rinsed glass wool and cap both ends. These caps should not be removed until the trap is fitted into the train. See Fig. 1 for details.

The dimensions and XAD-2 capacity of the sorbent trap, and the volume of gas to be sampled, should be varied as necessary to ensure efficient collection of the species of interest. Some illustrative data are presented in Table 1.

10.1.2 Preparation of Collection Train

During preparation and essembly of the sampling train, keep all train openings where contamination can enter covered until
	SARLE SIZE	ATTA YOU ATTA O	DIGALISON FOR	TINUL POLICY	w prstars		•	
			Cherge		Max. Som	Le Sise (cient Cep	(]]]]]]]]]]]]]]]]]]]	
Trap	Depth	ne (me) Djameter	ef X-D-2 Resin (g)	riev Equivalent to 43 cm/sec	Octane .	bensene	Pheao I	
EA 55	8		130	165 Len (5.9 efm)	150	3.0	240	
קו	R	54.	9	40 Lee (1.5 efe)	\$\$	0.9	2	
Battalle	20	R	6	18 Lpm (0.65 cfm)	1	4 . 0	2	

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just prior to assembly or watil sampling is about to begin. Contion: Do not use scalant greases in assembling the train.

Place opproximately 100 gms of water in each of the first two impingers with a graduated cylinder, and leave the third impinger supty. Place approximately 200 to 300 g or more, if macessary, of silics got in the last impinger. Meigh each impinger (stem included) and record the weights on the inpingers and on the data sheet.

Assemble the train as shown in Fig. 1.

Place crushed ice in the water bath around the impingers.

10.1.3 Leak Check Procedures

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10.1.3.1 Initial Leak Check

The train, including the probe, will be leak checked prior to being insurted into the stack after the ampling train has been assoubled. Turn on and set (if applicable) the heating/cooling system(s) to cool the sample gas yet reasin at a temperature sufficient to avoid condensation in the probe and connecting line to the first impinger (approximately 120°C). Allow time for the temperature to stabilize. Leak check the train at the sampling site by plugging the norrie with a TPE® plug and pulling a 380 mm Bg (12 in. Ag) vacuum. A leakage, rate in excees of 4% of the average compling rate or 0.0037 m²/min (0.02 cfm) whichever is less, is unacceptable. Sampling must cease if pressure during saupling exceeds the lesk check pressure.

The following leak_check instruction for the sampling train described in APTD-0576" and APTD-0581" may be helpful. Start the pump with bypass valve fully open and coarse adjust valve conplately closed. Partially open the coarse adjust valve and elowly close the bypass valve until 380 mm Mg (12 in. Mg) vacuum is reached. Do not reverse the direction of the bypass value. This will cause water to back up into the probe. If 340 an Ag (12 in. Ng) is exceeded during the test, either lesk check at this higher vacuum or and the leak check as described below and start the test

When the lesk check is completed, first slowly remove the TPE® plug from the inlet to the probe then innediately turn off the vacuum pump. This prevents the vater in the impingers from being farcad backward into the probe.

10.1.3.2 Leak Checks During a Test

A lask check shall be performed before and after a change of port during a test. A leak check shall be performed before and after a component (e.g., filter or optional water knockout trap) is changed during a test.

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Such leak chocks shall be performed according to the procedure iven in Section 10.1.3.1 of this method except that it shall be prformed at a vacuum equal to ar greater than the highest value performed at a vacuum equal to ar greater than the highest value performed at a vacuum equal to ar greater than the highest value performed at a vacuum equal to ar greater than the highest value performed at a vacuum equal to ar greater than the test. If the leakage rate is pund to be no greater than 0.00057 m /min (0.02 ft /min) or 4% of the average sampling rate (whichever is smaller) the results are comptable. If, however, a higher leakage rate is observed, the peter shall either: (1) record the leakage rate and then correct to volume of gas sampled since the last leak check as shown in petion 10.1.3.4 of this method, or (2) weld the test.

3.1.3.3 Post-Test Leak Check

A leak check is mandatory at the end of a test. This leak heck shall be performed in accordance with the procedure given in action 10.1.3.1 except that it shall be conducted at a vacuum qual to or greater than the highest value recorded during the get. If the leakage rate is found to be no greater than 0.00057 "/min (0.02 ft /min) or 4% of the average sampling rate (whichver is smaller), the results are acceptable. If, however, a igher leakage rate is observed, the tester shall eithert (i) ecord the leakage rate and correct the volume as ges sampled ince the leak the test.

0.1.3.4 Correcting for Exceptive Leekage Rates

The equation given in Section 11.3 of this method for calcuating V (atd), the corrected volume of gas sampled, can be used a written unless the leakage rate observed during any leak check after the start of a test exceeded L, the maximum acceptable leakage rate (see definitions below). If an observed leakage rate accede L, then replace V in the equation in Section 11.3 with the following expression:

$$\{V_{\mathbf{n}} = \mathbf{L}^{\mathbf{n}} (L_{\mathbf{i}} - L_{\mathbf{n}}) \quad \boldsymbol{\theta}_{\mathbf{i}} = L_{\mathbf{p}} - L_{\mathbf{n}} (\boldsymbol{\theta}_{\mathbf{p}})$$

wherei

- V = Volume of gas sampled as measured by the dry gas m meter (decf).
- L Harimum acceptable leakage rate equal to 0.00057 m³/mim. (0.02 ft²/mim) or 42 of the average sampling rate, whichever is smaller.
- L Leakage rate observed during the post-test leak check, p = /min (ft /min).
- L Leskage rate observed during the lesk check performed prior to the "i th" lesk check (i = 1,2,3...m), m/min (++-)(=tn).

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- Sampling time interval between two successive leak checks beginning with the interval between the first and second leak checks, min.
- - Sampling time interval between the last (n th) lask check p and the end of the test, min.

Substitute only for these laskages $(L_{\underline{1}} \text{ or } L_{\underline{2}})$ which exceeded $L_{\underline{3}}$.

10.1.3.5 Train Operation

Buring the sampling run, a compling rate within 10% of the selected compling rate shall be maintained. Data will be comeidered acceptable if readings are recorded at least every 3 min. and not more than 10% of the point readings are in encase of +10% and the average of the point readings is within +10%. Buring the run, if it becomes mecasary to change any system component in any part of the train, a look check must be performed prior to restarting.

For each run, record the data required on the data sheets. An example is shown in Fig. 4. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment and when sampling is helted.

To begin sampling, remove the norrie cap, verify (if applicable) that the probe and sorbent module temperature control systems are working and at temperature and that the probe is properly positioned. Position the probe at the sampling point. Immediately start the pump and adjust the flow rate.

If the stock is under eignificant sub-ambient pressure (height of impinger stom), take care to close the coarse adjust valve before inserting the probe into the stock to avoid water backing into the probe. If meassary, the pump may be turned on with the coarse adjust valve closed.

Buring the test run, make periodic adjustments to keep the probe temperature at the proper value. Add more ice and, if mecausary, solt to the ice bath. Also, periodically check the level and zero of the manueter and maintain the temperature of sorbant module at or less than 20°C but above 0°C.

If the pressure drop across the train becomes high enough to make the sampling rate difficult to maintain, the test run shall be terminated unless the replacing of the filter corrects the problem. If the filter is replaced, a lask check shall be performed.

At the end of the sample run, turn off the pump, remove the probe and norrie from the stack, and record the final dry gas meter reading. Perform the post test leak check.*

	MPINGER TEMPERATURE				-						Ī
100 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	BAMPLE BOX	XAD-2									-
1 101 HUM 1 101 HUM	A CUM		T								-
	A METER AATUME										
	DRY GA TEMPE M.ET										-
2 2011 7 1.470 Ar Bete Merice	STACK TEMPERATURE (19).**										
	REAL PLAN	ACTUAL									•
ATIC 87 T 800 874 800 874	0001CE 11 D#1510 (AH), N	DESMED									•
Benth	VELOCITY NEAD (As,), N	Ş .									
	PIADERS 2, 17 a	ACTUAL									
	GAS WETER	024230									
Provide the second seco	CLOCK TANE (24 M (24 M (24 M (24 M)										
	TRAVER TRAVE										

10.2 Sample Recovery

Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period.

When the probe can be safety handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the trols and close off both onds with hexane-rinsed aluminum foll. Soal off the inlet to the train with a ground glass cap or beneve-tinsed eluminum foil.

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Transfer the probe and impinger essenbly to the cleanup eres. This area should be clean and enclosed so that the chances of contenfacting or looing the sample will be minimized. He suching shall be allowed.

Inspect the train prior to and during disassembly and note any abuormal conditions. e.g., broken filters, color of the impinger liquid, etc. Treat the samples as follows:

10.2.1 Container No. 1

Either seal the ends of the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Were pair of precleaned tweesars to bandle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfor to the container any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and/or a sharp-adgad blade. Seal the container.

10.2.2 Sorbeat Modules

Remove the porbent module from the train and cap it off.

10.2.3 Cyclene Catch

If the optional cyclose is used, quantitatively recover the particulate into a sample container and cap.

10.2.4 Sample Container No. 2

Quantitatively recover esterial deposited in the norsie. probe, transfer line, the front half of the filter holder, and the cyclone, if used, first by brushing and then by sequentially rissing with acetone and than because three times each and add all these tinges to Container No. 2. Mark level of liquid on contaiser.

10.2.5 Sample Container No. 3

Rings the back half of the filter holder, the connecting line between the filter and the condenser and the condenser (if using the separate condenser-sorbest trap) three times each with acetone

DATA FIELD

PTK AM

UKALI

kane collecting all rinnes in Container 3. If using the od condenser-serbent trap, the rinne of the condenser shall formed in the laboratory efter temoval of the MAD-2. If the isl water knockout trap has been employed, it shall be id and recorded and its contents placed in Container 3 slong the rinnes of it. Rinne it three times each with acotone, imane. Mark level of liquid on container.

Sample Conteiner No. 4

move the first impinger. Wipe off the outside of the jer to remove excessive water and other material, weigh (stem led), and record the weight on data sheet. Pour the contents inses directly into Container No. 4. Rinse the impinger stilly three times with acotone, and hexane. Mark level of j on container.

7 Sample Container No. 5

move the second and third impingers, wipe the sutside to a accessive water and other debris, weigh (stem included) and d weight on data sheet. Empty the contents and rinses into iner No. 5. Rinse each with distilled BI water three times. level of liquid on container.

8 Silica Gel Container

enove the last impinger, wipe the outside to remove excessive and other debria, weigh (stem included), and record weight to sheet. Fince the silica gel into its marked container.

CALCULATIONS

erry out calculations, retaining at least one extra decimal a beyond that of the acquired data. Round off figures after calculations.

Nomenclature

- Total weight of chlorinated organic compounds in stack gas sample, mg.
- Concentration of chlorinated organic compounds in atack gas, µg/o, corrected to standard conditions of 20°C, 760 an Mg (68°F, 29.92 in. Ng) on dry basis.
- Cross-sectional area of nozzle, m² (ft²).
- Water vapor in the gas stream, proportion by volume.
- 1 Percent of isokinetic sampling.
 - unteht of water, is g/g-mole (18

- Pbar Barometric pressure at the sampling site, mm Hg (in. Hg).
- P Absolute stack gas pressure, mm Hg (in. Hg).
- P = Standard absolute pressure, 760 mm Ng (29.92 in. Ng).
- R = Ideal gas constant, 0.06236 mm Hg-m³/^oK-g-mole (21.63 in. Hg-ft / R-lb-mole).
- T_ Absolute average dry gas motor comperature ^oK (^oR).
- T_ Absolute average stack gas temperature ⁰K (⁰R).
- T_{atd} = Standard absolute temperature, 293°K (68°F).
- n Total mass of liquid collected in impingers and silics gel.
- Metalume of gas sample ... massured by dry gas metar, dcm (dcf).
- V (std) Volume of gas sample measured by the dry gas mater corrected to standard conditions, dacm (doct).
- V_u(std) Volume of water vapor in the gas sample corrected to standard conditions, scm (scf).
- Stack gas velocity, calculated by combustion calculation, m/sec (ft/sec).
- Y Meter box correction factor.
- All Average pressure differential across the orifice meter, mm H₂O (in. H₂O).
- O Total sampling time, min.
- 13.6 Specific gravity of mercury.
 - 60 Sec/min.
- 100 Conversion to percent.
- 11.2 Average Dry Gas Motor Temperature and Average Orifice Pressure Drop

See data pheat (Fig. 5).

DUV

11.3 Dry Gas Volume

Correct the cample volume measured by the dry gas meter to standard conditions $\{20^{6}C, 760 \text{ mm Mg} (68 \pm F, 23.92 \text{ in. MG})\}$ by using Equation 1.

 $V_{n}(atd) = Y V_{n} \frac{T_{atd}}{T_{n}} \frac{P_{har} + \frac{A^{n}}{13.6}}{P_{atd}} = K_{1}V_{n} \frac{P_{har} + \frac{A^{n}}{13.6}}{T_{n}}$ (1)

wheret

K, - 0.3855 [•]K/mm Mg for metric units

- 17.65 "R/in. Mg for English units

11.4 Yolune of Water Yaper

where I

$$R_2 = 0.00134 \text{ m}^3/\text{m}1$$
 for metric units
= 0.0472 fc³/ml for English units

11.5 Noisturg Content

$$P_{uo} = \frac{\Psi_{u}(atd)}{\Psi_{u}(atd) + \Psi_{u}(atd)}$$
(3)

If liquid droplets are present in the gas stress assume the stress to be esturated and use a psychrometric chart to obtain an approximation of the moisture percentage.

11.6 Parcant Iaobimetic Sampling

$$1 - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) \left(P_{bor} + \frac{1}{4} - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + \left(\Psi_{B} - K_{B}\right) - \frac{100 T_{B} \left[K_{4} - n_{1c} + n_{1c} +$$

wherei

 $R_4 = 0.003454$ mm Hg = $n^3/n1 = {}^{\circ}K$ for metric units = 0.002669 in Hg = $tt^3/n1 = {}^{\circ}R$ for English units

11.7 Concentration of Chlorinsted Organic Compounds in Stack Gau

Determine the concentration of chlorinated organic compounds in the stack gas according to Equation 3.

-23-

vhere:

DKAFI

(2)

$$K_{\rm s} = 35.31 \ {\rm fc}^3/{\rm m}^3$$

C_ - K_ - V (etd)

12. QUALITY ASSURANCE (QA) PROCEDURES

The positive identification and quantification of apacific compounds in this assessment of stationary conventional combustion sources is highly dependent on the integrity of the apoples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in this section were designed to monitor the performance of the sampling methods and to provide information to take corrective actions if problems are observed.

Field Blanks

The field blanks should be submitted as part of the samples collected at each particular testing site. These blanks should consist of materials that are used for sample collection and storage and are expected to be handled with exactly the same procedure as each sample modium.

Blank Train

For each series of test tune, act up a blank train in a manner identical to that described above, but with the probe inlet capped with basane-rinsed aluminum fail and the exit and of the last impinger capped with a ground glass cap. Allow the train to remain assembled for a period equivalent to one test run. Recover the blank sample as described in Sac. 7.2.

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DRA

ANALYTICAL PROCEDURES TO ASSAY STACK EFFLUENT SAMPLES AND RESIDUAL COMBUSTION PRODUCTS FOR POLYCHLORINATED DIBENZO-p-DIOXINS (PCDD) AND POLYCHLORINATED DIBENZOFURANS (PCDF)

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Prepared By

GROUP C - ENVIRONMENTAL STANDARDS WORKSHOP

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Scope and Applicability of Hethod

The analytical procedures described here are applicable for the rmination of polychiorinated dibenzo-p-dioxins (PCDD) and dibenzons (PCDF) in stack effluents from combustion processes. These methods also applicable to residual combustion products such as bottom and ipitator ash. The methods presented entail addition of isotopicallyled internal standards to all samples in known quantities, extraction he sample with appropriate organic solvents, preliminary fractionation cleanup of the extracts using a sequence of liquid chromatography mns, and analysis of the processed extract for PCDD and PCDF, using led gas chromatography - mass spectrometry (GC-MS). Various ormance criteria are specified herein which the analytical data satisfy for quality assurance purposes. These represent minimum eria which must be incorporated into any program in which PCDD PCDF are determined in combustion product samples.

The method presented here does not yield definitive information on concentration of individual PCDD/PCDF isomers, except for 2,3,7,8-achlorodibenzo-p-dioxim (TCDD) and 2,3,7,8-letrachlorodibenzofuran F). Rather, it is designed to indicate the total concentration of isomers of several chlorinated classes of PCDD/PCDF (that is, total a-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins and nzofurans). Of the 75 separate PCDD and 135 PCDF isomers, there 22 ICDD, 38 TCDF, 14 PeCDD, 28 PeCDF, 10 HxCDD, 16 HxCDF, 2 MpCDD, CDF, 1 OCDD and 1 OCDF.⁴

The analytical method presented herein is intended to be applicable determining PCDD/PCDF present in combustion products at the ppt to level, but the sensitivity which can ultimately be achieved for a n sample will depend upon the types and concentrations of other chemical ounds in the sample.

The method described here must be implemented by or under the rvision of chemists with experience in handling supertoxic materials analyses should only be performed in rigorously controlled, limited ss laboratories. The quantitation of PCDD/PCDF should be accomplished by analysts experienced in utilizing capillary-column gas chromatographyspectrometry to accomplish quantitation of chlorocarbons and similar ounds at very low concentration.

-1-

The toxicological data which are available for the PCDD and PCDF are far from complete. That is, the toxicological properties of all of the isomers comprising the 75 possible PCDD and 135 possible PCDF are not presently known. However, a considerable body of toxicological data exists for 2,3,7.8-TCDD which indicates that. in certain animal species, this compound is lethal at extraordinarily low does and causes a wide range of systemic affects, including hepatic disorders, carcinoma and birth defects. While much less data is available regarding the toxicology of 2,3,7,8-TCDF, sufficient data is available to form the basis for the belief that 2,3,7,8-TCDF is similar in its toxicological properties to 2,3,7,8-TCOD. Aelatively little is known about the toxicology of the higher chlorinated PCOD and PCDF (that is, penta through octachiorinated PCDD/PCDF), although there is some data to suggest that certain penta-, hexa-, and hepta- PCOD/PCOF isomers are hazardous. In view of the extraordinary toxicity of 2,3,7,8-TCOD and in view of the exceptional biological activity of this compound (on the basis of enzyme induction assays) and of compounds having similar molecular structures. extensive precautions are required to preclude exposure to personnel during handling and analysis of materials containing these compounds and to prevent contamination of the laboratory. Specific safety and handline procedures which are recommanded are given in the Appendix to this protocol.

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The abbreviations which are used to designate chlorinated dibenzo-pdioxins and dibenzofurans throughout this document are as follows: PCDD - Any or all of the 75 possible chlorinated dibenzo-p-dioxin isomers PCDF - Any or all of the 135 possible chlorinated dibenzofuran isomers TCDD - Any or all of the 135 possible tetrachlorinated dibenzo-p-dioxin isomers TCDF - Any or all of the 138 possible tetrachlorinated dibenzofuran isomers TCDF - Any or all of the 138 possible tetrachlorinated dibenzofuran isomers PCDD - Any or all of the 14 possible pentachlorinated dibenzo-p-dioxin isomers PeCDF - Any or all of the 28 possible pentachlorinated dibenzofuran isomers MACDD - Any or all of the 10 possible hexachlorinated dibenzo-p-dioxin isomers NACDF - Any or all of the 16 possible hexachlorinated dibenzo-p-dioxin isomers NACDF - Any or all of the 16 possible hexachlorinated dibenzo-p-dioxin isomers NACDF - Any or all of the 16 possible hexachlorinated dibenzo-p-dioxin isomers NACDF - Any or all of the 16 possible hexachlorinated dibenzo-p-dioxin isomers NPCDD - Any or all of the 2 possible heptachlorinated dibenzo-p-dioxin isomers NPCDF - Any or all of the 4 possible heptachlorinated dibenzo-p-dioxin isomers NPCDF - Any or all of the 4 possible heptachlorinated dibenzo-p-dioxin isomers NPCDF - Any or all of the 4 possible heptachlorinated dibenzo-p-dioxin isomers NPCDF - Any or all of the 4 possible heptachlorinated dibenzofuran isomers NPCDF - Any or all of the 4 possible heptachlorinated dibenzofuran isomers

Specific isomers. - Any of the abbreviations cited above may be converted to designate a specific isomer by indicating the exact positions (carbon atoms) where chlorines are located within the molecule. For example, 2,3,7,8-1CDD refers to only one of the 22 possible TCDD isomers - that isomer which is chlorinated in the 2,3,7,8 positions of the dibenzo p-dioxin ring structure.

. Reagents and Chemicals

The following reagents and chemicals are appropriate for use in these rocedures. In all cases, equivalent materials from other suppliers ay also be used.

2.1 Potassium Hydroxide, Anhydrous, Granular Sodium Sulfate and ulturic Acid (all Reagent Grade): J. T. Baker Chemical Co. or Fisher cientific Co. The granular sodium sulfate is purified prior to use by placing a beaker containing the sodium sulfate in a 400°C oven for our hours, then removing the beaker and allowing it to cool in a desiccator. tore the purified sodium sulfate in a bottle equipped with a Teflonined screw cap.

2.2 Hexane, Methylene Chloride, Benzene, Methanol, Toluene, Isooctane: "Distilled in Glass" Burdick and Jackson.

2.3 Tridecane (Reagent Grade): Signa Chemical Co.

2.4 Basic Alumina (Activity Grade 1, 100 - 200 mesh): ICH Pharmaceuticals. Immediately prior to use, the alumina is activated by heating for at least 16 hours at 600°C in a muffle furnace and then allowed to cool in a desiccator for at least 30 minutes prior to use. Store pre-conditioned alumina in a desiccator.

2.5 Silica (Bio-Sil A. 100/200 mesh): Bio-Rad. The following procedure is recommended for conditioning the Bio-Sil A prior to use. Place an appropriate quantity of Jio-Sil A in a 30 mm x 300 mm long glass tube (the silica gel is held in place by glass wool plugs) which is placed in a tube furnace. The glass tube is connected to a prepurified nitrogen cylinder, through a series of four traps (stainless steel tubes, 1.0 cm 0.D. x 10 cm long). 1) Trap No. 1 - Mixture comprised of Chromosorb W/AW (60/80 mesh coated with 5% Apiezon L), Graphite (UCP-1-100), Activated Carbon (50 to 200 mesh) in a 7:1.5:1.5 ratio (Chromosorb W/AN, Apiezon L obtained from Supelco, Inc., Graphite obtained from Ultracarbon Corporation, 100 mesh, 1-H-USP; Activated Carbon obtained from Fisher Scientific Co.); 2) Trap No. 2 - Holecular Sleve 13 X (60/80 mesh), Supelco, Inc.; 3) Trap No. 3 - Carbosleve S (80/100 mesh) obtained from Supelco, Inc.; 4) The Bio-Sil A is heated in the tube for 30 minutes at 180°C while purging with nitrogen (flow rate 50-100 mL/minute), and the tube is then removed from the furnace and allowed to cool to room temperature. Methanol (175 mL) is then passed through the tube, followed by 175 mL methylene chloride. The tube containing the silica is then returned to the furnace, the nitrogen purge is again established (50-100 mL flow) and the tube is heated at 50°C for 10 minutes, then the temperature is gradually increased to 100°C over 25 minutes and maintained at 180°C for 90 minutes. Heating muran is continued until the tube



2.6 Silica Gel Impregnated With Sulfuric Acid: Concentrated sulfuric acid (44 g) is combined with 100 g Bio-Sil A (conditioned as described abovej in a screw capped bottle and agitated to mix thoroughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The H₂SO₄-silica gel is stored in a screw-capped bottle (Tefion-lined cap).

2.7 Silica Gel Impregnated with Sodium Hydroxide: 1N Sodium hydroxide (39 g) is combined with 100 g Bio-Sil A (conditioned as described above) in a screw capped bottle and agitated to mix throughly. Aggregates are dispersed with a stirring rod until a uniform mixture is obtained. The NaOH-silica gel is stored in a screw-capped bottle (lefton-lined cap).

2.8 Carbon/Celite;

Carbon: AX-21 Carbon, Anderson Development Co., Adrian, Mich. 49221 Celite 545: Fisher Scientific Co

Combine AX-21 Carbon (10.7 g) with Celite 545 (124 g) in a 250 mL glass bottle fitted with a Teflon-lined cap. Agitate the mixture to combine thoroughly. Store in the screw-capped bottle.

2.9 Sepralyte Diol (40µ): Analytichem International

2.10 Nitrogen and Hydrogen (Ultra High Purity): Matheson Scientific

3. Apparatus and Naterials

The following apparatus and materials are appropriate for use in these procedures. In all cases, equivalent items from other suppliers may also be used.

3.1 Glassware used in the analytical procedures (including the Soxhlet apparatus and disposable bottles) is cleaned by rinsing successively three times with methanol and then three times with methylene chloride, and finally drying it in a 100°C oven. Bottles cleaned in this manner are allowed to cool to room temperature and are then capped using Teflonlined lids. Teflon cap liners are rinsed as just described but are allowed to air-dry. More rigorous cleaning of some glassware with detergent may be required prior to the solvent rinses, for example, the glassware employed for Soxhlet extraction of samples.

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3.1.1 Sample Vessels: 125 mL and 250 mL flint glass bottles fitted with screw caps and teflon cap liners, and glass test tubes, VMR-Scientific.

3.1.2 Jeflon Cap Liners: Scientific Specialities Service, Inc.

3.1.3 Soxhlet Apparatus: Extraction apparatus, Allihn condenser, Kimax Brand, American Scientific Products Cat. No. E6252-2A.

3.1.4 Gravity Flow Liquid Chromatographic Columns: Custom Fabricated (Details of the columns are provided in later sections).

3.1.5 Micro-vials (3.0 mL): Meliance Glass,

3.2 Capillary Gas Chromatographic Columns: Two different columns are required if data on both 2,3,7,8-TCDD and 2,3,7,8-TCDF, as well as on the total PCOD/PCOF by chlorinated class, are desired. The appropriate columns are: 1) A fused silica column (60 M x 0.25 mm J.D.) coated with D8-5 (0.25 µ film thickness), J & W Scientific. Inc., Rancho Cordova, Calif. is utilized to separate each of the several tetra-through octachlorinated CDDs and CDFs, as a group, from all of the other groups. While this column does not resolve all of the isomera within each chlorinated group, it effectively resolves each of the chlorinated aroups from all of the other chlorinated aroups and therefore provides data on the total concentration of each group (that is, total tetra-, penta-, hexa-, hepta- and octa CDDs and CDFs). This column also resolves 2,3,7,8-TCDD from all of the other 21 TCDD isomers and this isomer can therefore be determined quantitatively if proper calibration procedures are applied as described further in a later section. This column does not completely resolve 2.3.7.8-1CDF from the other TCDF isomers, and if a peak corresponding in retention time to 2,3,7,8-TCOF is observed in the analysis using this column, then a portion of the sample extract must be reanalyzed using the second GC column described below if isomer - specific data on 2,3,7,8-TCDF is desired. 2) A fused silica column (30 N x 0.25 mm l.D.) coated with DB-225 (0.25 µ film thickness). J & W Scientific, inc., Rancho Cordova, Calif., must be utilized to obtain quantitative data on the concentration of 2,3,7,8-TCDF, since this column adequately resolves 2,3,7,8-TCDF from the other TCDF isomers.

3.3 Balance: Analytical Balance, readibility, 0.0001 g.

3.4 Nitrogen Blowdown Concentration Apparatus: N-Evap Analytical Evaporator Nodel 111, Organomation Associates Inc.

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4. Instrumentation

Gas Chromatograph-Nass Spectrometer-Data System (GC/MS/DS): The instrument system used to analyze sample extracts for PCDD/PCDF comprises a gas chromatograph (fitted for capillary columns) coupled directly or through an enrichment device to a mass spectrometer which is equipped with a computer-based data system. The individual components of the GC/MS/DS are described below.

4.1 Gas Chromatograph (GC): The chromatograph must be equipped with an appropriate injector and pneumatic system to permit use of the specified glass or fused silica capillary columns. It must also incorporate an oven which can be heated in a reproducible, programmed temperature cycle. The injector should be configured for splitless/ split injections. The GC column performance should be verified at the beginning of each 8 hour work period or at the beginning of each series of analyses if more than one set of samples is analyzed during an 8 hour shift. Extracts of complex combustion products and effluents may contain numerous organic residues even after application of the extensive prefractionation/cleanup procedures specified in this method. These residues may result in serious deviation of GC column performance and therefore, frequent performance checks are desirable. Using appropriate calibration mixtures, as described below, the retention time windows for each chlorinated class of CDDs/CDFs must be verified. In addition, the GC columnities willight must be demonstrated to effectively separate 2,3,7,8-TCOD from all other TCDD isomers if data on 2,3,7,8-TCDD alone is desired with at least 20% valley definition between the 2,3,7,8- isomer and the other adjacent-eluting TCDD isomers. Typically, capillary column peak widths (at half-maximum peak height) on the order of 5-10 seconds are obtained in the course of these analyses. An appropriate GC temperature program for the analyses described herein is discussed in a later section (see Table 1).

4.2 Gas Chrometograph-Mass Spectrometer Interface: The GC-MS interface can include enrichment devices. Such as a glass jet separator or a silicone membrane separator, or the gas chromatograph can be directly coupled to the mass spectrometer source. If the system has adequate pumping of the source region. The interface may include a diverter value for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass or glass-lined stainless steel. The interface components must be compatible with temperatures in the neighborhood of 250°C, which is the temperature at which the interface is typically maintained throughout analyses for PCOD/PCOF. The GC/MS interface must be appropriately configured so that the separation of 2,3,7,8-TCDD from the other TCDD isomers which is achieved in the gas chromatographic column is not appreciably degraded. Cold spots and/or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. If the latter are observed, thorough cleaning of the injection port. interface and connecting lines should be accomplished prior to proceeding.

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4.3 Mass Spectrometer (NS): The mass spectrometer used for the inalyses described here is typically a double-focusing sector or nuadrupole instrument equipped with an electron impact source (70 ev). mintained at 250°C, and a standard electron multiplier detector. If possible, it is desirable to have both low and high resolution capability with the mass spectrometer used, since confirmation of data obtained by low resolution HS using high resolution HS is sometimes desirable. Alternatively, a combination of mass spectrometers can be used for this purpose. The static resolution of the instrument must be maintained at a minimum of 1:500 (with a 10% valley between adjacent masses) if operating in the low resolution MS mode, and a minimum resolution of 1:10,000 is desirable for operation in the high resolution mode. The mass spectrometer must also be configured for rapid computercontrolled selected-ion monitoring in both high and low resolution operating modes. At a minimum, two ion-masses characteristic of each class of chlorinated dioxins should be monitored, and these are two ions in the molecular ion isotopic cluster. It is desirable for increased confidence in the data to also monitor the fragment ions arising from the loss of COC1 from the molecular ion. In order to accomplish the requisite rapid multiple ion monitoring sequence during the time period defined by a typically capillary chromatographic peak (the base of the chromatographic meak is typically 15-20 seconds in width), the fallowing MS performance parameters are typically required (assumine a 4-ion monitorine sequence for each class of PCDD/PCDF); duell time/ ion-mass, =100 msec.; minimum number of data points/chronatographic peak, 7 . The mass scale of the mass spectrometer is calibrated using high boiling perfluorokerosene and/or some other suitable mass standard depending upon the requirements of the GC-MS-DS system utilized. The actual procedures utilized for calibration of the mass scale will be unique to the particular mass spectrometer being employed. A list of the appropriate ions to be monitored in the PCDD/PCDF analyses described herein is presented in a later section (see Table 1).

4.4 Data System: A dedicated computer-based data system, capable of providing the data described above, is employed to control the rapid selected-ion monitoring sequence and to acquire the data. Both digital data (peak areas or reak heights) as well as peak profiles (displays of intensities of ion-masses monitored as a function of time) should be acquired during the analyses, and displayed by the data system. This raw data (mass chromatograms) should be provided in the report of the data.

5. Calibration Standards

A recommended set of calibration standards to be used in the analyses described herein is presented below. Stock standard solutions of the various PCDD and PCDF isomers and mixtures thereof are prepared in a glovebox, using weighed quantities of the authentic isomers. These stock solutions are contained in appropriate volumetric flashs and are stored tightly stoppered, in a refrigerator. Aliquots of the stock standards are removed for direct use or for subsequent serial dilutions to prepare working standards. These standards must be checked regularly time) to ensure that solvent evaporation or other losses have not occurred which would alter the standard concentration. The several recommended standard solutions are as follows.

5.] Standard Mixture A: Prepare a stock solution containing the following isotopically-labelled PCDD and PCDF in isooctane at the indicated concentrations: $2.5ng./\mu$ ¹⁺C₁₂-2,3,7,8-TCDD, $2.5ng/\mu$ ¹⁺C₁₂-1,2,3,4,7,8-MKCDD, $25ng/\mu$ ¹⁺C₁₂-1,2,3,4,7,8-MKCDD, $25ng/\mu$ ¹⁺C₁₂-1,2,3,4,7,8-MKCDF, $25ng/\mu$ ¹⁺C₁₂-0,2,3,4,7,8-MKCDF, $25ng/\mu$ ¹⁺C₁₂-0,2,3,7,8-MKCDF, $25ng/\mu$ ¹⁺C₁₂-0,2,3,4,7,8-MKCDF, 25ng/

5.2 Standard B: Prepare a stock solution containing 1.0 ng of ${}^{37}Cl_{3}-2,3,7,0-TCDD/\muL$ of isooctane. This standard can be coinjected if desired, along with aliquots of the final sample extract to reliably estimate the recovery of the ${}^{35}Cl_{12}-2,3,7,0-TCDD$ surrogate standard.

5.3 Standard Mixture C: Prepare a stock solution containing 100 ng/ μ L of isooctane af each of the following PCDD and PCDF: 2,3,7,8-TCDF; 2,3,7,8-TCDD; 1,3,4,6,8-PeCDF, 2,3,4,6,7,8-HxCDF; 1,2,4,7.9-PeCOO; 1,2,3,8,9-PeCDD; 1,2,3,4,6,8-HxCDF; 2,3,4,6,7,8-HxCDF; 1,2,3,4,6,8-HxCDD, 1,2,3,4,6,7-HxCOD; 1,2,3,4,6,7,8-HpCDF; 1,2,3,4,7,8,9-HpCDF; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,9-HpCDO; 0CDF: and 0CDD. This isomer mixture is used to define the gas chromatographic retention time intervals or windows for each of the penta-, hexa-, hepta-, and octachlorinated groups of PCDD and PCDF. Each pair of isomers of a given chlorinated class which is listed here corresponds to the first and last eluting isomers of that class on the DB-5 capillary GC column (except for TCDD and TCDF). In addition, this isomer mixture is used to determine EC-MS response factors for representative isomers of each of the penta-, hexa-, hepta-, and octachlorinated groups of PCDD and PCDF. The later data are used in quantitating the analytes in unknown samples.

5.4 Standard Mixture D: Prepare a stock solution containing 50 pg/µL of isooctame of each of the following TCOD isomers: 1,3,6,8-TCOD; 1,2,3,7-TCOD; 1,2,3,9-TCDD; 2,3,7,8-TCOD; and 1,2,8,9-TCOD. Two of the isomers in this mixture are used to define the gas chromatographic retention time window for TCODs (1,3,6,8-TCOD is the first eluting TCDD

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b. Some of the PCDD/PCDF isomer standards recommended for this method are available from Cambridge Isotope Laboratories, Cambridge, Massachusetts. Other PCDD/PCDF standards are available from the Brehm Laboratory, Wright State University, Dayton, Ohio, from the U.S. EPA Standard Repository at Research Triangle Park, North Carolina and possibly from other laboratories Not all of the indicated isotopically-labelled PCDD/PCDF internal standards recommended here are presently available in quantities sufficient for widespread distribution, but these are expected to be available in the near future.

isomer and 1,2,8,9-TCDD is the last eluting TCDD isomer on the BB-5 GC columni). The remaining isomers serve to demonstrate that the 2.3.7.8-TCUD isomer is resolved from the other nearest eluting TCUD isomers. and that the column therefore yields quantitative data for the 2,3,7,8-1CDD isomer alone.

5.5 Standard Mixture E: Prepare a stock solution containing 50 pg/ul of isooctane of each of the following TCDF isomers: 1,3,6,8-TCDF; 2,3,4,8-TCDF: 2.3.7.8-TCDF, 2.3.4.7-TCDF; and 1.2.8.9-TCDF. This isomer mixture is used to define the ICOF gas chromatographic retention time window (1.3.6.8- and 1.2.8.9-ICDF are the first and last eluting ICDFs on the DB-5 capillary column) and to demonstrate that 2,3,7,8-TCDF is uniquely resolved from the adjacent-eluting ICDF isomers.

6. Procedures for Addition of Internal Standards and Extraction of Samples

Both liquid and solid samples will be obtained for PCDD/PCDF analyses as a result of the application of an appropriate stack sampling procedure. Samples

resulting from the sampling train will include the following (these will be provided to the analytical laboratory as separate samples in the form indicated): 1) particulate filter and particulates thereon; 2) particulates from the cyclone (if used); 3) combined aqueous solutions from the impingers; 4) the intact XAD-resin cartridge and the resin therein; 5) combined aqueous rinse (if used) solutions from rinses of the nozzle, probe, filter holder, cyclone (if used), impingers, and all connecting lines; 6) combined acetone rinse solutions from rinses of the nozzle, probe, filter holder, cyclone (if used), impingers, and all connecting lines; 7) combined hexame rinse solutions from rinses of the nozzle, probe, filter, cyclone (if used), impingers, and all connecting lines. In addition, samples of bottom ash, precipitator ash, incinerator feed materials or fuel, guench liquids, and materials from effluent control devices may also be provided for analyses.

In general, the volumes of all liquid samples received for analyses are measured and recorded, and where appropriate, solid samples or aliquots thereof are weighed. Any samples which are homogeneous (as for example, a single liquid phase sample or a solid which can be thoroughly mixed) can be split prior to analyses, if desired, provided that this will still permit the attainment of the desired detection limits for the analytes of interest. Samples such as particulates from the sampling train which are generally collected in relatively small quantity, are preferably analyzed in total.

6.1 Organic Liquid Samples (Acetone and Hexane Solutions). Combine the acetone and hexame rinse solution and concentrate to a volume of about 1-5 mL using the nitrogen blowdown apparatus (a stream of dry nitrogen)

Ulist while neating the sample gently on a water bath. Rinse the vessels which contained the original solutions three times with small portions of hexane and add these to the concentrated solutions and concentrate further to near dryness. This residue will likely contain particulates which were removed in the rinses of the train probe and nozzle. Combine the residue (along with three rinses of the final sample vessel) in the Soxhlet apparatus with the filter and particulates, and proceed as described under Solid Sample below.

6.2 Aqueous Liquids

Add an appropriate quantity of the isotopically-labeled internal standard mixture (Standard Hixture A described earlier) to the aqueous liquid sample (or an aliquot thereof) in a screw-capped bottle fitted with a Teflon-lined cap. Add approximately 25% by volume of hexane to the spiked aqueous sample, seal the bottle and agitate on a shaker for a period of three hours. Allow the vessel to stand until the aqueous and organic layers separate, then transfer the organic layer to a separate sample bottle. Repeat the hexane extraction sequence two additional times and combine the organic fractions with that from the first extraction. Proceed with the sample fractionation and cleanup procedures

6.3 Solid Samples

Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene and reflux for a period of one hour. Remove the toluene and discard it, retaining the silica gel, or if desired, retain a portion of the toluene to check for background contamination. For extraction of particulates, place the entire sample in the thimble onto the bed of precleaned silica gel (1 cm. thick), and top with the precleaned glass wool retained from the initial Soxhlet cleaning procedure. Add the appropriate quantity of the isotopically-labelled internal standard mixture (Standard Mixture A described earlier) to the sample in the Souhlet thimble. Charge the Soxhlet with toluene and reflux for a period of 16 hours. After extraction, allow the Soxhlet to cool, remove the toluene extract, and transfer it to another sample vessel. Concentrate the extract to a volume of approximately 40 ml by using the nitrogen blowdown apparatus described earlier. Proceed with the sample fractionation and cleanup procedures described below.

7. Procedures for Cleanup and Fractionation of Sample Extracts

The following column chromatographic sample clean-up procedures are used in the order given, although not all may be required. In general, the silica and alumina column procedures are considered to be a minimum requirement. Acceptable alternative cleanup procedures may be used provided that they are demonstrated to effectively transmit a

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epresentative set of the analytes of interest. The column chromatoraphic procedures listed here have been demonstrated to be effective or a mixture consisting of 1,2,3,4-TCDD, 2,3,7,8-TCDD, 2,3,6,8-TCDF, ,2,4,8-TCDF, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDD, 1,2,4,7,8-PeCDF, 1,2,3,4,7,8xCDD, 1,2,4,6,7.9-MxCDF, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,8,9-HpCDF, CDD and OCDF

An extract obtained as described in the foregoing sections is oncentrated to a volume of about 1 mL using the nitrogen blowdown pparatus, and this is transferred quantitatively (with rinsings) to be combination silica gel column described below.

7.1 Combination Silica Gel Column: Pack one end of a glass :olumn (20 mm. 0.0. x 230 mm in length) with glass wool (precleaned) ind add, in sequence, 1 g silica gel, 2 g base-modified silica gel, 1 g silica gel, 4 g acid-modified silica gel, and 1 g silica gel. [Silica gel and modified silica gel are prepared as described in the Reagents sections of this protocol.) Preelute the column with 30 mL hexane and discard the eluate. Add the sample extract in 5 mL of bexane to the column along with two additional 5 ml rinses. Elute the column with an additional 90 mL of bexane and retain the entire eluate. Concentrate this solution to a voiume of about 1 ml.

7.2 Basic Alumina Column: Cut off a 10 mL disposable Pasteur glass pipette at the 4 mL graduation mark and pack the lower section with glass wool (precleaned) and 3 g of Noelm basic alumina (prepared as described in the Reagent section of this protocol). Transfer the concentrated extract from the combination silica column to the top of the column and elute the column sequentially with 15 mL of hexane, 10 mL of 8% methylene chloride-in-hexane and 15 mL of 50% methylene chloride-in-hexane, discarding the first two eluste fractions and retaining the third eluste fraction. Concentrate the latter fraction to about 0.5 mL using the nitrogen blowdown apparatus described earlier.

7.3 PX-21 Carbon/Celite 545 Column: Take a 9 inch disposable Pasteur pipette and cut off a 0.5 inch section from the constricted tip. Insert a filter paper disk at the top of the tube, 2.5 cm. from the constriction. Add a sufficient quantity of PX-21 Carbon/Celite 545 (Prepared as described in the reagent section of this protocol) to the tube to form a 2 cm. length of the Carbon-Celite. Insert a glass wool plug. Preelute the column in sequence with 2 mL of 508 benzene-in-ethyl acetate, 1 mL of 508 methylene chloride-in-cyclohexane and 2 mL of hexane, and discard these eluates. Load the extract (in 1 mL of hexane) from the alumina column onto the top of the column, along with 1 mL hexane rinse. Elute the column with 2 mL of 508 methylene chloride-in-hexane and 2 mL of 508 benzene-in-ethyl acetate and discard these eluates. Invert the column and reverse elute it with 4 mL of toluene, retaining this eluate. Concentrate the eluate and transfer it to a Reacti-Vial for storage. Store extracts in a freezer, shielded from light, prior

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to GC-MS analysis. If desired, still another column chromatographic clean-up step can be employed prior to concentration of the extract,

7.4 Silica/Diol Micro Column Cleanup: After the above clean-up steps small amounts of highly colored polar compounds may be present in complex samples. These are removed, if necessary, by the following glass Pasteur pipette, followed by 3 mm of sepralyte (Analytichem International), 6 mm of silica gel and finally 3 mm of sodium sulfate. The column is pre-wet with hexame, the sample is applied in 100 µL of 100% hexame and eluted with hexame, collecting 1.5 ml.

8. Procedure for Analysis of Sample Extracts for PCDD/PCDF Using Gas Chromatography-Mass Spectrometry (GC-MS).

8.1 Sample extracts prepared by the procedures described in the foregoing are analyzed by GC-MS utilizing the following instrumental parameters. Typically, 1 to 5 μ L portions of the extract are injected into the GC. Sample extracts are first analyzed using the D8-5 capitlary GC column to obtain data on the concentrations of total tetra-through octa-CDDs and CDFs, and on 2,3,7,8-TCDD. If tetra-CDFs are detected in this analysis, then another aliquot of the sample is analyzed in a separate run, using the D8-225 column to obtain data on the concentration

8.2 Gas Chromatograph

8.2.1 Injector: Configured for capillary column, splitless/split injection (split flow on 60 seconds following injection), injector temperature, 250°C.

8.2.2 Carrier gas: Hydrogen, 30 lb head pressure.

B.2.3 Capillary Column 1: For total tetra-through octa - CDDs/CDFs and 2,3,7,8-TCOD, 60 M x 0.25 mm i.D. fused silica DB-5; temperature programmed (see Table 1 for temperature program). Capillary Column 2: for 2,3,7,8-TCOF only, 60 M x 0.25 mm i.D. fused silica DB-225, temperature programmed (180°C for 1 min., then increase from 180°C to 240°C 0 5°C/min., hold at 240°C for 1 min.)

8.2.4 Interface Temperature: 250°C

8.3 Mass Spectrometer

8.3.1 Ionization Mode: Electron impact (70 eV)

8.3.2 Static Resolution: 1:600 (10% valley) or 1:10,000 depending upon requirement. Usually the sample extracts are initially analyzed using low resolution HS, then if PCDD/PCDF are detected, it is desirable to analyze a second portion of the sample extract using high resolution MS.

8.3.3 Source Temperature: 250°C

8.3.4 Ions Monitored: Computer-Controlled Selected-Ion Monitoring, See Table 1 for list of ion masses monitored and time intervals during which ions characteristic of each class of CDDs and CDFs are monitored.

8.4 Calibration Procedures:

8.4.1 Calibrating the MS Mass Scale: Perfluoro Kerosene, decafluorotriphenyl phosphine, or any other accepted mass marker compound must be introduced into the MS, in order to calibrate the mass scale through at least m/z 500. The procedures specified by the manufacturer for the particular MS instrument used are to be employed for this purpose. The mass calibration should be rechecked at least at 8 hr. operating intervals.

8.4.2 Table 1 shows the GC temperature program typically used to resolve each chlorinated class of PCOD and PCOF from the other chlorinated classes, and indicates the corresponding time intervals during which ions indicative of each chlorinated class are monitored by the HS. This temperature program and ion monitoring time cycle must be established by each analyst for the particular instrumentation used by injecting aliquots of Standard Mixtures C, D. and E (See earlier section of this protocol for description of these mixtures). It may be necessary to adjust the temperature program and ion monitoring cycles slightly based on the observations from analysis of these mixtures.

8.4.3 Checking GC Column Resolution for 2,3,7,8-TCDD and 2,3,7,8-TCDF: Utilize the column-resolution TCDD and TCDF isomer mixtures (Standard Mixtures D and É, containing 50 pg/μ], respectively of the appropriate TCDD and TCDF isomers) to verify that 2,3,7,8-TCDD and 2,3,7,8-TCDF are separated from the other TCDD and TCDF isomers, . respectively. A 20% valley or less must be obtained between the mass chromatographic peak observed for 2,3,7,8-TCDD and adjacent peaks arising from other TCDD isomers, and similar separation of 2,3,7,8-TCDF from other neighboring TCDFs, is required. Standard Mixture D is utilized with the DBS column and Standard Mixture E with the DB-225 column. Analyze the column performance standards using the instrumental parameters specified in Sections 8.2 and 8.3, and in Table 1. The column performance evaluation must be performed each time a new column is installed in the gas chromatograph, and at least once during each 8 hour operating period. Providing that the same column is employed for a

period of time, its performance can also be gauged by noting the peak width (at 1/2 peak height) for 2,3,7,8-TCDD or for 2,3,7,8-TCDF. If this peak width is observed to broaden by 20% or more as compared to the usual width for satisfactory pperation, then the column resolution is suspect and must be checked. If the column resolution is found to be insufficient to resolve 2,3,7,8-TCDD and 2,3,7,8-TCDF from their neighboring TCDD and TCDF isomers, respectively, (as measured on the two different columns used for resolving these two isomers), then a new D8-5 and/or D8-225 GC column must be installed.

8.4.4 Calibration of the GC-MS-DS system to accomplish quantitative analysis of 2,3,7,8-TCDD and 2,3,7,8-TCDF, and of the total tetrathrough octa-CDDs and CDFs contained in the sample extract, is accomplished by analyzing a series of at least three working calibration standards. Fach of these standards is prepared to contain the same concentration

each of the stable-isotopically labelled internal standards used here (Standard Mixture A) but a different concentration of native PCDD/PCDF (Standard Hixture C). Typically, mixtures will be prepared so that the ratio of native PCDD and PCDF to isotopically-labelled PCDD and PCDF will be on the order of 0.1, 0.5 and 1.0 in the three working calibration mixtures. The actual concentrations of both native and isotopically-labelled PCOD and PCDF in the working calibration standards will be selected by the analyst on the basis of the concentrations to be measured in the actual sample extracts. At the time when aliguots of each of the standards are injected (and also when injecting aliquots of actual sample extracts), if desired, an aliquot of a standard containing typically 1 ng of $\frac{1}{1}$ Cl₃-2,3,7,8-TCDD (Standard B) can be drawn into the micro syringe containing the calibration solution described above (or the sample extract) and this is then co-injected along with the sample extract in order to obtain data permitting calculation of the percent recovery of the ${}^{11}C_{12}$ -2,3,7,8-TCOD internal standard. Equations for calculating relative response factors from the calibration data derived from the calibration standard analyses, and for calculating the recovery of the 13C11-2.3.7.8-TCDD and the other isotopically-labelled PCDD and PCDF, and the concentration of native PCDD and PCDF in the sample (from the extract analysis) are summarized below. In these calculations, as can be seen, 2.3.7.8-TCDD is employed as the illustrative model. However, the calculations for each of the other native dioxins and furans in the sample analyzed are accomplished in an analoous manner. It should be noted that in view of the fact that stable-isotopically labelled internal standards corresponding to each tetra- through octachlorinated class are not used here fowing to limited availability at this time) the following approach is adopted: For quantitation of tetrachlorinated dibenzofurans 13C12-2,3,7,8-TCDF is used as the internal standard. For quantitation of tetrachlorodibenzo-p-dioxins, ${}^{19}C_{12}-2,3,7,8$ -TCDD is used as the internal standard. For quantitation of PeCDD, HxCDD, PeCDF, and HxCDF, the corresponding stable-isotopically labelled HxCDD and HxCDF internal standards are used. For quantitation of HpEDD, OCDO, and HpCDF, OCDF, the isotopicallylabelled OCDD and OCDF, respectively, are used. Inherent in this approach is the assumption that the response factors for each of the isomers f each chlorinated class are the same, and in the case of the pentaid hepta-CDDs and CDFs, the assumption is made that the responses for nese two classes are equivalent to those for the tetra-isomers and the cta-isomers, respectively.

8.4.5 Equations for Calculating Response Factors, Concentration of .3.7,8-TCDD in An Unknown Sample, and Receveries of Internal Standards.

- quation 1: Response Factor (RRF) for native 2,3,7,8-TCDD using ³³C12-2,3,7,8-TCDD as an internal standard.
 - $RRF_{d} = (A_sC_{1s}/A_{1s}C_s)$

where: A₂ = SIM response for 2,3,7,8-TCDD ion at m/z 320 + 322

- A₁₅ = SIN response for ¹³C₁₂-2,3,7,8-TCDD internal standard ion at m/z 332
- Cis = Concentration of the internal standard (pg./pL.)
- C_ = Concentration of the 2,3,7,8-TCDD (pg./wL.)
- Equation 2: Response Factor (RRF) for ³³CL -2,3,7,8-TCDD, the co-injected external standard
 - $RRF_f = (A_{is}C_{es})/(A_{es}C_{is})$
 - where: $A_{15} = SIM$ response for ${}^{13}C_{12}-2,3,7,8-TCDD$ internal standard ion at m/z 332
 - A = SIN response for co-injected ³²Cl₄-2,3,7,8-TCDD external standard at m/z 328 - 0.009 (SIN response for native 2,3,7,8-TCDD at m/z 322)

 C_{ie} = Concentration of the internal standard (pg./µL.)

 C_{es} = Concentration of the external standard (pg./µL.)

Equation 3: Calculation of concentration of native 2,3,7,8-TCDD using ${}^{30}C_{33}$ -2,3,7,8-TCDD as internal standard

Concentration, pg./g. = $(A_g) (I_g)/(A_{ig})(RRF_d)(W)$

- where: $A_g = SIM$ response for 2,3,7,8-TCDD ion at m/z 320 + 322
 - A₁₅ = SIM response for the ¹³C₁₂-2,3,7,8-ICDD internal standard ion at m/z 332
 - Is Amount of internal standard added to each sample (pg.)
 - i = Weight of soll or waste in grams
 - RRF_d Relative response factor from Equation 1

Equation 4: Calculation of % recovery of ¹⁰C₁₂-2,3,7,8-TCDD internal standard

- **5** Recovery = $100(A_{1s})(E_s)/(A_{ns})(I_1)(E_{ns})$
 - A₁₅ = SIM response for ¹³C₁₂-2,3,7,8-TCDD internal standard ion at m/z 332
 - A = SIM response for ³⁷Cl₂-2,3,7,8-TCDD external standard fon at m/z 328 - 0.009 (SIM Response for native 2,3,7,8-TCDD at m/z 322)
 - E = Amount of ^{\$3}Cl₅-2,3,7,8-TCDD external standard co-injected with sample extract (ng.)
 - 1 " Theoretical amount of ¹³C₁₂-2,3,7,8-TCDD internal standard in injection
 - RRF_F = Relative response factor from Equation 2

As noted above, procedures similar to these are applied to calculate analytical results for all of the other PCDD/PCDF determined in this method.

8.5 Criteria Which GC-MS Data Must Satisfy for Identification of PCDD/PCDF in Samples Analyzed and Additional Details of Calculation Procedures.

In order to identify specific PCDD/PCDF in samples analyzed, the GC-MS data obtained must satisfy the following criteria:

8.5.1 Mass spectral responses must be observed at both the molecular and fragment ion masses corresponding to the ions indicative of each chlorinated class of PCDD/PCDF identified (see Table 1) and intensities of these ions must maximize essentially simultaneously (within + 1 second). In addition, the chromatographic retention times observed for each PCDD/PCDF signal must be correct relative to the appropriate stable-isotopically lahelled internal standard and must be consistent with the retention time windows established for the chlorinated group to which the particular PCDD/PCDF is assigned.

8.5.2 The ratio of the intensity of the molecular ion $(H)^*$ signal to that of the $(H+2)^*$ signal must be within \pm 10% of the theoretically expected ratio (for example, 0.77 in the case of 10%); therefore the acceptable range for this ratio is 0.69 to 0.85).

8.5.3 The intensities of the ion signals are considered to be detectable if each exceeds the baseline noise by a factor of at least 3:1. The ion intensities are considered to be quantitatively measurable if each ion intensity exceeds the baseline noise by a factor of at least 5:1[°].

8.5.4 For reliable detection and quantitation of PCDF it is also desirable to monitor signals arising from chlorinated diphenyl ethers which, if present could give rise to fragment lons yielding ion masses identical to those monitored as indicators of the PCDF. Accordingly, in Table 1, appropriate chlorinated diphenyl ether masses are specified which must be monitored simultaneously with the PCDF ion-masses. Only when the response for the diphenyl ether ion mass is not detected at the same time the PCDF ion mass can the signal obtained for an apparent PCDF be considered unique.

B.5.5 Measurement of the concentration of the congeners in a chlorinated class using the methods described herein is based on the assumption that all of the congeners are identical to the calibration standards employed in terms of their respective chemical and separation properties and in terms of their respective gas chromatographic and mass spectrometric responses. Using these assumptions, for example, the ${}^{13}C_{11}$ -2,3,7,8-1CDD internal standard is utilized as the internal calibration standard for all of the 22 TCDD isomers or congeners. Furthermore, the concentration of the total TCDD present in a sample extract is determined by calculating, on the basis of the standard procedure outlined above, the concentration of each 1CDD isomer peak (or peaks for multiple TCDD isomers, where these coelute) and these individual concentrations are subsequently summed to obtain the concentration of "total" 1CDD.

^{C.} In practice, the analyst can estimate the baseline noise by measuring the extension of the baseline immediately prior to each of the two mass chromatographic peaks attributed to a given PCDD or PCDF. Spurious signals may arise either from electronic noise or from other organic compounds in the extract. Since it may be desirable to evaluate the judgement of the analyst in this respect, copies of original mass chromatograms must be included in the report of analytical results.

8.6 Frequently, during the analysis of actual sample extracts, extraneous compounds which are present in the extract (those organic compounds not completely removed during the clean-up phase of the analysis) can cause changes in the liquid and gas chromatographic elution characteristics of the PCDD/PCDF (typically retention times for the PCDD/PCDF are prolonged). Such extrameous organic compounds, when introduced into the mass spectrometer source may also result in a decrease in the sensitivity of the MS because of suppression of ionization, and other affects such as charge transfer phenomena. The shifts in chromatographic retention times are usually general shifts, that is, the relative retention times for the PCDD/PCDF are not changed, although the entire elution time scale is prolonged. The analyst's intervention in the GC-MS operating sequence can correct for the lengthened GC retention times which are sometimes observed due to the presence of extraneous organics in the sample extract. For example, using the program outlined in Table 1. if the retention time observed for 2,3,7,8-TCDD (which normally is 19.5 minutes) is lengthened by 30 seconds or more, appropriate adjustments in the programming sequence outlined in Table 1 can be made, that is, each selected ion-monitoring program is delayed by a length of time proportionate to the lengthening of the retention time for the 2,3,7,8-TCDD isomer. In the case of ionization suppression, this phenomenon is inherently counteracted by the internal standard approach. However, if loss of sensitivity due to ionization suppression is severe. additional clean-up of the sample extract may be required in order to achieve the desired detection limits.

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9. Quality Assurance/Quality Control

9.1 Quality assurance and quality control are ensured by the following provisions:

9.1.1 Each sample analyzed is spiked with stable isotopically labelled internal standards, prior to extraction and analysis. Recoveries obtained for each of these standards should typically be in the range from 60-90%. Since these compounds are used as true internal standards however, lower recoveries do not necessarily invalidate the analytical results for native PCDD/PCDF, but may result in higher detection limits than are desired.

9.1.2 Processing and analysis of at least one method blank sample is accomplished for each set of samples (a set being defined as 20 samples or less).

9.1.3 It is desirable to analyze at least one sample spiked with representative native PCDD/PCDF for each set of 20 or fewer samples. The result of this analysis provides an indication of the efficacy of the entire analytical procedure. The results of this analysis will be considered acceptable if the detected concentration of each of the native

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CDD/PCDF added to the sample is within $\pm 50\%$ of the known concentration. An appropriate set of native isomers to be added here is a set such a that indicated for Standard Mixture C.)

9.1.4 At least one of the samples analyzed out of each set (of 20 amples or less) is analyzed in duplicate and the results of the duplicate nalysis are included in the report of data.

9.1.5 Performance evaluation samples prepared by EPA,or other aboratories, which contain representative PCDD/PCDF in concentrations pproximating those present in typical field samples being analyzed but unknown to the analyzing lab) should be periodically distributed a laboratories accomplishing these analyses.

9.1.6 Sources of all calibration and performance standards used in the nalyses and the purity of these materials must be specified in the data report.

). Data Reporting

10.1 Each report of analyses accomplished using the protocol lescribed herein will typically include tables of results which include the following:

10.1.1 Complete identification of the samples analyzed (sample numbers and source).

10.1.2 The dates and times at which all analyses were accomplished. This information should also appear on each mass chromatogram included with the report.

10.1.3 Raw mass chromatographic data which consists of the absolute intensities (based on either peak height or peak area) of the signals observed for the ion-masses monitored (See Table 1).

10.1.4 The calculated ratios of the intensities of the molecular ions for all PCDD/PCDF detected.

10.1.5 The calculated concentrations of native 2,3,7,8-TCDD and 2,3,7,8-TCDF, and the total concentrations of the congeners of each class of PCDD/PCDF for each sample analyzed, expressed in nanograms TCDD per gram of sample (that is, parts-per-billion) as determined from the raw data. If no PCDD/PCDF are detected, the notation "Not

(or detection limits) are reported.

10.1.6 The same raw and calculated data which are provided for the actual samples will also be reported for the duplicate analyses, the method blank analyses, the spiked sample analyses and any other QA or performance samples analyzed in conjunction with the actual sample set(s).

10.1.7 The recoveries of the internal standards in percent.

10.1.8 The recoveries of the native PCOD/PCDF from spiked samples in percent.

10.1.9 The calibration data, including response factors calculated from the three point calibration procedure described elsewhere in this protocol. Data showing that these factors have been verified at least once during each 8 hour period of operation or with each separate set of samples analyzed must be included.

10.1.10 The weight or quantity of the original sample analyzed.

10.1.11 Documentation of the source of all PCDD/PCDF standards used and available specifications on purity.

10.1.12 In addition to the tables described above, each report of analyses will include all mass chromatograms obtained for all samples analyzed, as well as for all calibration, GC column performance, and GC "window" definition runs and results of column performance checks.

10.1.13 Any deviations from the procedures described in this protocal which are applied in the analyses of samples will be documented in detail in the analytical report.

11. Typical Data Indicative of Method Performance - Precision and Accuracy.

11.1 The method described herein has typically been employed to quantitatively determine 2,3,7,8-TCOD in combustion product samples at concentrations as low as 10 picograms/gram and as high at 100 ν g/g. Concentrations of the other PCDD/PCDF which can be detected typically fall within the range of 20 picograms/isomer/gram of sample, to 100 picograms/g of sample. Of course, the limits of detection which can be practically achieved are dependent on the quantity of sample available

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:ind ther rfer orga ·es ic micl _ d th unt present in the sample. With respect to precision, the average deviation of data obtained from the analyses of a number of aliquots of the same sample containing the 2,3,7,8-1CDD isomer in the 250-300 ppb range is estimated to be +10% or better. Data on the precision of quantitation of multiple PCOD/PCDF in a single sample are not as yet available. As yet, there is inadequate interlaboratory and performance evaluation data available to specify the accuracy which can be expected of the analytical procedures described herein.

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	TABLE 1. Security	of Derstiens in		tion of Itl (Cont.)		
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rameters given mere are applicable for a 80-meter fused silica capillary BC column coated with BB-5.

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RECONVENDED SAFETY AND HANDLING PROCEDURES

FOR LABORATORIES CONDUCTING PCDD/PCDF ANALYSES

APPENDIX

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ecommended Safety and Handling Procedures in Connection with implementing he Analytical Protocal for Determination of PCDD/PCDF in Combustion Products

1. The human toxicology of PCOD/PCOF is not well defined at present, 1though the 2,3,7,8-TCOD isomer has been found to be acnegenic, arcinogenic, and teratogenic in the course of laboratory animal .tudies. The 2,3,7,8-TCOD is a solid at room temperature, and has a elatively low vapor pressure. The solubility of this compound in water is only about 200 parts-per-trillion, but the solubility in 'arious organic solvents ranges from about 0.001% to 0.14%. The physical roperties of the 135 other tetra-through octachlorinaed PCOD/PCOF have not wen well established, although it is presumed that the physical roperties of these congeners are generally similar to those of the ',3,7,8-TCOD isomer. On the basis of the available taxicological ind physical property data for TCOD, this compound, as well as the other 'COD and PCOF, should be handled only by highly trained personnel about are thoroughly versed in the appropriate procedures, and who anderstand the associated risks.

2. PCDD/PCDF and samples containing these are handled using essentially the same techniques as those employed in handling radioactive or infectious materials. Well-ventilated, controlled-access laboratories are required, and laboratory personnel entering these laboratories should mear appropriate safety clothing, including disposable coveralls, shoe covers, gloves, and face and head masks. During analytical operations which may give rise to aerosols or dusts, personnel should wear respirators couldned with activated carbon filters. Eve protection equipment (preferably full face shields) must be worn at all times while working in the analytical laboratory with PCDD/PCDF. Various types of gloves can be used by personnel, depending upon the analytical operation being accomplished. Latex gloves are generally utilized. and when handling samples thought to be particularly hazardous, an additional set of gloves is also worn beneath the latex gloves (for example, Playtex gloves supplied by American Scientific Products, Cat. No. 67216). Bench-tops and other work surfaces in the laboratory should be covered with plastic-backed absorbent paper during all analytical processing. When finely divided samples (dusts, soils, dry chemicals) are being processed, removal of these from sample containers. as well as other operations, including weighing, transferring, and mixing with solvents, should all be accomplished within a glove box. Glove boxes, hoods and the effluents from mechanical vacuum pumps and gas chromatographs on the mass spectrometers should be vented to the atmosphere preferably only after passing through MEPA particulate filters and vapor-sorbing charcoal.

3. All laboratory ware, safety clothing and other items potentially contaminated with PCDD/PCDF in the course of analyses must be carefully secured and subjected to proper disposal. When feasible, liquid wastes are concentrated, and the residues are placed in approved steel hazardous waste drums fitted with heavy gauge polyethylene liners. Glass and combustible items are compacted using a dedicated trash compactor used only for hazardous waste materials and then placed in the same type of disposal drum. Disposal of accumulated wastes is periodically accomplished by high temperature incineration at EPA-approved facilities.

4. Surfaces of laboratory benches, apparatus and other appropriate areas should be periodically subjected to surface wipe tests using solvent-wetted filter paper which is then analyzed to check for PCOD/PCDF contamination in the laboratory. Typically, if the detectable level of TCOD or TCDF from such a test is greater than $50ng/m^2$, this indicates the need for decontamination of the laboratory. A typical action limit in terms of surface contamination of the other PCOD/PCDF (summed) is $500ng/m^2$. In the event of a spill within the laboratory, absorbent paper is used to wipe up the spilled material and this is then placed into a hazardous waste drum. The contaminated surface is subsequently cleaned thoroughly by washing with appropriate solvents (methylene chloride followed by methanol) and laboratory detergents. This is repeated until wipe tests indicate that the levels of surface contamination are below the limits cited.

5. In the unlikely event that analytical personnel experience skin contact with PCDD/PCDF or samples containing these, the contaminated skin area should immediately be thoroughly scrubbed using mild scap and water. Personnel involved in any such accident should subsequently be taken to the nearest medical facility, preferably a facility whose staff is knowledgable in the toxicology of chlorinated hydrocarbons. Again, disposal of contaminated clothing is accomplished by placing it in hazardous waste drums.

6. It is desirable that personnel working in laboratories where PCDD/PCDF are handled be given periodic physical examinations (at least yearly). Such examinations should include specialized test;, such as those for urinary porphyrins and for certain blood parameters which, based upon published clinical observations, are appropriate for persons who may be exposed to PCDD/PCDF. Periodic facial photographs to document the onset of dermatologic problems are also advisable.

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