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Sampling and Analysis Methods for Hazardous Waste Combustion

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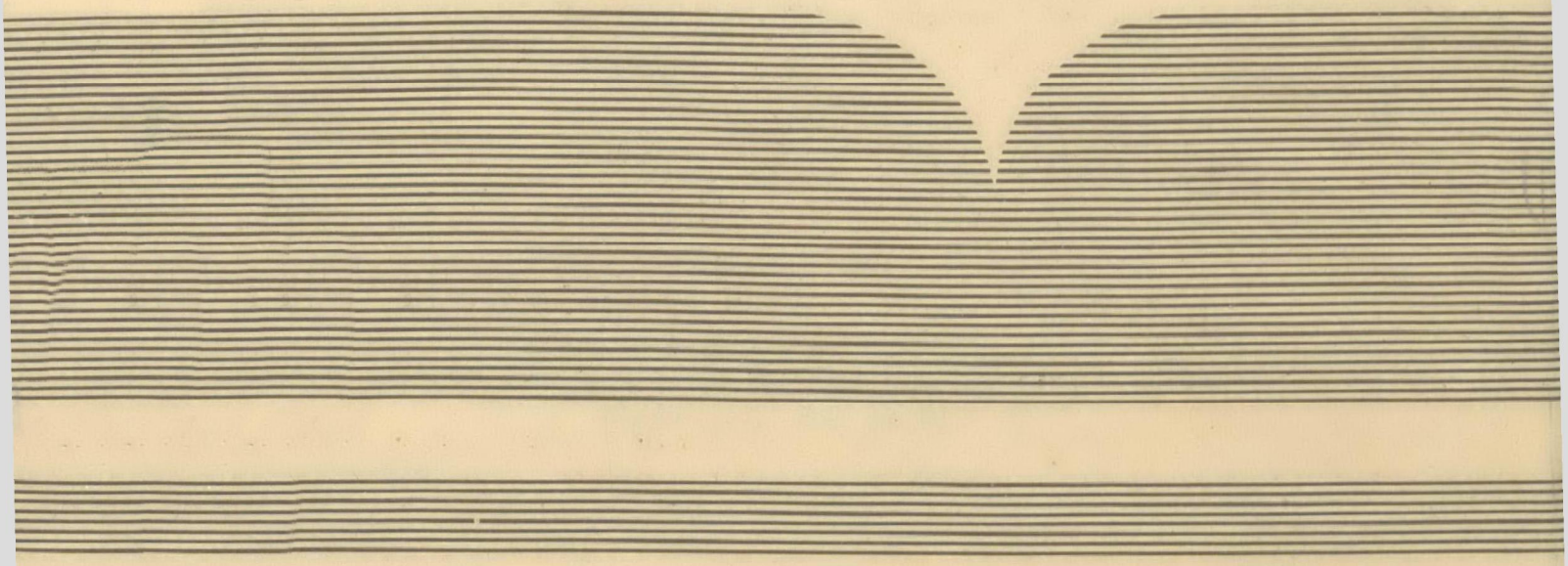

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SAMPLING AND ANALYSIS METHODS FOR HAZARDOUS WASTE COMBUSTION

by

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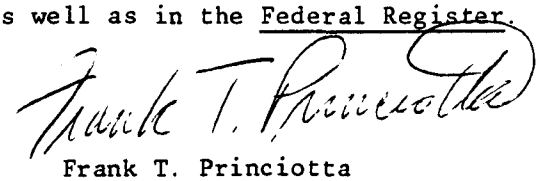
This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

This report has been produced by EPA's Office of Research and Development as part of on-going studies in support of regulatory programs and of EPA's Office of Solid Waste, EPA Regional Offices, and appropriate State Agencies. The document contains state-of-the-art sampling and analysis methods for determination of hazardous waste incinerator performance. It is intended as a reference work to be used by personnel of the regulatory groups, personnel associated with engineering R&D, and the regulated community.

Inclusion in this report does not mean that the sampling or analysis method is an official EPA method. Official test methods for hazardous waste related programs are published in SW-846 "Test Methods for Evaluating Solid Waste," as well as in the Federal Register.



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ABBREVIATIONS AND GLOSSARY OF TERMS

AAS	Atomic Absorption Spectroscopy
Accuracy	The difference between a single value or the mean of a set of results and the value which is accepted as the correct (true) value for the quantity measured.
AFID	Alkali Flame Ionization Detector
amu	Atomic Mass Unit (1 amu = 9.314×10^8 eV)
APCD	Air Pollution Control Device
Appendix VIII	Hazardous Constituent List (40 C.F.R. Part 261)
ASTM	American Society for Testing and Materials
atm	Atmosphere (1 atm = 1.013×10^5 Pa = 760 Torr)
Btu/lb	British Thermal Unit per Pound (1 Btu/lb = 2.3244×10^3 J/Kg = 0.556×10^{-3} kcal/g)
Btu/h	British Thermal Unit per Hour (1 Btu/h = 2.931×10^{-1} W)
C	Corrosivity Test--RCRA Characteristic
C.F.R.	Code of Federal Regulations
CI	Chemical Ionization Mode (Mass Spectrometry)
cm	Centimeter (10^{-2}m)
CO	Carbon Monoxide
Coliwasa	Composite Liquid Waste Sampler
CV	Coefficient of Variation
2,4-D	2,4-Dichlorophenoxyacetic acid
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene

DDT	Dichlorodiphenyltrichloroethane
D.E.S.	Diethylstilbestrol
DFTPP	Decafluorotriphenylphosphine
Directed Analysis	Qualitative confirmation of compound presence and identity. Also, quantitative data of known quality for a set of constituents that might reasonably be expected to be present in the waste based on professional judgment and/or the results of proximate and survey analyses.
DNPH	Dinitrophenylhydrazine
DRE	Destruction and Removal Efficiency--the measure of the mass emission rate of a principal organic hazardous constituent (POHC) in the output stack gas versus the mass feed rate of the same POHC in the influent waste.
dscf	Dry Standard Cubic Foot (1 dscf = 2.8317×10^{-2} dscm)
dscm	Dry Standard Cubic Meter
E	Extraction Procedure Toxicity Test--RCRA Characteristic
ECD	Electron Capture Detector
EI	Electron Impact Ionization Mode (Mass Spectrometry)
EP	Extraction Procedure
EPA	U.S. Environmental Protection Agency
ESP	Electrostatic Precipitator
eV	Electron Volt (1 eV = 1.602×10^{-19} J)
Excess Air	Air flow rate above that required to achieve theoretically complete combustion.
FPD	Flame Photometric Detector
ft	Foot (1 ft = 3.0480×10^{-1} m)
FT-IR	Fourier Transform-Infrared Spectroscopy
g	Gram (10^{-3} kg)

gal	Gallon (1 gal = 3.785×10^{-3} m^3)
GC	Gas Chromatography
GC/AFID	Gas Chromatography/Alkali Flame Ionization Detector
GC/ECD	Gas Chromatography/Electron Capture Detector
GC/MS	Gas Chromatography/Mass Spectrometry
GC/MS/DS	Gas Chromatography/Mass Spectrometry/Data System
GC/NPD	Gas Chromatography/Nitrogen-Phosphorus Detector (Alkali Flame Ionization Detector)
GC/TD	Gas Chromatography/Thermionic Detector
gr	Grain (1 gr = 6.48×10^{-5} kg)
GRAV	Gravimetric Analysis
h	Hour
HCl	Hydrochloric Acid
HPLC	High Performance Liquid Chromatography
HPLC/UV	High Performance Liquid Chromatography/ Ultraviolet Spectroscopy
I	Ignitability Test--RCRA Characteristic
ICAP	Inductively Coupled Argon Plasma Atomic Emission Spectroscopy
I.D.	Internal Diameter
in	Inch (1 in = 2.54×10^{-2}m)
IR	Infrared Spectroscopy
Isokinetic Sampling	Collection of stack gas samples under conditions such that the linear velocity of gas through the sampling nozzle is equal to that of the undisturbed gas stream at the sample point.
Isothermal	With or at equal temperatures.
J	Joule

kcal	Kilocalorie (1 kcal = 4.184×10^3J)
K-D	Kuderna-Danish Evaporative Concentrator
kg	Kilogram (10^3g)
L	Liter (1L = 1.00×10^{-3} m^3)
LC	Liquid Chromatography
LC/EC	Liquid Chromatography/Electrochemical Detector
LOD	Loss on Drying
LOI	Loss on Ignition
LRMS	Low Resolution Mass Spectrometry
µg	Microgram (10^{-6}g)
µL	Microliter (10^{-6}L)
µM	Micrometer (10^{-6}m)
m	Meter
m^3	Cubic Meter
M5	Method 5 Sampling Train
mg	Milligram (10^{-3}g)
min	Minute (1 min = 60 sec)
mL	Milliliter (10^{-3}L)
mm	Millimeter (10^{-3}m)
MM5	Modified Method 5 Sampling Train
MS	Mass Spectrometry
mV	Millivolt (10^{-3}V)
MW	Molecular Weight
NDIR	Non-Dispersive Infrared Analyzer
NFPA	National Fire Protection Association

ng	Nanogram (10^{-9}g)
nm	Nanometer (10^{-9}m)
NO_x	Nitrogen Oxides (NO, NO_2, etc.)
N.O.S.	Not Otherwise Specified
O.D.	Outer Diameter
Opacity	Measurement of the optical density of stack gas emissions of an incinerator.
Pa	Pascal
PCB(s)	Polychlorinated Biphenyl(s)
POHC(s)	Principal Organic Hazardous Constituent(s)
P_2O_5	Phosphorus Pentoxide
ppb	Part Per Billion
	One part in 10^9. For gaseous mixtures, a volume:volume basis is typically used and 1 ppb is on the order of 1 $\mu g/m^3$: $\mu g/m^3 = ppb \times \frac{RT}{MW}$ where RT = 22.4 L/mole at 0° and 1 atm = 24.5 L/mole at 25° and 1 atm For liquid materials, a weight:volume basis is most commonly used and 1 ppb = 1 µg/L ($\approx$ 1 µg/kg for liquids with density $\approx$ 1). For solid materials, a weight:weight basis is most commonly used and 1 ppb = 1 µg/kg.
ppm	Part Per Million
	One part in 10^6 (see ppb). 1 ppm $\approx$ 1 mg/m^3 gaseous streams 1 ppm = 1 mg/L liquid streams 1 ppm = 1 mg/kg solid streams
Precision	The reproducibility of measurements within a set of independent replicate determinations. The relative standard deviation expressed as a percentage of the mean is a common measure of precision.

Proximate Analysis	Provides data relating to the physical form of the waste and provides an approximate mass balance as to the composition of the waste.
psi	Pounds Per Square Inch (1 psi = 6.8948×10^3 Pa)
PVC	Polyvinyl Chloride
QA	Quality Assurance
QC	Quality Control
R	Reactivity Test--RCRA Characteristic
RCRA	Resource Conservation and Recovery Act of 1976
RI	Refractive Index Detector
rpm	Revolutions Per Minute
RSD	Relative Standard Deviation
SASS	Source Assessment Sampling System
s	Second
SCFM	Standard Cubic Feet per Minute
SD	Standard Deviation
Segregation	Heterogeneity in a sample
Semivolatiles	Organic species with moderate vapor pressure sufficient to allow analysis by gas chromatography, generally have boiling points of 100°C or higher, molecular weights of 100-400, seven to twenty carbon atoms per molecule.
SO_x	Sulfur Oxides (SO_2, SO_3)
Sparging	Removal of the volatile constituents of a sample by bubbling an inert gas stream through the sample.
Surrogate	A known compound added to a sample which is chemically similar to a POHC of interest so that an estimate of the accuracy of the analytical measurement and an assessment of the overall efficiency of the analytical procedures can be made.

Survey Analysis	Provides an overall description of the sample in terms of the major organic compounds and major inorganic compounds that are present in the sample. The analysis provides a qualitative description of the overall chemistry of the sample.
T	Transmittance
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
TCD	Thermal Conductivity Detector
TCDD(s)	Tetrachlorodibenzo-p-dioxin(s)
TCO	Total Chromatographicable Organics
TGA	Thermogravimetric Analysis
THEED	Tetrahydroxyethylenediamine
TLC	Thin Layer Chromatography
TOC	Total Organic Carbon Content
TOX	Total Organic Halogen Content
2,4,5-TP	2,4,5-Trichlorophenoxypropionic acid
TSDF	Hazardous Waste Treatment, Storage, and Disposal Facility
UV	Ultraviolet Spectroscopy
V	Volt
VOA	Volatile Organics Analysis
Volatiles	Organic species with appreciable vapor pressure at room temperature, generally have boiling points of 100°C or lower, molecular weights less than 200, one to seven carbon atoms per molecule.
W	Watt
W_{in}	Mass feed rate of one POHC in the waste stream feeding the incinerator.
W_{out}	Mass emission rate of the same POHC (see W_{in}) present in exhaust emissions prior to release to the atmosphere.

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I. ABSTRACT

As part of the Resource Conservation and Recovery Act of 1976, the U.S. Environmental Protection Agency (EPA) has proposed regulations for owners and operators of facilities that treat hazardous wastes by incineration to ensure that these incinerators will be operated in an environmentally responsible manner. The primary criterion upon which the operational specifications are based is the destruction and removal efficiency (DRE) of the incinerator. The DRE value, defined in terms of waste input and stack output levels of designated principal organic hazardous constituents (POHCs) must be equal to or greater than 99.99 percent.

In support of the DRE requirement, this report is a reference that describes the sampling and analysis methods for measuring the hazardous constituents (as defined in 40 C.F.R. Part 261, Appendix VIII) which might be designated as POHCs in the various influent and effluent streams of incineration facilities. The sampling and analysis methods for these constituents are described in the text. Also included are concise summary sheets for all recommended methods which state the name and number of the method, the types of samples and specific analytes to which the method applies, a brief description of the method, instrument and operating conditions, and reference(s) to more detailed descriptions of the procedure. Technician-level protocols are thus incorporated by reference rather than by reproduction in this report. In addition to presenting the methods for sampling and analysis of POHCs at these facilities, information concerning additional sampling and analysis requirements, general strategies for preparing sampling and analysis plans to meet the regulatory requirements, and guidelines for reporting and documentation are discussed.

Appendix A provides physical/chemical data (structure, CAS Registry Number, molecular weight, melting point, boiling point, and heat of combustion, when available) for all hazardous constituents listed in 40 C.F.R. Part 261, Appendix VIII (May 20, 1981). Additional appendices list specific compounds from Appendix VIII, with appropriate sampling (Appendix B) and analysis (Appendix C) methods. Mass spectral analytical ions for compounds analyzed by gas chromatography/mass spectrometry (GC/MS) are tabulated in Appendix E.

This report has been submitted in partial fulfillment of Contract No. 68-02-3111, Technical Directive No. 124, by Arthur D. Little, Inc. (Case No. 82480-54), under the sponsorship of the U.S. Environmental Protection Agency/Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina.

II. INTRODUCTION

A. PURPOSE

As part of the Resource Conservation and Recovery Act (RCRA), the EPA has promulgated proposed, interim, and final regulations for owners/operators of facilities which treat hazardous wastes by incineration to ensure that the incinerators are operated in an environmentally responsible manner (1). The regulations cover a range of activities, including operational performance standards, waste analysis, trial burns, monitoring and inspections, record-keeping and reporting, emission control criteria, fugitive emissions control, and closure of the facility. Details for each incinerator facility are authorized via facility permits.

In the permitting process, permitting officials use best professional judgment to determine the performance parameters which must be followed for each facility. The permit writer makes use of available technical advisory information contained in the "Guidance Manual for Hazardous Waste Incinerator Permits" (2) and the "Engineering Handbook for Hazardous Waste Incineration" (3). These documents provide engineering information in terms of waste and effluent characterization, incinerator design, control technology, facilities requirements, environmental impacts, and cost evaluations. Additional supporting documentation for the permit writer and for the incinerator facility owners/operators is available to address points raised during the permitting process.

This report is considered to be an additional supporting document. The primary criterion upon which all operational specifications are based is the destruction and removal efficiency (DRE) of the incinerator. This value, defined in terms of waste input and stack output levels of the principal organic hazardous constituent(s) (POHC(s)) designated in the trial burn permitting process, must be equal to or greater than 99.99 percent, according to the permitting standards for hazardous waste incineration. This report addresses the sampling and analysis methods to be used when measuring the levels of the POHC(s) in the various streams of an incinerator facility (inlet waste, stack gas, process water, fly ash, and bottom ash) for the purpose of calculating a DRE value for the incinerator. This compilation of sampling and analysis methods expands upon and augments the information contained in the "Guidance Manual for Hazardous Waste Incinerator Permits" (2).

The purpose of this report was an initial attempt to gather the sampling and analysis procedures for the benefit of the owners/operators of hazardous waste incineration units, permit application writers, the permit reviewer, and the chemical analyst. Since this report is an initial attempt, the information on sampling techniques and analytical procedures should be considered more as a guidance rather than a

prescription. These protocols lack definitive data on accuracy and precision because of limited use within the context of hazardous waste incineration. As new data are developed, the precision and accuracy data will be made available through updated versions of this manual or other documents. It is important that users of these protocols provide information on verified techniques, new procedures, and other relevant matters to the EPA so that updates can be made available.

B. SCOPE

This report describes the sampling and analysis methods which are appropriate to the measurement of POHCs in hazardous waste incineration facility streams. The material in this report has been divided into sections which address different aspects of the sampling and analysis approach for hazardous waste incinerators.

Regulatory requirements for the sampling and analysis activities are briefly reviewed, with emphasis on the data needs for trial burns. During trial burns, the sampling and analysis methods need to allow measurement of those POHCs which are expected to be present in the effluents, the level of particulate matter in the stack exhaust gas, and (in some cases) the concentration of hydrochloric acid in the stack gas. Also during trial burns, waste samples must be characterized to establish limits on the waste compositions which may be incinerated. During routine facility operations, the incoming wastes are examined periodically to determine if the composition of the waste has changed. Some gaseous species, such as carbon monoxide (CO), are monitored continuously as an indicator of the combustion efficiency of the process. Periodically, at a frequency not specified in the current regulations, the influent and effluent streams may be tested to monitor compliance with the DRE criteria and general incinerator performance.

Section III explains the strategies involved in preparing sampling and analysis plans to meet regulatory requirements. These strategies include approaches to the selection of POHCs which are likely to be present in the waste streams and combustion effluents. In addition, other strategies for monitoring of indicator species and characterization of liquid and solid effluents are included.

This report contains separate sections for sampling methods (Section IV), preparation methods (Section V), and analysis methods (Section VI), in terms of the various types of streams and sample media which will be encountered. Section VII describes general methods which will aid in the collection of high-quality sampling and analysis data; it also discusses the reporting and documentation concerns for the sampling and analysis of incinerator emissions. Other aspects of the reporting requirements are fully discussed in the permit writer's guidance document (2).

C. USE OF REPORT

In this report, the procedures are primarily briefly described with reference to other documents which contain more detailed procedural information. Existing collections of sampling and analysis methods, such as "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods" SW-846 (4) or "Samplers and Sampling Procedures for Hazardous Waste Steams" (5), are incorporated into this report only by reference.

The structure of this report permits quick access for the user. Concise method summary sheets for each sampling, preparation, and analysis method are grouped at the end of their respective sections. Many tables have been prepared which cross-reference specific methods to the individual hazardous constituents from 40 C.F.R. Part 261, Appendix VIII. Appendix A summarizes the physical and chemical data (structure, molecular weight, melting point, boiling point, and heat of combustion), of each hazardous constituent listed in Appendix VIII, if available. Appendices B and C reference each hazardous constituent by recommended sampling and analysis method.

III. SAMPLING AND ANALYSIS STRATEGY TO MEET REGULATORY REQUIREMENTS

A. INTRODUCTION

Section 3004 of the Resource Conservation and Recovery Act (RCRA) of 1976 requires the Administrator of the U.S. Environmental Protection Agency to promulgate such performance standards for owners and operators of hazardous waste treatment, storage, and disposal facilities (TSDFs) as may be necessary to protect human health and the environment. Section 3004 standards not only establish the levels of environmental protection that hazardous waste TSDFs must achieve, but also mandate the criteria against which applications for permits must be measured. The facility standards are thus key elements in the system mandated by RCRA for management of hazardous wastes.

The RCRA regulations that relate specifically to hazardous waste incineration are incorporated in the Code of Federal Regulations, Title 40 (40 C.F.R.) Parts 122, 264, and 265. Under Part 122 which regulates EPA administered permit programs, Subpart A presents definitions and general program requirements, while Subpart B specifies additional requirements for hazardous waste permitting programs under RCRA. Under Parts 264 (Permitting Standards) and 265 (Interim Status Standards), Subpart B presents general facility standards, including general waste characterization requirements, while Subpart O relates specifically to incinerators.

1. General Facility Standards

The General Facility Standards as they relate to the sampling and analysis of hazardous waste are identical in the interim status (§265.13) and permitting (§264.13) standards. The general waste analysis requirement is that the owner or operator must obtain a detailed chemical and physical analysis of a representative sample of waste. At a minimum, the analysis must generate all information that is needed to treat, store, or dispose of waste in accordance with RCRA requirements and/or conditions of an operating permit. In addition to this detailed analysis of a representative waste sample, the owner/operator must "inspect" each shipment of waste to determine whether it matches the identity specified on the manifest. The sampling and analysis or inspection methods to be used must be specified in a written plan, which may become part of a RCRA Part B permit application.

2. Interim Status Standards for Incinerators

In addition to the general waste analysis, the Part 265, Subpart O, incinerator standards require that the owner/operator sufficiently analyze any waste that he has not previously burned in his

incinerator, so that he can (a) establish steady-state (normal) operating conditions, and (b) determine the type of pollutants which might be emitted.

The interim status standards for incinerators specify no explicit requirements for sampling and analysis of stack exhaust gas, or other incinerator effluents.

3. Permitting Standards for Incinerators

The Part 264, Subpart O, incinerator standards include requirements for waste analysis, three performance standards that include implicit sampling and analysis requirements, and also some operating/monitoring/inspection requirements. The waste analysis requirements are cross-referenced to the Part 122 Hazardous Waste Permit Program regulations and include analyses to determine the heating value of the waste, viscosity or physical form, identification of any hazardous constituents (listed in 40 C.F.R. Part 261, Appendix VIII) present in the waste to be burned, and an approximate quantification of any hazardous constituents identified in the waste.

The Part 264 performance standards (§264.343) relate to:

- The destruction and removal efficiency (DRE) for each principal organic hazardous constituent (POHC) designated in the permit. The DRE, defined in terms of the mass emission rate of a POHC in the stack exhaust gas vs. the mass feed rate of the same POHC in the waste, must be $\geq$ 99.99%. The DRE performance standard implicitly requires sampling and analysis to quantify the designated POHC(s) in the waste stream and in the stack gas during a trial burn.

- A limitation on hydrochloric acid emissions from the stack of an incinerator. This performance standard implicitly requires, in some cases, sampling and analysis to quantify hydrochloric acid in the stack gas and/or to determine the efficiency of air pollution control devices.

- A limitation on stack emissions of particulate material to $\leq$ 180 mg/dscm ($\leq$ 0.08 gr/dscf), corrected to a standard excess air level. This performance standard implies measurement of the particulate emission rate.

The sampling and analysis requirements of the Part 264 performance standards are described here as implicit because, during routine operational burns, compliance with specified operating requirements is acceptable in lieu of actual demonstrated compliance with the performance standards. The operating requirements (§264.345) and monitoring/inspection requirements (§264.347), in turn, specify that the carbon monoxide (CO) level in the stack exhaust gas must be monitored continuously; this is the only explicit chemical sampling and analysis requirement imposed on all operating incinerators by the Part 264 regulations.

On a case-by-case basis, the permit to operate an incinerator may specify additional operating requirements that necessitate other types of sampling and analysis on a routine basis. The permit may also include requirements for sampling and analysis to demonstrate actual compliance with the performance standards on an annual or other periodic schedule.

4. Hazardous Waste Permit Program

The Part 122, Subpart B, requirements for hazardous waste incineration permit programs under RCRA mandate that the owner/operator of an incineration facility must either:

- submit results of a trial burn which demonstrate facility operating conditions under which the waste can be incinerated in accordance with the Part 264.343 performance standards, or

- submit data based on waste analysis and on other trial or operational burns sufficient to specify operating conditions under which the waste can be incinerated in accordance with the Part 264.343 performance standards.

(An exemption to these requirements may be sought in the case of incineration of waste that is hazardous only because it has the characteristic(s) of Ignitability, Corrosivity, or Reactivity (in some cases), as defined in Part 261, Subpart C, of the RCRA regulations and that contains insignificant concentrations of hazardous components, as defined by Appendix VIII of Part 261.)

Sampling and analysis requirements for waste characterization are the same in the case of a trial burn (§122.27) or alternative data submission (§122.25). The analysis of the waste must include:

- heating value of the waste (in the form and composition in which it will be burned),

- viscosity or physical form,

- identification and approximate quantification of any hazardous organic constituents that are listed in Appendix VIII of Part 261 and are known or suspected to be present in the waste, and

- quantification of those hazardous constituents that may be designated as principal organic hazardous constituents (POHCs) for purposes of demonstrating compliance with the DRE performance standard.

Sampling and analysis requirements for incinerator effluent characterization (stack gas) in the event that a trial burn is conducted include:

- quantitative analysis of the stack exhaust gas for concentration (mass emissions) of the designated POHC(s),
- quantitative analysis of the stack exhaust gas for the concentration (mass emissions) of particulate matter,
- quantitative analysis (in some cases) of the stack exhaust gas for the concentration of hydrochloric acid for purposes of calculating a removal efficiency and/or emission rate,
- determination of the oxygen concentration in the stack exhaust gas for the purpose of calculating the excess air level in the exhaust gas, and
- continuous monitoring of carbon monoxide in the stack exhaust gas.

It is important to emphasize that most of the sampling and analysis procedures described in this report relate to trial burns. It is further important to note that only a small fraction of the procedures specifically selected to address an individual POHC will generally be applied in any single trial burn.

For operating burns, the only explicit sampling and analysis requirement is the determination of carbon monoxide in the stack gas. Although the permit writer or the state/local authorities may impose additional monitoring requirements in some instances, it is not anticipated that comprehensive sampling of the stack gas effluent or directed analysis of POHCs will be required except in trial burn situations.

B. WASTE CHARACTERIZATION STRATEGY

1. Sampling

Acquisition of a representative sample of hazardous waste for subsequent chemical analysis is accomplished by preparing a composite of several subsamples of the waste. Sampling tactics for the collection of subsamples, as specified in "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (4), generally involve grab sampling of liter/kilogram-sized portions of waste materials. To ensure that the bulk of the waste is accurately represented by the composite sample, the sampling strategy requires collection of a minimum of three subsamples which provide an integration over both the depth and the surface area of the waste as contained in drums, tanks, holding ponds, etc. The composite sample prepared in the field is split into at least three replicate samples prior to shipment to the analytical laboratory. This

is primarily a precaution against breakage or loss of a sample, but it also provides the potential for a check on the homogeneity of the composite sample.

To ensure that sampling and analysis results will be adequately documented, chain-of-custody procedures are incorporated into sampling protocols. The sampling protocols also include explicit provisions for ensuring the safety of the personnel collecting the samples.

2. Analysis

The overall strategy for waste characterization includes test procedures to determine the characteristics of the waste and analysis procedures to determine the composition of the waste. The analysis procedures for determining the composition of the waste are divided into three sections:

- Proximate Analysis
- Survey Analysis
- Directed Analysis

Figure 1 provides an overview of this analytical approach. The discussion below provides a capsule description of each major element of this scheme and the utility of the resulting information in the hazardous waste incineration permitting process.

a. Characteristics

The characteristics of the waste sample in terms of Ignitability (I), Corrosivity (C), Reactivity (R), and Extraction Procedure Toxicity (E) are determined according to the procedures and guidelines presented in 40 C.F.R. Part 261, Subpart C, and in SW-846 (4). These tests are performed on a sample from each waste stream unless there is sufficient information from the engineering analysis to indicate that the waste does not meet the I, C, R, and/or E criteria. This information is relevant to the Part 264, Subpart B, general waste analysis requirement in that the data affect procedures for safely storing, handling, and disposing of the waste at the facility. The data are also relevant to possible exclusion from the trial burn requirements of Part 122. The I, C, R, and E test data for each hazardous waste to which the tests are applicable are generally available from the waste generator and manifest or shipping papers received by the incineration facility owner/operator.

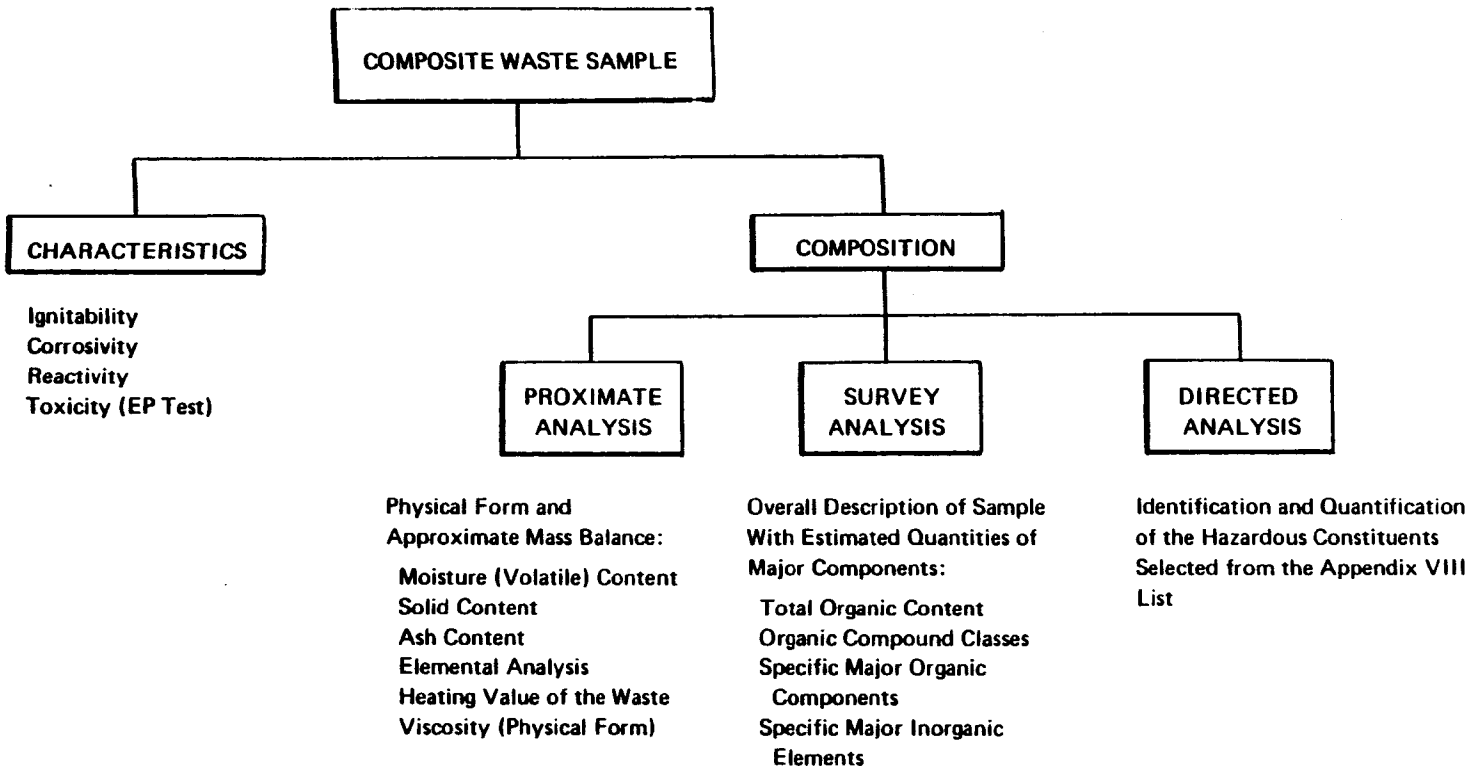


FIGURE 1 OVERVIEW OF THE ANALYTICAL APPROACH FOR WASTE CHARACTERIZATION

b. Composition--Proximate Analysis

The proximate analysis provides data relating to the physical form of the waste and provides an approximate mass balance as to its composition. This analysis includes determination of:

- moisture (volatile), solid, and ash content;
- elemental composition (carbon, hydrogen, nitrogen, sulfur, phosphorus, fluorine, chlorine, bromine, iodine);
- heating value of the waste; and
- viscosity or physical form.

This information meets the waste analysis requirements of the Part 264, Subpart O regulations and is also responsive to the general waste analysis requirements of Subpart B.

The elemental composition data allow prediction of a high concentration of potentially significant combustion products (NO_x, SO_x, P_2O_5, hydrogen halides and halogens). These data also facilitate an informed selection of the Appendix VIII hazardous constituents that might be present/not present in the waste by indicating whether the overall waste composition, and hence the types of components present, are consistent with the expectations based on best professional judgment. For example, if bromine were not expected to be present in the waste, the organobromine compounds from Appendix VIII would have been excluded from the directed analysis based on professional judgment. If bromine were, in fact, found in the waste at 0.5 percent level by weight, the list of compounds sought by directed analysis would be expanded to include the organobromines. It might also be possible, in some cases, to rule out some categories of Appendix VIII compounds on the basis of elemental analysis data when conservative professional judgment could not have excluded them.

c. Composition--Survey Analysis

The survey analysis is designed to provide an overall description of the sample in terms of (1) the major types of organic compounds, and (2) the major inorganic elements (metals) that are present. The survey analysis package includes determination of:

- total organic content by chromatographic (TCO) and gravimetric (GRAV) procedures,
- organic compound class types present by infrared (IR) and probe mass spectrometric procedures,
- major organic components by gas chromatographic/mass spectrometric (GC/MS) or high performance liquid chromatographic/infrared (HPLC/IR) or high performance liquid chromatographic/mass spectrometric (HPLC/LRMS) procedures, and

- metals by inductively coupled argon plasma emission spectroscopic (ICAP) and atomic absorption spectroscopic (AAS) procedures.

The type of data generated by the survey analysis allows a qualitative description of the overall chemistry of the sample. This information is important in deciding which of the hazardous constituents listed in Appendix VIII are present in the waste, and may lead to the selection of alternative, previously unsuspected POHC(s). Knowledge of the major components of the sample is also important in predicting the identity of hazardous by-products of combustion, or other emissions that may require sampling and analysis.

d. Composition--Directed Analysis

The directed analysis portion of the waste characterization scheme provides qualitative confirmation of the presence and identity of specific compounds and quantitative data with appropriate quality control measures for the Appendix VIII constituents that might reasonably be expected to be present in the waste based on professional judgment and/or on the results of proximate and survey analysis. It is important to note that directed analysis does not involve screening of every waste sample against the complete Appendix VIII hazardous component list. A preliminary judgment is made as to the compounds or types of compounds that are actually present.

For the organic directed analysis, a high resolution separation technique--fused silica capillary gas chromatography--and a high specificity detection technique--mass spectrometry--are used wherever possible. This approach ensures adequate qualitative and quantitative analysis on a cost-effective basis for a variety of waste types and process chemistries. Although gas chromatography/mass spectrometry (GC/MS) instrumentation is sophisticated and the initial capital cost of the instrumentation is high, the analytical technique is widely available in contractor laboratories, routine analytical service laboratories, and EPA laboratories. The combination of highly specific and reliable compound identification, high sensitivity, good quantitative capability, and the capability for the determination of multiple components in a single analysis make GC/MS the analytical method of choice for both waste and effluent organic analyses. Alternative organic analysis procedures using gas chromatography with less specific detectors generally require additional sample preparation and multiple analyses, and may still prove inadequate in terms of selectivity and elimination of interferences from non-target compounds.

For the inorganic directed analysis, atomic absorption spectroscopy (AAS) and inductively coupled argon plasma emission spectroscopy (ICAP) for metals and ion chromatography (IC) for anions are the primary analytical procedures.

The results of the directed analysis establishes that the waste contains the suspected pollutant(s) and demonstrates the concentration rate at which the pollutant(s) may be expected to be found. Directed analysis is also used to confirm and quantify unexpected hazardous components identified in the survey analysis. These data from the quantitative analysis of confirmed, identified contaminants of documented toxicity (Appendix VIII compounds) are essential for the selection of POHCs and the prediction of hazardous by-products of combustion.

e. Selection of POHC(s)

The criteria for selection of the POHC(s) (typically one to six specific constituents per waste stream) include:

- the expected difficulty of thermal degradation of the various hazardous organic constituents in the waste, and
- the concentration of those constituents in the waste.

Designation of the POHC(s) will be negotiated on a case-by-case basis for each permit application. It is important to note that it is not necessarily, nor even generally, true that all Appendix VIII compounds present in the waste will be designated as POHCs for trial burn purposes. The intent is to select a few specific compounds as indicators of satisfactory incinerator performance when burning a particular waste. It is necessary that the compounds selected provide a sufficiently stringent test of the incinerator performance in terms of the DRE to ensure that incineration of the waste can be carried out in an environmentally sound fashion. This criterion mandates selection of the more thermally stable constituent(s) as the POHC(s). At the same time, however, it is also necessary that the designated POHC(s) be present in the waste in sufficiently high concentration that they are capable of being detected in the stack gas at emission levels corresponding to $\leq$0.01 percent of their mass feed rate in the waste. This is a particularly important constraint for wastes that are to be incinerated with substantial quantities of auxiliary fuel which effectively dilutes the concentration of the POHC(s) in the exhaust gas. Although the burning of auxiliary fuel might not affect the mass emission rate of the POHC(s), it would lead to an increased volumetric flow of stack gas and thus to a decreased concentration of the POHC(s) in the stack exhaust gas. This lower concentration directly affects the detection limit achievable for a given stack gas sample size (e.g., 5 or 30 dscm).

It is recommended that, whenever possible, the permit writer select the POHC(s) present in the waste at 1000 ppm or higher. If it is considered desirable to designate as a POHC a thermally stable compound present at the hundreds of parts per million level, the trial burn permit application must include calculations and supporting data to indicate that 0.01 percent of the mass feed rate of that component in the waste could, in fact, be detected in the stack effluent. A waste

concentration of 100 ppm probably represents a practical lower level below which determination of 99.99 percent DRE may require extraordinary sampling, analysis, and quality control procedures, which may significantly increase the sampling and analysis costs for that trial burn.

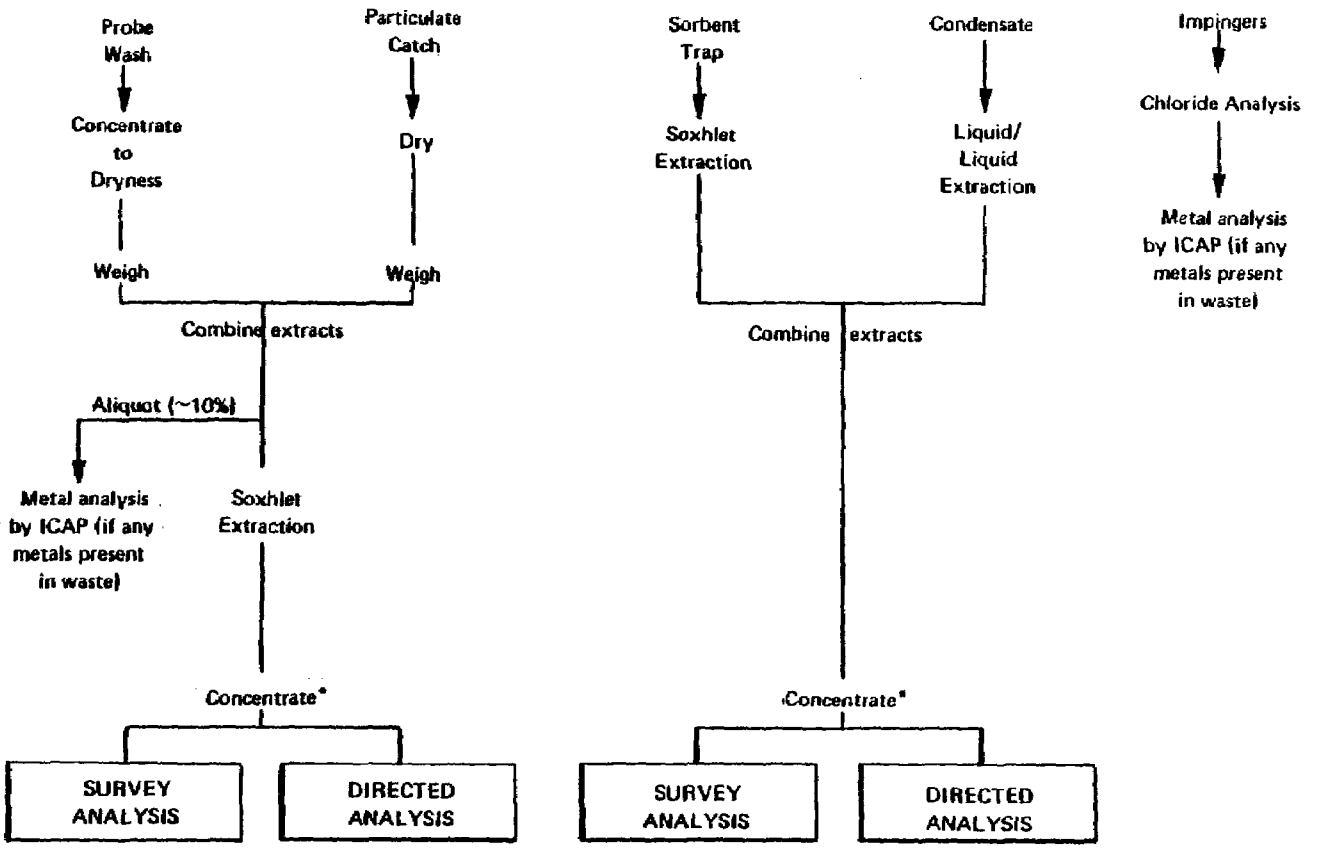
For a waste material that is a listed hazardous waste under RCRA (40 C.F.R. Part 261, Subpart D), the constituents which caused the Administrator to list the waste as toxic (tabulated in Appendix VII of 40 C.F.R. Part 261) would be logical candidates for designation as POHC(s) if these constituents were organic chemicals. However, many of the listed wastes are considered hazardous on the basis of their content of metals which are not, by definition, POHCs; Appendix VII contains relatively few organic chemicals.

C. STACK GAS EFFLUENT CHARACTERIZATION STRATEGY

The overall strategy for hazardous waste incinerator stack gas effluent characterization to determine compliance with the Part 264 performance standards is to collect replicate 3 to 6 hour (5-30 dscm) samples of stack exhaust gas, using a comprehensive sampling train, such as a modified EPA Method 5 (MM5) train (6) or the EPA/IERL-RTP Source Assessment Sampling System (SASS) (7). Either of these trains provides a sample sufficient for determination of particulate mass loading, concentrations of particulate and vapor phase organics, concentration of HCl, and concentrations of particulate and volatile metals.

Directed analyses for POHC(s) in the stack exhaust gas samples are performed on these MM5/SASS samples. The same sample (probe wash and particulate catch composite) may be used for determination of the particulate mass loading, determination of the non-volatile metal content, and subsequent extraction of non-volatile organic components. The semi-volatile organic components of the stack exhaust gas are collected in the sorbent trap and condensate portions of the MM5 or SASS train. More volatile organic constituents require additional sampling procedures. The extracts of the various parts of the MM5/SASS train may be combined for analysis of the concentration of POHC(s). For burns of wastes that could also produce significant emissions of HCl, a special reagent (caustic) in the impinger solution of a Method 5, or either a MM5 or SASS train is used to collect the HCl in the stack exhaust gas; the concentration of HCl is then quantified as chloride by ion chromatography. Figure 2 shows an overview of the analysis scheme for stack gas samples.

The directed analyses shown in Figure 1 are performed on triplicate samples. Although two samples would allow an average level of a POHC to be determined, at least three samples should be analyzed in order to compute an error bound for the measured values. The incremental cost of the replicate sampling and analysis is warranted by the increased confidence in the resulting data; quantitative results from a single sampling and analysis run should not generally be considered as an



*As an alternative, the extracts from particulate and vapor portions of the train may be combined prior to analysis.

FIGURE 2 OVERVIEW OF AN ANALYSIS SCHEME FOR STACK GAS SAMPLES FROM A COMPREHENSIVE SAMPLING TRAIN

acceptable indicator of performance. The survey analysis, which is a qualitative screen of the collected material to ensure that potentially hazardous, but unexpected, emissions are not overlooked, need be performed on no more than one stack gas sample.

During a trial burn, the oxygen level in the stack gas is measured using an Orsat analyzer, as detailed in 40 C.F.R. Part 60, Appendix A, Method 3 (6), so that the particulate loading may be corrected to a standard excess air level.

For both trial and operating burns, on-line monitors (non-dispersive infrared instruments) are used to provide continuous readings of the carbon monoxide (CO) level in the incinerator effluent.

D. ADDITIONAL EFFLUENT CHARACTERIZATION STRATEGY

The basic strategy for sampling scrubber water, ash, and other residues (if any) is to prepare composite samples from grab subsamples, collected using the same types of sampling devices and tactics used for waste characterization. This sampling is required only during trial burns in accordance with 40 C.F.R. Part 122.27. These additional effluent samples are analyzed for the designated POHC(s) to determine appropriate disposal or subsequent treatment methods, and to ensure that significant discharges of the POHC(s) in other media do not go undetected. A target detection limit of 0.01-0.5 percent of the mass feed rate of each POHC in the waste should be achievable with a reasonable sample size.

E. SELECTION OF SPECIFIC SAMPLING AND ANALYSIS METHODS

The preceding discussion has briefly described the RCRA regulations that define the sampling and analysis requirements for hazardous waste incineration and presented an overview of the strategic sampling and analysis approaches that have been developed to meet these requirements. Subsequent sections of this document present descriptions of the sampling, sample preparation, and analysis methods that are recommended for implementation of this strategy. This portion of Section III illustrates, by means of a hypothetical example, the transition from strategy, as described, to the tactics and methods described in the following chapters. The example is somewhat oversimplified in the interest of clarity, but it should demonstrate how to use this document in the development and evaluation of a hazardous waste incineration trial burn plan. The following discussion deals with sampling and analysis considerations only and does not address adequacy of incinerator design, operating conditions, or other engineering considerations.

1. Scenario

The owner/operator of an incineration facility seeks a RCRA permit to treat chlorinated organic waste material.

The facility is a liquid-injection incinerator with a capacity of 10×10^6 Btu/h (2.931×10^6 W); it is equipped with a wet scrubber for acid gas removal. A waste oil (<0.1% chlorine) is burned as auxiliary fuel. The proposed operating conditions for hazardous waste incineration include: combustion zone temperature of 2000°F (1100°C), residence time of 2 s with 150 percent excess air.

The waste is still bottom from the production of tetrachloroethene (tetrachloroethylene). Based on engineering analysis, it is expected to be a non-viscous organic liquid with a heating value <5000 Btu/lb ($<1.163 \times 10^7$ J/kg). The major components of the waste are expected to be highly chlorinated species such as hexachlorobenzene, hexachlorobutadiene, and the like.

2. Strategy

It is hypothesized that there are insufficient data from other trial or operating burns to specify operating conditions under which this type of facility has been demonstrated as being in compliance with the Part 264 performance criteria when burning this type of waste. Therefore, a trial burn will be required.

It is also hypothesized that there are data available from the waste generator which are sufficient to develop the trial burn plan. Therefore, additional analysis of the waste will not be necessary to support the trial burn permit application. The POHC(s) for which destruction and removal efficiencies are to be demonstrated in the trial burn must be designated, based on review of existing information and/or additional analysis of a representative sample of the waste.

Since the owner/operator plans to operate his facility under one set of temperature-residence time-excess air conditions when treating hazardous waste, the trial burn will consist of three replicate tests under that set of operating conditions.

The trial burn sampling and analysis strategy must address:

- the waste analysis requirements of 40 C.F.R. Part 122,
- the performance standards of 40 C.F.R. Part 264, Subpart O, and
- the monitoring requirements of 40 C.F.R. Part 264, Subpart O.

a. Sampling Strategy

During each of the three replicate tests, the following samples must be obtained:

- one composite sample of the waste actually treated,
- one time-averaged (3-4 hour) sample of stack gas, and
- one composite sample of spent scrubber water.

No bottom ash or fly ash streams (other than the stack particulate emissions) are expected to be generated as effluents from this facility.

b. Analysis Strategy

The waste must be analyzed to determine:

- heating value of the waste,*
- viscosity or physical form,*
- quantity of organically-bound chlorine* (this analysis is not mandatory; however, the data obtained may be helpful in determining a potential for HCl emissions),
- identity and approximate quantity of known or suspected Appendix VIII constituents,* and
- quantity of the designated POHC(s) for the trial burn.

The stack gas must be analyzed to determine:

- quantity of the designated POHC(s) for the trial burn,
- quantity of particulate matter emissions,
- quantity of hydrochloric acid emissions,
- carbon monoxide level, and
- oxygen level (excess air level determination).

The scrubber water must be analyzed to determine:

- quantity of the designated POHC(s) for the trial burn.

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*It has been hypothesized, for this example, that this information was available from the waste generator. Some or all of these determinations may be repeated on the actual composite waste sample.

3. Tactics and Methods

a. Selection of POHCs

Table 1 summarizes the information that is hypothetically available from the generator of the waste in this example. The major organic components that appear to be candidates for selection as the POHC(s) are listed in Table 2, along with their relevant physical/chemical properties (from Appendix A).

It is hypothesized that the permit writer designates hexachlorobutadiene, hexachlorobenzene, and hexachloroethane as the POHCs. All three species are present in significant concentration in the waste and will remain at >1000 ppm concentration, even if the waste were cut by as much as 1:10 with auxiliary fuel in order to limit the total chlorine feed rate and to maintain an adequate heating value in the total incinerator feed. Fully chlorinated species, such as these, are generally considered to be highly resistant to thermal degradation, and thus provide a set of "worst case" POHCs for DRE determination.

b. Selection of Sampling Methods

For sampling of wastes, as well as the liquid and solid effluents, the choice of method is based primarily on the nature of the medium. Review of available methods indicates that dipper (Method S002) and tap sampling (Method S004) is appropriate for collection of discrete subsamples of waste feed and of spent scrubber water, respectively, at regular time intervals over the duration of each trial burn. These subsamples are then combined to form the corresponding composite samples for each test.

For sampling of stack gas, both the nature of the medium and the nature (volatility, stability) of the POHC(s) and other target species affects the choice of a sampling method. Appendix B lists recommended sampling methods for each candidate POHC. Table 3 summarizes these recommendations for the candidate POHCs in this hypothetical example. The MM5/SASS approach collects all the candidate POHCs and also suffices to determine compliance with the two other performance standards of 40 C.F.R. Part 264. The particulate matter emission rate is determined from the mass of material collected in the probe wash, cyclone (if any), and filter of the MM5 train, prior to extraction for POHC analysis. The hydrochloric acid emission rate is determined by using a caustic scrubbing solution in the impinger portion of the MM5 train and determining the hydrochloric acid level, as chloride, by ion chromatography.

In addition to the procedures chosen for the collection of the POHCs, it is necessary to specify procedures to accomplish the required monitoring for carbon monoxide and excess air (oxygen determination) levels in the stack gas.

TABLE 1

AVAILABLE INFORMATION ON COMPOSITION
OF HYPOTHETICAL WASTE

Visual Inspection: The waste is a pitch black, non-viscous liquid with obvious particulate loading. It has a pungent odor and fumes slightly when the cap is removed.

Loss on Ignition: Ignition at 600°C resulted in a 99.8% loss of mass.

Higher Heating Value: The waste does not burn in a bomb calorimeter; its higher heating value is estimated at ∿2000 Btu/lb (∿1.11 kcal/g).

Combustion Analysis: The waste was found to contain: 21.35% C; 0.13% H; 0.07% N; 0.02% S; 75.52% Cl.

Infrared Spectrum: The IR shows no -COOH, -OH, -NH, or C=O functionality. Most of the spectral peaks can be attributed to hexachlorobutadiene. Hexachlorobenzene peaks are also present.

LRMS: The major components identified are mass 258, 6 Cl's, C_4Cl_6 or hexachlorobutadiene and, less abundant, mass 282, 6 Cl's, C_6Cl_6 or hexachlorobenzene.

GC/MS: This analysis confirms that hexachlorobutadiene is the major component and hexachlorobenzene is present at about 10% of the C_4Cl_6 concentration. Other peaks in the chromatogram correspond to hexachloroethane (∿4%), tetrachloroethanes (∿3%), tetrachloroethene (∿0.1%) plus four others at about 0.5% concentration of the C_4Cl_6 concentration.

Summary: All of the available evidence suggests that this waste contains essentially no tetrachloroethene, that hexachlorobutadiene makes up about 65% of the waste, and that there are perhaps a dozen other components at 1-5% concentration. All of the minor components appear to be chlorinated, with hexachlorobenzene the most abundant.

TABLE 2

CANDIDATE POHCs FOR HYPOTHETICAL WASTE

Compound	Approximate Concentration in Waste	B.P. (°C)	ΔH^1 kcal/mol[2] (kcal/g)	MW (g/mol)
Hexachlorobutadiene[3]	65 %	215	553 (2.12)	260.74
Hexachlorobenzene[3]	6 %	323-326	510 (1.79)	284.76
Hexachloroethane[3]	2 %	186.8	109 (0.46)	236.72
Tetrachloroethane				
1,1,1,2-	1.5%	130.5	233 (1.39)	167.84
1,1,2,2-		146.5	233 (1.39)	167.84
Tetrachloroethene (Tetrachloroethylene)	0.1%	121.0	197 (1.19)	165.82

[1] Standard Enthalpy of Combustion

[2] 1 kcal/g = 1.8 x 10^3 Btu/lb

[3] Designated as POHC for the trial burn

TABLE 3

RECOMMENDED STACK SAMPLING METHODS FOR CANDIDATE POHCs IN HYPOTHETICAL TRIAL BURN EXAMPLE

Candidate POHC	Stack Sampling Method	
	Number	Description
Hexachlorobutadiene[1]	S008[2]	MM5 - Sorbent
Hexachlorobenzene[1]	S008[2]	MM5 - Particulate and Sorbent
Hexachloroethane[1]	S008[2]	MM5 - Sorbent
Tetrachloroethane(s)	S008[2]	MM5 - Sorbent
Tetrachloroethene (Tetrachloroethylene)	S008[2]	MM5 - Sorbent

[1]Designated as a POHC for the trial burn.

[2]Method S009 (SASS) could also be selected. A specially fabricated glass-lined SASS train might be necessary to withstand the hydrochloric acid concentration expected in the stack gas.

c. Selection of Sample Preparation Methods

The procedures used in the preparation of field samples for subsequent analysis of the designated POHC(s) and other target species are determined both by the nature of the sample medium and the nature of the species sought.

The samples which have been collected for Test No. 1 of the trial burn include a composite sample of still bottom waste (organic liquid/sludge), one composite sample of spent scrubber water (aqueous liquid), and one time-integrated stack gas sample collected with a MM5 comprehensive sampling train. The stack gas sample is composed of several discrete subsamples (Figure 2) which are prepared individually--probe wash and filter catch (solid), sorbent trap (solid), condensate (aqueous liquid), and impinger solution (aqueous liquid).

Representative aliquots of samples must be obtained prior to subsequent extraction procedures. Method P001 is appropriate for obtaining representative aliquots of both the waste and scrubber water samples. For the various MM5 samples, aliquots are not necessary since the entire sample is usually extracted. The target species (hexachlorobutadiene, hexachlorobenzene, and hexachloroethane) require the addition, prior to extraction, of a surrogate to monitor the recovery of the neutral extractable organics (Method P014). (For the probe wash and filter catch samples, the surrogate(s) are added after the samples have been dried to constant weight, and the particulate loading obtained.)

The appropriate extraction procedure is primarily determined by the sample medium. Review of available extraction procedures suggests that liquid/liquid extraction (Method P021a) is appropriate for aqueous liquid samples (scrubber water and MM5 train condensate), solvent dilution (Method P023) for organic liquids (still bottom waste), and liquid/solid extraction in a Soxhlet apparatus (Method P024b) for the solid samples (combined probe wash and filter catch and the sorbent trap from the MM5 train). The resulting sample extracts are then concentrated (Method P031) for subsequent analysis procedures, assuming further cleanup procedures (Methods P041-P045) are not needed to remove interferences. All extracts from the MM5 train samples (probe wash/filter catch, sorbent, and condensate) are combined prior to the concentration step to yield one sample extract for analysis. A representative aliquot (Method P001) of the impinger solution is removed for analysis of chloride by ion chromatography.

d. Selection of Analysis Methods

The analytical procedures used for qualitative identification and quantitative determination of POHC(s) and other target species are determined primarily by the nature (volatility, polarity) of the species sought.

Appendix C lists recommended analysis methods for each candidate POHC after the appropriate sample preparation steps (described in Section IV) have been performed. Table 4 summarizes the recommended analysis methods for the candidate POHCs in this hypothetical example. Note that a single analytical method suffices to determine all of the hexachloro- species of concern here, while an additional method would be recommended if it were desired to include the tetrachloroethanes and tetrachloroethene.

4. Results and Calculations

Chapter VI includes formats for reporting the results of specific analyses and Chapter VII deals with overall reporting and documentation procedures. This section of Chapter III supplements these discussions and those available in other resources (2-5), by showing the calculations of DRE, corrected particulate loading, and HCl emissions for the hypothetical example described above. Again, this example has been somewhat oversimplified for purposes of illustration.

According to 40 C.F.R. Part 264, the DRE for each POHC is calculated as:

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} \times 100\%$$

where:

W_{in} = mass feed rate of one POHC in the waste stream feeding the incinerator, and

W_{out} = mass emission rate of the same POHC present in stack exhaust gas emissions.

a. Calculation of W_{in}

$$W_{in}\ (lb/h) = \frac{C_w \times FR_w}{100}$$

where:

C_w = concentration of POHC in waste (%), and

FR_w = mass feed rate of waste to the incinerator (lb/h).

Assume that quantitative analysis of a representative aliquot drawn from the composite waste sample from Test No. 1 of the trial burn gave the following concentrations:

TABLE 4

RECOMMENDED ANALYSIS METHODS FOR CANDIDATE POHCs IN HYPOTHETICAL TRIAL BURN EXAMPLE

Candidate POHC	Analysis Method	
	Number	Description
Hexachlorobutadiene[1]	A121	GC/MS Extractables
Hexachlorobenzene[1]	A121	GC/MS Extractables
Hexachloroethane[1]	A121	GC/MS Extractables
	A101	GC/MS Volatiles
Tetrachloroethane(s)	A101	GC/MS Volatiles
Tetrachloroethene (Tetrachloroethylene)	A101	GC/MS Volatiles

[1]Designated as POHC for the trial burn.

hexachlorobutadiene:	63.0%
hexachlorobenzene:	9.4%
hexachloroethane:	1.1%

Further, assume that the 10 x 10^6 Btu/h thermal capacity of the facility was met by blending waste 1:10 with waste oil to give a feed mixture that was 7.5% chlorine and had a heating value of 16,400 Btu/lb (3.8 x 10^7 J/kg). The total mass feed rate to the incinerator was therefore 600 lb/h (272.2 kg/h), 540 lb/h (245 kg/h) of which was auxiliary fuel (waste oil) and 60 lb/h (27 kg/h) was chlorinated waste.

The W_{in} values for the three POHCs are therefore:

POHC		W_{in}
hexachlorobutadiene	(.630 x 60)	37.8 lb/h
hexachlorobenzene	(.094 x 60)	5.64 lb/h
hexachloroethane	(.011 x 60)	0.66 lb/h

b. Calculation of W_{out}

$$W_{out}\ (lb/h) = C_s \times ER_s \times 1.32 \times 10^{-4}$$

where:

C_s = concentration of POHC in the stack gas effluent (mg/dscm),

ER_s = volumetric flow rate of stack gas (dscm/min), and

1.32×10^{-4} = conversion factor from mg/min to lb/h.

Assume that quantitative analysis of the extract prepared from the time-integrated comprehensive sampling train sample from Test No. 1 of the trial burn gave the following concentrations in the sampled gas:

hexachlorobutadiene	0.080 mg/dscm
hexachlorobenzene	0.020 mg/dscm
hexachloroethane	$\leq$0.004 mg/dscm

Further, assume that the average measured volumetric flow of stack gas during Test No. 1 of the trial burn was 3200 dscf/min (90 dscm/min).

The W_{out} values for the three POHC therefore would be:

POHC		W_{out}
hexachlorobutadiene	$0.080 \times 90 \times 1.32 \times 10^{-4}$	9.5×10^{-4} lb/h
hexachlorobenzene	$0.020 \times 90 \times 1.32 \times 10^{-4}$	2.4×10^{-4} lb/h
hexachloroethane	$<0.004 \times 90 \times 1.32 \times 10^{-4}$	$< .48 \times 10^{-4}$ lb/h

c. Calculation of DRE

$$DRE = \left(\frac{W_{in} - W_{out}}{W_{in}} \right) \times 100\%$$

POHC	DRE
hexachlorobutadiene	99.997%
hexachlorobenzene	99.996%
hexachloroethane	>99.993%

Note that compliance with a four-nines DRE performance standard could not have been demonstrated in this particular example for a component present at <1% in the waste itself (or <1000 ppm in the 1:10 waste:fuel blend fed to the incinerator), unless the detection limit for that component in the stack gas were <4 µg/dscm.

In this hypothetical example, compliance with a $\geq$99.99% DRE performance standard has been demonstrated, in one test, for each of the three POHCs. If these results were supported by data from the other two replicate trial burn tests, the four-nines DRE could be considered to have been established.

d. Calculation of HCl Emissions

An incinerator which burns highly chlorinated hazardous waste capable of producing significant stack gas emissions of hydrogen chloride (HCl) must be monitored and/or controlled for the HCl emissions.

The hypothetical waste in this example contains approximately 75 percent chlorine by weight (Table 1). At the proposed 60 lb/h feed rate of waste (blended 1:10 with auxiliary fuel for a total feed of 600 lb/h or 9.8×10^6 Btu/h), the maximum HCl emission rate would be 45 lb/h (chlorine basis) or 46 lb/h (21 kg/h) as HCl. This is sufficiently high to warrant concern for potential HCl emissions and to indicate the necessity for stack measurement of HCl.

The stack emission rate of HCl can be calculated from:

$$HCl_{out}\ (lb/h) = C_{in} \times ER_s \times 1.32 \times 10^{-4}$$

where:

C_{in} = concentration of HCl (as Cl^-) in the stack gas effluent and collected in the impingers,

ER_s = volumetric flow rate of the stack gas (dscm/min), and

1.32×10^{-4} = conversion factor from mg/min to lb/h.

Assume that quantitative analysis of the impinger/condensate solution from the time-integrated comprehensive sampling train from Test No. 1 of the trial burn gave 34 mg/dscm HCl in the stack gas effluent.

The stack emission rate of HCl is calculated by:

$$HCl_{out} = 34\ mg/dscm\ (90\ dscm/min)\ (1.32 \times 10^{-4})$$

$$= 0.40\ lb/h\ HCl$$

This emission level is <1% of the 46 lb/h of HCl potentially generated from the waste, indicating that the removal efficiency of the wet scrubber was >99%, and the incinerator is shown to be in compliance with the Part 264 performance standard which limits HCl emissions from the stack.

e. Calculation of Particulate Loading

An incinerator burning hazardous waste must not emit particulate matter in excess of 180 milligrams per dry standard cubic meter when corrected to a standard excess air level (7 percent oxygen) in the stack gas according to the performance standard outlined in 40 C.F.R. Part 264.

Assume that prior to chemical analysis, particulate samples from the stack effluent of the hypothetical waste (from probe washes and filter catches of the time-integrated comprehensive sampling train) were dried and weighed. The hypothetical particulate loading from these measurements was calculated to be 80 mg/dscm at the actual excess air level of the stack exhaust gas. The excess air level was determined to be 150 percent based on a measured oxygen level of 12.8 percent.

The measured oxygen level is corrected to a standard excess air level and a corrected particulate loading calculated as specified in the Part 264 regulations, according to the following formula:

$$P_c \text{ (mg/dscm)} = P_m \times \frac{14}{21 - Y}$$

where:

P_c = corrected concentration of particulate matter (mg/dscm),

P_m = measured concentration of particulate matter (mg/dscm), and

Y = measured concentration of oxygen in the stack gas using the Orsat method for oxygen analysis of dry flue gas (%).

The corrected particulate loading is then 140 mg/dscm (0.06 gr/dscf).

Therefore, it is determined that this total particulate emission level is in compliance with the Part 264 performance standard which specifies that particulate emissions cannot exceed 180 mg/dscm (0.08 gr/dscf).

f. Summary

It is apparent that this sample of hypothetical waste when burned under these conditions complies with the Part 264, Subpart O, incinerator performance standards as they relate to:

- destruction and removal efficiency-
  All three POHCs showed compliance with the $\geq$99.99% DRE performance standard;

- limitation on HCl emissions-
  The HCl emission rate of 0.40 lb/h shows compliance with a $\geq$99% removal standard for HCl; and

- limitation on stack emissions of particulate material-
  The corrected particulate loading of 140 mg/dscm shows compliance with the 180 mg/dscm standard for particulate loading (corrected to a standard excess air level).

If these results are supported by data from two replicate hypothetical waste samples, compliance could be considered to have been established.

IV. SAMPLING PROCEDURES

A. OVERVIEW

The sampling methods which are required for the ultimate analysis of POHCs in hazardous wastes and incinerator effluents during trial burns may be required to address a variety of media. The hazardous waste prior to incineration may be a solid, liquid, slurry, or sludge. Following combustion, POHCs may be found in solids (e.g., bottom ash, fly ash/ESP catches), liquids (scrubber water), or the stack gas with its entrained particulate material. In this discussion, the sampling methods appropriate to each influent and effluent stream of a hazardous waste incinerator are discussed. Each sampling method is described in an outline which also indicates the sample matrix and the general hardware requirements for the sampling method. Reference to a primary source, where a complete detailed description of the method can be found, is also included.

Liquid and gaseous sampling methods are likely to be most important for both routine and trial burn monitoring. It is expected that most hazardous wastes to be incinerated will be liquids, sludges, or slurries. Often these wastes will be contained in drums following transportation from the generator to the disposal facility. Such wastes are amenable to sampling with a Coliwasa (composite liquid waste sampler). During trial burns, the calculation of the destruction and removal efficiency (DRE) value for the designated POHC(s) requires the measurement of the POHC(s) in the stack gas following all emission control devices. The required DRE value, 99.99 percent minimum, for each POHC places severe constraints on the sampling system for stack exhaust gases. It should be remembered that only during the trial burn does specific POHC sampling occur. During routine incinerator operation, sampling requirements are significantly less.

B. SAMPLING METHODS FOR INFLUENT STREAMS

The preferred sampling method for the influent streams to a hazardous waste incinerator depends upon the exact form of the influent (solid, sludge, liquid, etc.). This section presents a summary description of the general methods which are to be used for the sampling of the influent streams to a hazardous waste incinerator. Table 5 summarizes the sampling devices appropriate for hazardous waste sampling and Table 6 summarizes typical sampling points for most waste containers.

The basic strategy for sampling of influent waste streams to a hazardous waste incinerator during a trial burn is the compositing of individual grab samples of the influent waste. To obtain a representative sample of the waste, the number and frequency of the grab samples collected

TABLE 5

CHOICE OF SAMPLERS FOR HAZARDOUS WASTES

Waste Type	Sampler	Limitations/Comments
Liquids, sludges and slurries in drums, vacuum trucks, barrels, and similar containers	Coliwasa	Not for containers >1.5m deep.
	a) Plastic	Not for wastes containing ketones, nitrobenzene, dimethylformamide, mesityl oxide, or tetrahydrofuran (5).
	b) Glass	Not for wastes containing hydrofluoric acid and concentrated alkali solutions.
Liquids and sludges in ponds, pits or lagoons	a) Dipper	Cannot be used to collect samples beyond 3.5m; dip and retrieve sampler slowly to avoid bending the tubular aluminum handle.
	b) Weighted Bottle	May be difficult to use on viscous liquids; the bottle may also be used as the sample container.
Wastes in storage tanks	Weighted Bottle	May be difficult to use on viscous liquids; the bottle may also be used as the sample container.
Powdered or granular solids in bags, drums, or containers	a) Thief	Limited application for sampling moist and sticky solids and when the diameter of the solids is greater than 0.6 cm.
	b) Trier	May incur difficulty in retaining a core sample of very dry granular materials during sampling.
Dry wastes (in shallow containers) and surface soil	Trowel	Not applicable to sampling deeper than 8 cm. Difficult to obtain a reproducible sample mass.
Waste piles	Waste Pile Sampler	Not applicable to sampling solid wastes with dimensions greater than one-half the diameter of the sampling tube.

Source--References 2, 4, and 5.

TABLE 6

SAMPLING POINTS FOR MOST WASTE CONTAINERS

Container	Sampling Point
Drum (bung on one end)	Withdraw sample through the bung opening.
Drum (bung on side)	Lay drum on side with bung up; withdraw sample through the bung opening.
Barrels, fiberdrums, buckets, sacks, or bags	Withdraw samples through the top of barrels, fiberdrums, buckets, and similar containers, or through fill openings of bags and sacks; withdraw sample through the center of the containers and to different points diagonally opposite the point of entry.
Vacuum truck (or similar)	Withdraw sample through open hatch; sample all other hatches.
Ponds, pits, lagoons	Divide surface area into an imaginary grid;* take three samples, if possible: one sample near surface, one sample at mid-depth or at center, and one sample at the bottom; repeat the sampling at each grid over the entire pond or site.
Waste piles	Withdraw subsurface sample through at least three different points near the top of pile to points diagonally opposite the point of entry.
Storage tanks	Withdraw sample from the top through the sampling hole.
Soils	Divide the surface area into an imaginary grid;* sample each grid.

*The number of grids is determined by the desired number of samples to be collected which, when combined, will give a representative sample of the waste.

Source--References 2, 4, and 5.

will vary, depending upon the engineering design of the waste feed system. In general, a minimum of three individual grab samples will be composited to ensure adequate integration over time (for continuous feed processes) or over mass (for batch feed processes).

1. Sampling Methods for Liquid Wastes

a. Coliwasa (Method S001)

The most important liquid sampler for use in sampling hazardous wastes is the composite liquid waste sampler (Coliwasa). The design of this device is both simple and inexpensive, and permits the sampling of both free-flowing liquids and slurries, including multiphase wastes. Coliwasa samples may be collected rapidly, thus minimizing the exposure of the sample collector to the potential hazards of the waste. In addition, although not commercially available, the Coliwasa sampler is simple to fabricate and inexpensive enough that contaminated parts may be discarded after a single use if the parts cannot be easily cleaned.

The fabrication of a Coliwasa has been thoroughly documented (5), with the selection of the sampling tube material (PVC or borosilicate glass tubing) for a particular waste determined by the components of the waste, as described in Table 5. To collect a waste sample, the Coliwasa is slowly lowered into the waste container, a liquid sample is removed from the waste, and the waste sample is transferred to a storage container. This process is repeated until the requisite quantity of sample has been collected. The primary limitation on the use of a Coliwasa is that the sample depth cannot exceed 1.5m. However, most of the liquid hazardous wastes which will be sent to incinerator facilities will probably be contained in drums, barrels, and tanks where this limitation will not be important.

b. Dipper or Pond Sampler (Method S002)

The dipper or pond sampler, permits collection of liquid samples in ponds, pits, lagoons, and tanks with open tops. The sampler consists of an adjustable clamp attached to the end of a multiple-piece telescoping aluminum tube; the clamp is used to secure a sampling beaker or bucket. This device is not sold commercially, but the pieces may be obtained from hardware or swimming pool stores (for the telescoping tube) and laboratory supply houses (for the clamp and beaker).

Dipper samples can be collected from open streams such as sluices or from open tanks where there is sufficient access to permit the insertion and removal of the dipper apparatus. A sample is collected by inverting the beaker and then slowly lowering it into the liquid to be sampled. At the appropriate depth, a rapid push-pull motion will rotate the beaker opening toward the surface and allow a waste sample to be collected. This device may be used to obtain samples as far as 3.5m from the edge of the tank and at different depths.

c. Weighted Bottle Sampler (Method S003)

The weighted bottle sampler usually consists of a glass bottle, a weight sinker, a bottle stopper, and a line which is used to raise and lower the bottle during sampling, as well as to open the bottle at the appropriate sampling depth. Descriptions of this device are found in ASTM Methods D-270 (8) and E-300 (9). These methods use a metallic bottle basket which also serves as the weight sinker. These devices may be either fabricated or purchased.

The use of a weighted bottle to sample liquids contained in storage tanks, wells, sumps, or other containers which cannot be adequately sampled with the other liquid sampling devices, involves lowering the bottle to the appropriate depth, uncapping it, and after completely filling it, withdrawing the sampler. Once out of the waste, the bottle may be capped, rinsed off, and used as the sample storage container. The sampler cannot be used to collect liquids that are incompatible with, or chemically react with, the weight sinker or the control lines.

d. Tap Sampling (Method S004)

Tap sampling is the appropriate method for sampling liquid wastes in pipes or ducts. Coliwasa sampling is not appropriate to the collection of liquids from moving streams. For liquids in motion, such as scrubber water which mixes while being recycled, a simple tap, either in the process line or in the storage reservoir, allows collection of a representative sample. For this method, a sampling line is attached to the tap and inserted into the sampling bottle. The tap is opened to permit a flow such that the sample fill-time exceeds five minutes. Both the sampling line and bottle are flushed several times prior to isolation of the sample. Excess waste should be returned to the feed tank or disposed of in accordance with facility procedures. This method is described fully in ASTM Method D-270 (8).

2. Sampling Methods for Solid Wastes

A wide variety of sampling tools are available for the sampling of solid materials. The most suitable of these methods for the sampling of hazardous waste are the grain sampler (thief), the sample corer (trier), and the trowel (scoop). The use of each sampler is described in detail in SW-846 (4).

a. Thief or Grain Sampler (Method S005)

The grain sampler, also called a thief, consists of two slotted telescoping tubes, usually made of brass or stainless steel. The outer tube has a conical pointed tip on one end which permits the sampler to penetrate the material being sampled. The sampler is opened and closed by rotating the inner tube. While open, the sampler is shaken to permit the free-flowing sample to fill the interior of the sampler.

b. Trier or Sample Corer/Waste Pile Sampler (Method S006)

A typical trier or sample corer consists of a long tube with a slot that extends almost the entire length of the tube. The waste pile sampler is essentially a large sample corer. While not commercially available, these samplers can be easily fabricated from sheet metal or plastic (PVC) pipe. The tip and edges of the tube slot are sharpened to allow the corer to cut a core of the material to be sampled when rotated after insertion into the material. The sampler is inserted into the waste at an oblique angle and withdrawn with the open portion pointed upwards. Sample corers are usually made of stainless steel with wooden handles, and can be purchased from laboratory equipment suppliers. Its use is similar to that of the grain sampler as discussed above. However, the trier is preferred over the grain sampler when the powdered or granular material to be sampled is moist or sticky.

The waste pile sampler is used to sample wastes in large heaps, with cross-sectional diameters greater than 1m. In addition, this sampler can be used to sample granular or powdered wastes in large bins, silos or barges where the grain sampler and corer are not long enough. This sampler will not collect representative samples when the diameter of the solid particles in the waste exceeds one-half the diameter of the tube.

c. Trowel or Scoop (Method S007)

A trowel looks like a small shovel. A laboratory scoop is similar to the trowel except that the blade on the trowel is usually more curved and has a closed upper end to permit the containment of material. A trowel can be purchased from hardware stores; the scoop can be purchased from laboratory equipment suppliers. An ordinary zinc-plated garden trowel can be used in some cases to sample dry granular or powdered materials in bins or other shallow containers. The laboratory scoop, however, is a better device because it is usually made of materials less subject to corrosion or chemical reactions, thus lessening the probability of sample contamination.

3. Sampling Methods for Slurry and Sludge Samples

Slurries and sludges may be sampled employing the methods described previously (such as the Coliwasa). Free-flowing sludges and slurries may be appropriately sampled as liquids. For compacted sludges, i.e., non-free-flowing, the solid waste samplers used for moist samples (such as corers and trowels) are appropriate.

4. Sampling Methods for Water Samples

Scrubber water and other liquid hazardous waste influents to a hazardous waste incinerator are usually sampled by the dipper or tap sampling method.

C. SAMPLING METHODS FOR EFFLUENT STREAMS

Sampling of the effluent streams of a hazardous waste incinerator serves several purposes. During trial burns, the measurement of POHCs in the stack gas effluent is an integral part of the calculation of DRE values to determine whether the incinerator meets its performance criteria. In addition, other effluent streams such as scrubber waters and solids, have to be monitored periodically to ensure that these effluents are disposed of in an environmentally acceptable manner.

1. Sampling Methods for Stack Gas

The sampling of stack gas components is most important to the hazardous waste incinerator permitting process. In general, the sampling apparatus for collecting stack gas effluents includes three major components: (a) an extractive probe which must be resistant to physical and chemical reactions with the gas being sampled; (b) one or more thermostatted compartments to maintain the gas at a temperature consistent with the collection medium, usually hot (200°C) for particulate collection and cool (20°C) for sorbent collection of the more volatile constituents; and (c) the sample collector. Some of the sampling devices integrate all three components into a single unit, while other methods require the addition of one or more components before they are suitable for use.

In general, the deployment of stack gas sampling trains for the measurement of emissions from a hazardous waste incinerator should parallel the procedures specified in EPA Methods 1-5 (6) for particulate emissions testing. Criteria for selection of sampling port locations and number, location of sampling points within a stack, and assurance of isokinetic sampling rates are comparable with the Modified Method 5 train and SASS train. These criteria are discussed in both EPA Methods (6) and in "Air Pollution (Volume III)" (10).

In addition to the Modified Method 5 and SASS trains, a volatile organic sampling train (VOST) has recently been developed for the collection of volatile POHCs at low concentrations in stack gas effluents.

a. Modified Method 5 Train (Method S008)

The Modified Method 5 (MM5) sampling train is one of the comprehensive sampling systems which is used to sample stack gas effluents. This system is based upon the design of units which normally are employed for sampling under EPA Method 5 (6). The modified system consists of a probe, an optional cyclone, a high-efficiency glass or quartz fiber filter stage, a sorbent module, four impingers, and some control hardware. The sorbent module, the modification to the basic system which permits trapping of volatile organic vapors, is mounted vertically atop the first impinger of the train. This impinger is empty and is used to collect the condensate which percolates through the sorbent resin module.

A diagram of this system is shown in Figure 3. Physical construction details and assembly details of this system have been described by Martin (11) and maintenance procedures have been described by Rom (12). This system may be used for either stack gas sampling or combustion zone sampling with differences only in the type of probe utilized.

For stack gas sampling, either medium-wall Pyrex glass tubing (for probes less than 2.1m (7 ft) in length) or 1.6 cm O.D. Inconel 825 tubing (for probes greater than 7 ft long) is wrapped with heating wire and a stainless-steel jacket. Samples are collected while the probe is heated to a gas temperature above the dew point of the stack gas. If sampling of combustion zone vapors is necessary or desirable for a particular trial burn, a water-cooled, quartz-lined sampling probe is used (13). A stainless-steel jacket surrounds the quartz probe liner, and the water cooling decreases the temperature of the exiting gas to about 205°C (400°F).

The ball or spherical joint of the probe connects to a glass cyclone with a collection flask attached. The use of the glass cyclone is optional. The purpose of the cyclone is to remove large quantities of particulates and prevent plugging of the filter. In gas streams where the particulate loading is expected to be minimal, the cyclone may be replaced with a glass tube connecting the probe to a glass filter holder. If the cyclone is not used, the cyclone outlet is connected to the glass filter holder. This holder is equipped with a very coarse, fritted glass filter support and a tared glass or quartz fiber filter. The cyclone, flask, and filter holder are contained in an electrically heated enclosed box which is thermostatically maintained at a temperature of 120°C $\pm$ 12°C (250°F $\pm$ 25°F) which is sufficient to prevent water condensation in this portion of the train.

Downstream of the heated filter, the sampled gas passes through a water-cooled module and then to a sorbent module that is filled with XAD-2 resin. The XAD-2 sorbent is a porous polymer resin with the capability of adsorbing a broad range of organic species. The sorbent module is expected to give efficient collection of vapor phase organic materials with boiling points $\geq$100°C (200°F) (14,15,16,17).

A diagram of a suitable sorbent module is shown in Figure 4. Alternative designs in which the cooling and sorbent portions are separate components are also acceptable and may be more conveniently cleaned. Before the sampled gas reaches the sorbent resin, it is cooled to a temperature of 20°C (70°F). This may cause some of the water vapor in the sampled stream to condense and, in turn, some organic vapor may become entrained in the condensate. For this reason, the condensate is allowed to percolate through the resin bed prior to being discharged into a collection vessel.

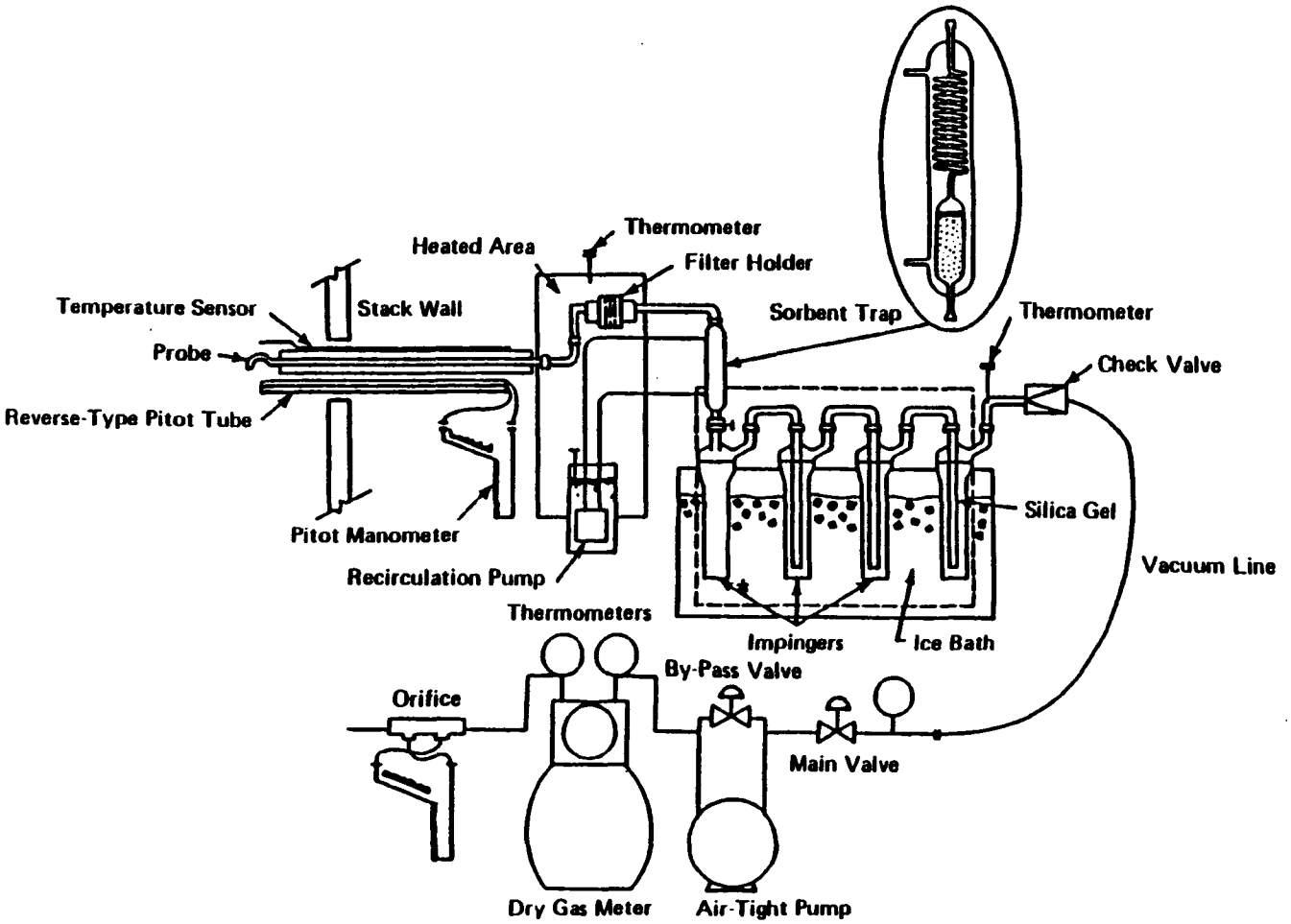

FIGURE 3 MODIFIED METHOD 5 TRAIN (MM5)

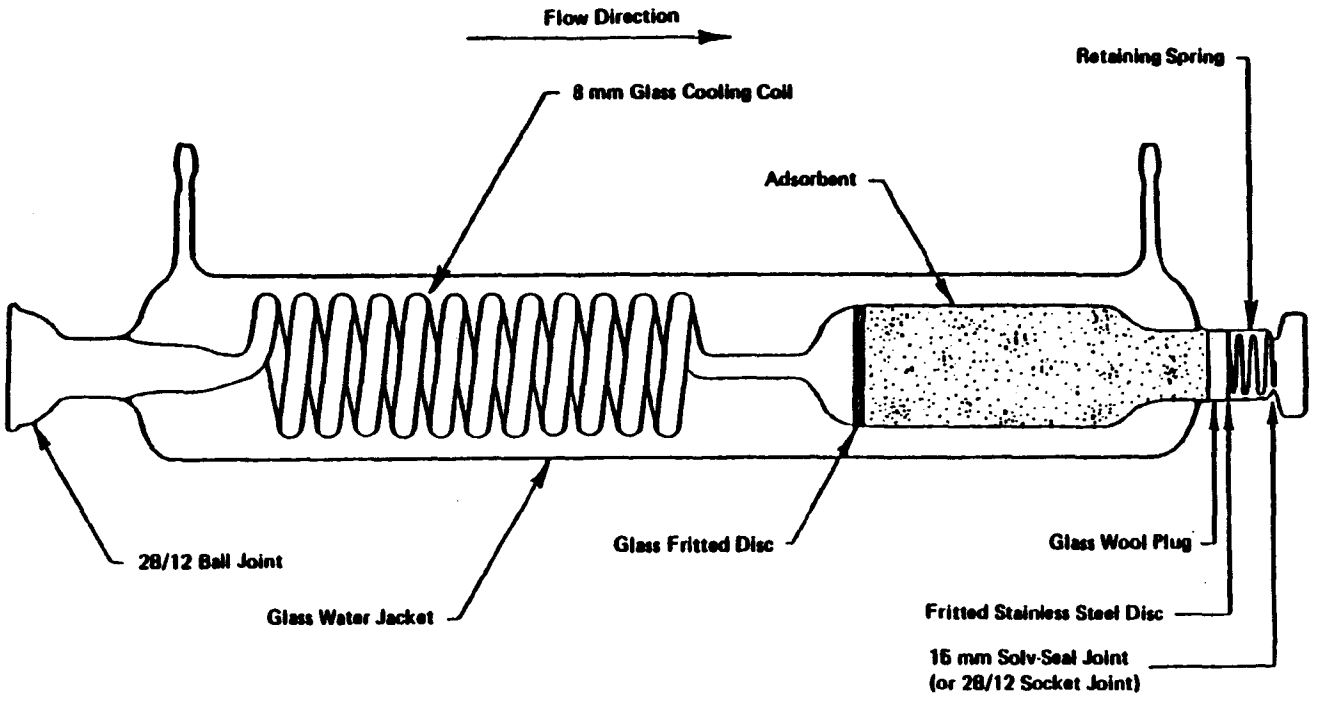

FIGURE 4 SORBENT MODULE

At the downstream side of the sorbent module, four impingers are connected in series and immersed in an ice bath. The first impinger, connected to the outlet of the sorbent module, is modified to have a very short stem, so that the sampled gas does not bubble through the collected condensate. An oversized impinger may be required for sampling high moisture streams since the first impinger collects the condensate, which passes through the sorbent module, for subsequent organic analysis. The second impinger is a modified version of a Greenberg-Smith design; initially it is filled with scrubbing solution. The selection of scrubbing solution is contingent upon the type of vapors that are suspected of being contained in the stack gas. A caustic solution such as sodium hydroxide or sodium acetate, is used to collect acidic gases such as HCl. (Sodium acetate may be used to prevent depletion of scrubbing reagent by carbon dioxide.) For collecting volatile metals (mercury, arsenic, selenium), a strongly oxidizing solution (such as the SASS silver-catalyzed ammonium persulfate) must be used. The third impinger is a Greenberg-Smith impinger with a tip; it is also filled with an appropriate scrubbing solution. The fourth impinger is typically filled with silica gel to absorb any moisture in the stack gas. Moisture removal is important to ensure accurate gas flow measurements and to prevent damage to the pumping system.

During operation, the MM5 train typically collects a 4-6 dry standard cubic meter (dscm) sample over a sampling time of 3-5 hours. A near isokinetic sampling rate is maintained throughout the sample collection.

b. Source Assessment Sampling System (SASS) (Method S009)

The Source Assessment Sampling System (SASS) is an alternative integrated stack gas sampling system. In many respects, the SASS train is about a five-fold scale-up of the MM5 train and collects a larger sample, typically 30 dscm over a 3-hour sampling period. This sampling train is appropriate whenever a large sample of stack gas (greater than 10 dscm) is required to ensure adequate detection limits.

The SASS train consists of a stainless-steel probe that connects to three cyclones and a filter in an oven module, a gas treatment section, and an impinger series (Figure 5). Size fractionation is accomplished in the cyclone portion of the SASS train, which incorporates three cyclones in series to provide large collection capacities for particulate matter nominally size-classified into three ranges: (a) >10 μm, (b) 3 μm to 10 μm, and (c) 1 μm to 3 μm. By means of a standard 142 or 230 mm filter, a fourth cut, <1 μm, can also be obtained. The gas treatment system follows the oven unit and is composed of four primary components: the gas cooler, the sorbent trap, the aqueous condensate collector, and a temperature controller. Volatile organic material is collected in a cartridge or "trap" containing XAD-2 sorbent, a macroreticular resin with the capability of adsorbing a broad range of organic species. The XAD-2 cartridge in the SASS train

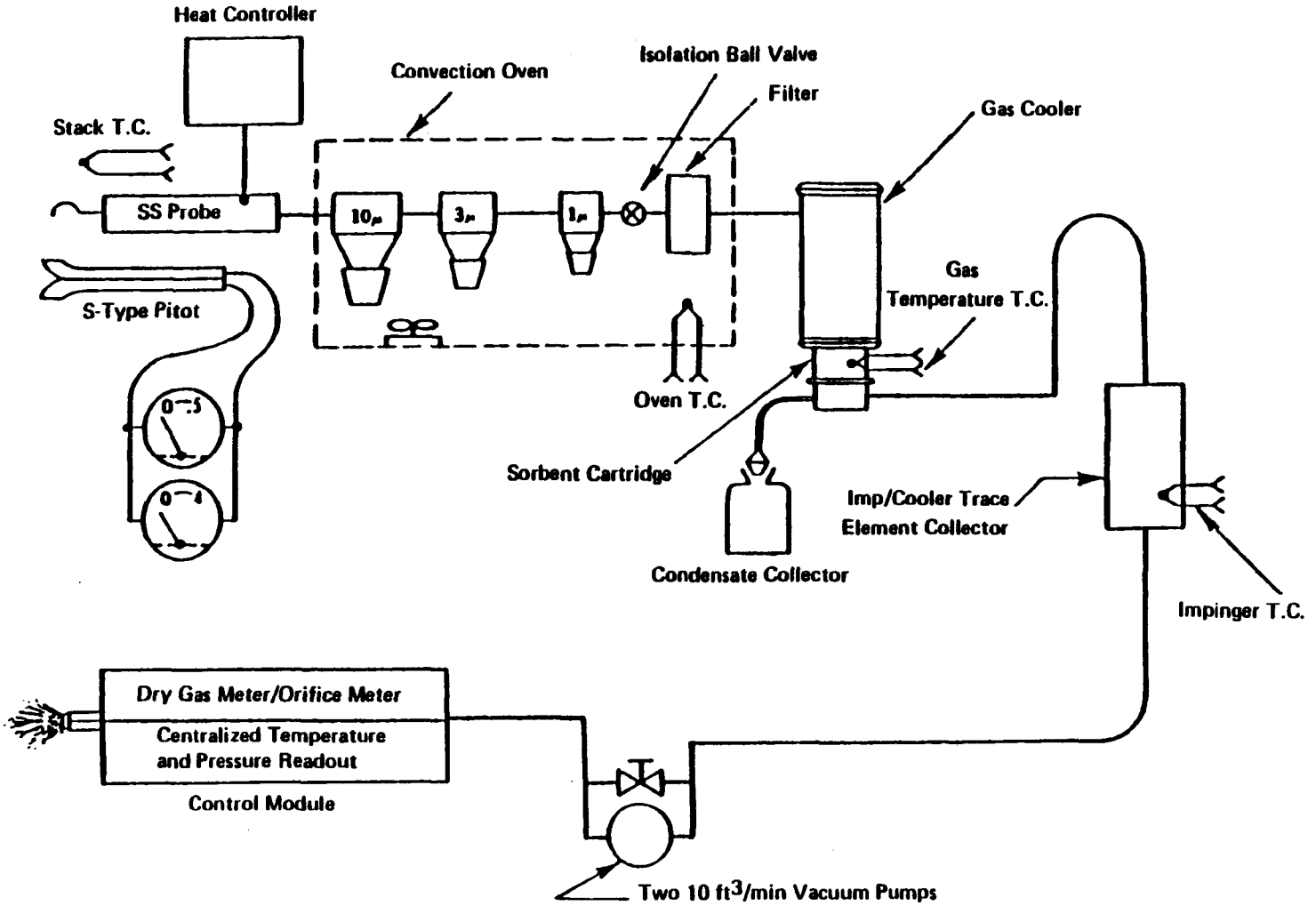

FIGURE 5 SOURCE ASSESSMENT SAMPLING SYSTEM (SASS)

is sized to ensure efficient collection of vapor phase organic materials with boiling points $\geq$ 100°C (200°F). Volatile inorganic elements are collected in a series of impingers that follow the condenser and sorbent system. Trapping of some inorganic species also may occur in the sorbent module. The last impinger in the series contains silica gel for moisture removal.

This train was not designed for traversing a stack or for sampling at stack gas temperatures above 260°C (500°F), although it could be adapted, with suitable modifications, to these sampling situations. In routine stack sampling, the stack to be sampled is velocity-traversed once to locate a position near the center of the stack which has an average stream velocity. The velocity at the sampling point, the stack temperature, and moisture content are used to calculate the size of the probe nozzle which will give approximately isokinetic sampling conditions (10). The appropriately sized nozzle is attached to the probe for the subsequent sampling effort.

c. Gas Bulb and Gas Bag Sampling Systems (Methods S010, S011)

In addition to the stack gas sample collected with the comprehensive sampling system, other gas phase stack samples may have to be collected during some particular trial burns if volatile organic species are among the designated POHCs for the purpose of calculating the DRE performance. This type of sample is required because the sorbent module and filter units contained within the comprehensive sampling system (MM5 or SASS) are not efficient for the collection of organic material with boiling points below 100°C (200°F). Therefore, organic materials with high volatility may pass through the comprehensive sampling system without being collected quantitatively.

To collect volatile POHC species, gas bulb samples of the stack exhaust gas should be obtained during each trial burn when constituent(s) of high volatility are designated as the POHC(s). The gas bulb may be either directly coupled to a point that is downstream from the sorbent module in a MM5 or SASS sampling train, or to a separate sampling line within the stack. The latter alternative is preferred since the flow in the comprehensive sampling system would not be disturbed.

For gas bulb sampling, the bulb is evacuated prior to connection to the sample line and then it is allowed to fill with stack gas effluent (or combustion zone effluent, if desired). Once the bulb is filled, the sample valve is closed and firmly sealed. The bulb is removed and shipped to the laboratory for analysis. A diagram of a typical gas bulb collection system is shown in Figure 6. An outer styrofoam container is used for thermal insulation during handling and for sample safety during shipping.

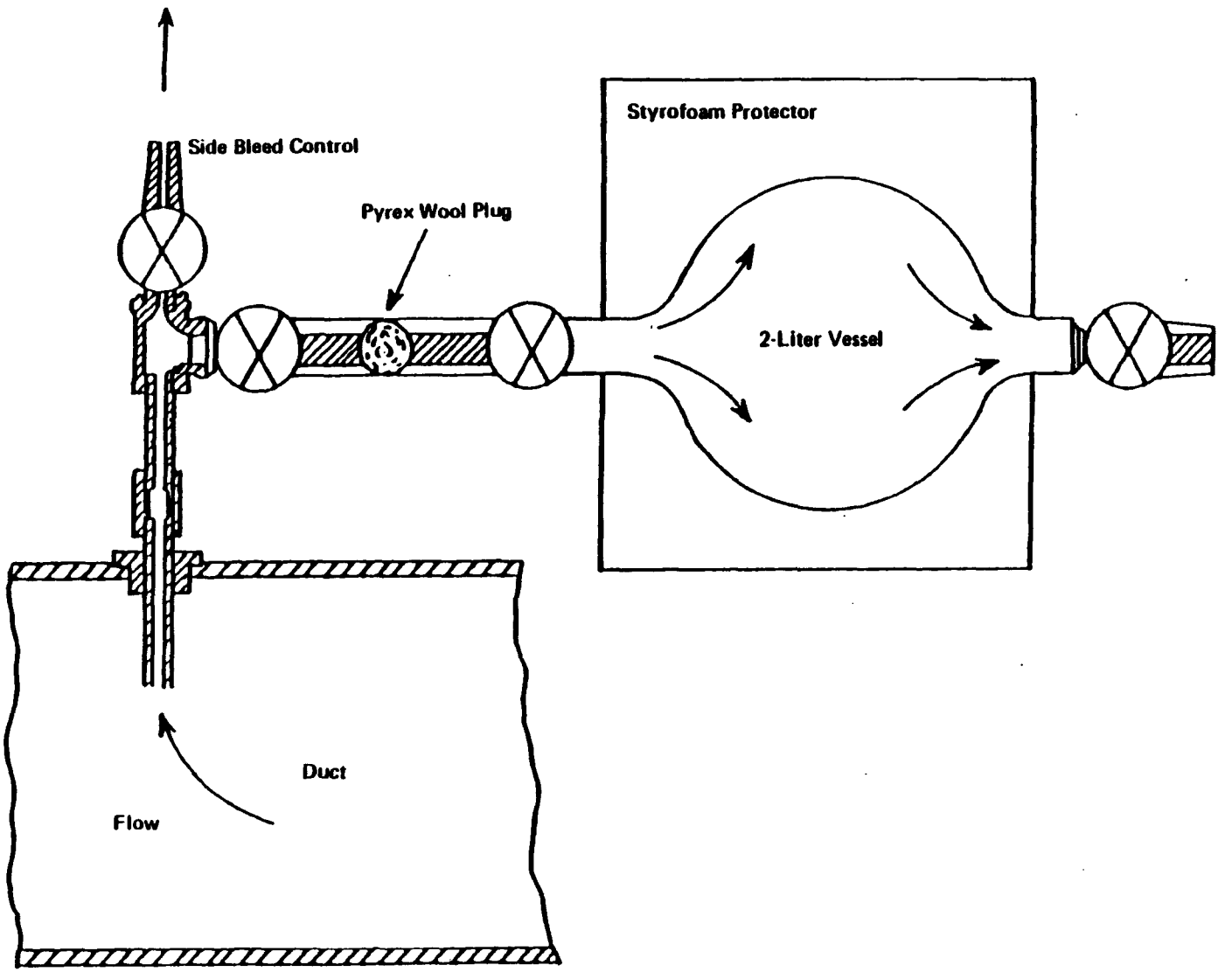

FIGURE 6 EVACUATED GRAB SAMPLING APPARATUS (FOR SUBATMOSPHERIC PRESSURES)

The amount of sample which has to be collected is a function of the limit of detection requirements for the POHC(s) which is being monitored. An alternative approach is to use gas bag sampling with an integrated sampling train, as shown in Figure 7. The gas bag collects a 10 to 30L gas sample which can be integrated over a reasonably long sampling time (e.g., 3 hours).

For gas bag sampling, a nonreactive probe is inserted into the stack and the gas sample is first bled or drawn through the probe, and then through an air-cooled condenser, or equivalent, at a rate which is regulated by a small diaphragm pump. The condenser serves to remove excess moisture from the gas stream and to cool the gas to a temperature which is compatible with the physical characteristics of the bag. A flow rate meter is used to adjust and measure the gas flow into the bag. Gas bag sampling should only be used for those components for which it is validated. Also, it is important that field blank gas bag samples (i.e., gas bags filled with air drawn from a cylinder) are collected at the same time that the field samples are collected.

d. Volatile Organic Sampling Train (VOST) (Method S012)

After reviewing previous editions of this document and also the results of previous hazardous waste incineration trial burns, it seems that the volatile hazardous constituents are important components in incinerator effluents. Thus, the need to develop a better and more sensitive sampling and analysis technique for these volatile constituents is apparent. Therefore, the concept of a volatile organic sampling train (VOST) was developed as an alternative to the use of the integrated gas bag sampling system, or the gas bulb sampling system for the collection of volatile POHCs. The VOST has since been evaluated by Midwest Research Institute (Kansas City, Missouri). A paper which describes the equipment and procedures used during a laboratory evaluation of the VOST, data from the collection, and analysis of four volatile constituents taken during the laboratory evaluation, a description of a field version of the VOST, and conclusions and recommendations from the study, has been included as Appendix F of this report.

The VOST which was evaluated consisted of a system designed to draw effluent gas at a flow rate of 1L/min through two traps (1.6 cm in diameter x 10 cm) in series (Figure 8). The first trap contained Tenax and was preceded by a gas cooler/condenser and followed by an impinger for condensate collection. A second trap, containing a section of Tenax and a section of charcoal, was located after the impinger. The purpose of the second trap was to collect very volatile compounds (e.g., vinyl chloride) which readily break through a Tenax trap. The concept also involved replacing both pairs of traps with fresh traps every 20 minutes (20L sample) over a 2 hour sampling period, for a total of six pairs of traps. The collection of several pairs of traps assures that the more volatile components will not break through

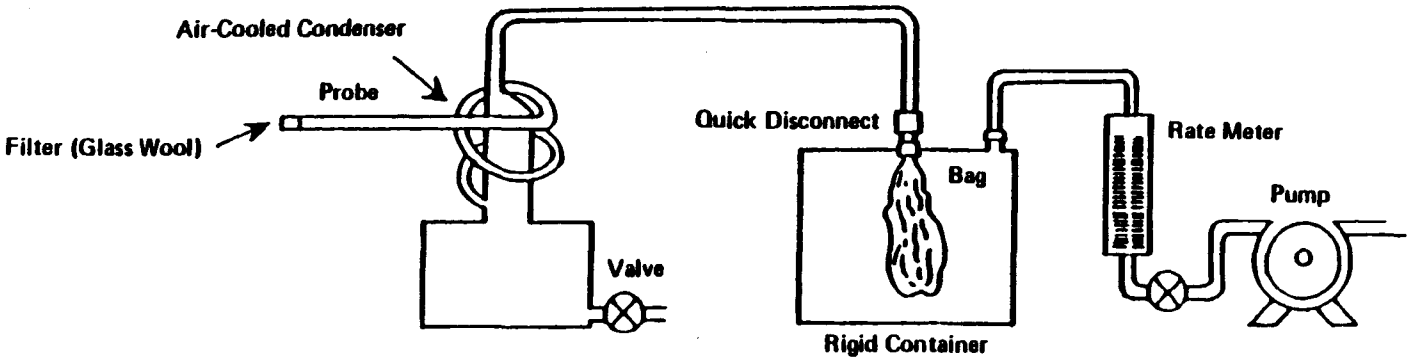

FIGURE 7 INTEGRATED GAS-SAMPLING TRAIN: GAS BAG

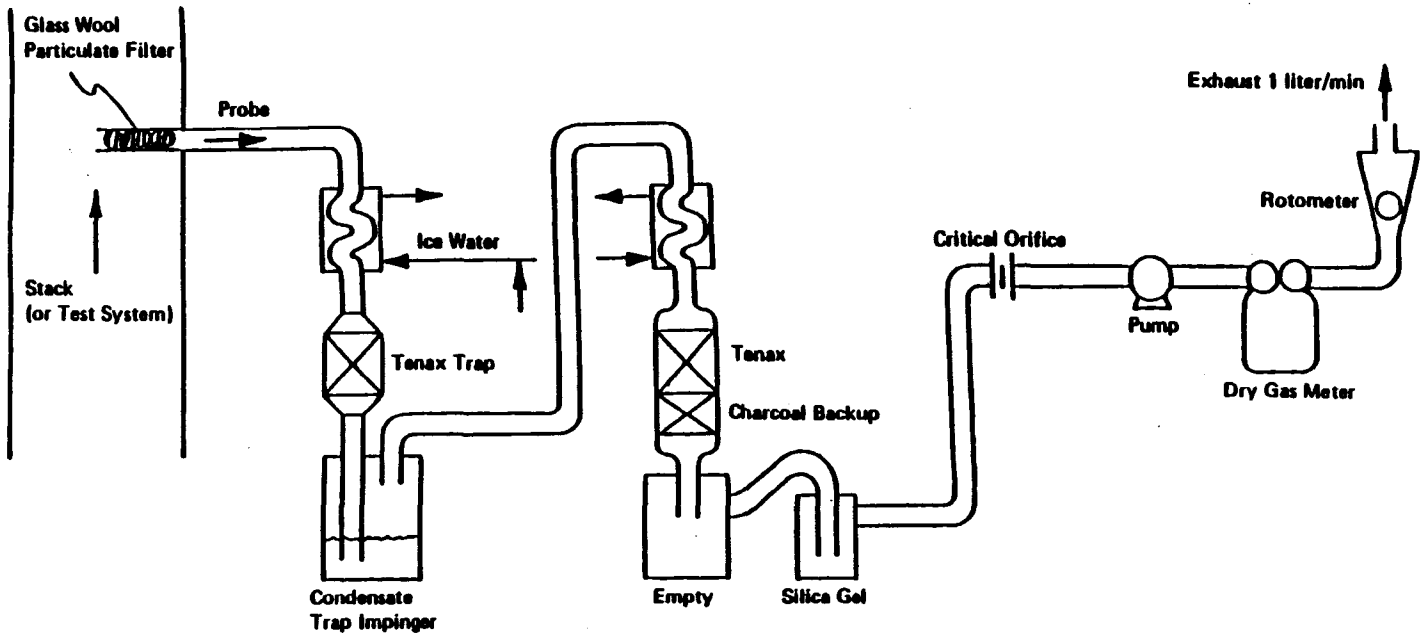

FIGURE 8 VOLATILE ORGANIC SAMPLING TRAIN (VOST)

both the front (Tenax) and back (Tenax/charcoal) traps. Also, a range of POHC concentrations are obtained since the contents of one or all pairs of traps can be combined for analysis.

Prior to sampling it may be useful to spike the Tenax and Tenax/charcoal traps with the compounds of interest to ensure that they can be thermally desorbed at the time of analysis. A set of blank traps should also be analyzed to determine background levels.

e. Specific Sorbent/Reagent Methods

Specific sorbents and reagents are used to collect POHCs which are subject to reaction or loss when collected using the previously described approaches. The use of specific sorbent/reagent sample collection methods requires devices similar to that shown previously for integrated gas bag samples. A nonreactive probe is inserted into the stack gas stream and gas collected at a controlled rate. A gas cooler is located before the sorbent or reagent collector to reduce the temperature of the gas stream to levels compatible with the collector. The sorbent appropriate to the POHC of interest is mounted in place of the gas bag shown in Figure 7. Special reagent solutions in impingers may be placed following the selected sorbent, as appropriate, to remove other POHCs and corrosive gases from the gas stream prior to the flow controllers. Table 7 summarizes the sorbents and special reagents to be used for the sampling of the specific POHCs.

These special-purpose sorbents/reagents may be incorporated into the Modified Method 5 or SASS train modules if the substitution for standard train components does not adversely affect collection of other POHCs. Alternatively, a separate MM5/SASS train to collect the compound types listed in Table 7 may be used.

f. Monitoring of Gaseous Combustion Products

As part of the routine documentation of the combustion performance of a hazardous waste incinerator, several parameters are monitored continuously in the incinerator stack. The primary component which needs to be monitored on a continuous basis, or with high frequency (once per hour), is the level of carbon monoxide (CO) in the stack effluent. This measurement is needed during trial burns as well as during routine incinerator operation. Plume color and plume opacity may also be measured frequently for control purposes, although routine documentation is not required.

In addition, the oxygen level in the incinerator effluent must be determined to allow correction of the measured particulate loading to a standard excess air level. It may also be necessary, in some cases, to measure the incinerator effluent for hydrochloric acid for the purpose of calculating a removal efficiency.

TABLE 7

SORBENTS AND SPECIAL REAGENTS FOR SPECIFIC POHCs

Compound Type	Sorbent
General-purpose--organics	XAD-2 resin
General-purpose--organics	Tenax GC
General-purpose--chlorinated organics	Florisil
General-purpose--nonpolar organics	Ambersorb XE-340
General-purpose--polar organics (better than XAD-2 resin for polar compounds)	XAD-8 resin
General-purpose--polar organics	Ambersorb XE-347

Compound Type	Special Reagent
Acidic compounds	Dilute caustic (such as 1% NaOH)
Basic compounds	Dilute acid (such as 1% HCl)
Volatile metals	Oxidizing reagents (such as ammonium persulfate)
Aldehydes	2,4-Dinitrophenylhydrazine in 2N HCl (or 2,3,4,5,6-Pentachlorobenzylhydrazine)

- Gaseous Sample Conditioner

On-line, continuous monitoring instrumentation for incinerator effluents involves a sample delivery system which provides a properly conditioned representative sample to the instrumentation for measurement. The sample delivery system needs to include a sampling probe and a gas conditioner. For stack gas sampling, Pyrex glass or stainless-steel probes may be used for the collection of particulates or gases. A gas conditioning process is generally required to remove particulate, cool, dilute and/or dehumidify the effluent prior to continuous analysis by instruments, such as carbon monoxide monitors.

- Carbon Monoxide Measurement

For measurement of the level of carbon monoxide (CO) in the incinerator effluent, a nondispersive infrared (NDIR) analyzer is recommended as the preferred analytical procedure (EPA Method 10 (6)). Selection of this instrument is consistent with the need to continuously monitor combustion efficiency by monitoring CO. Many commercial NDIR analyzers for CO are available; however, selection should be based on the EPA specifications described in EPA Method 10 (6). Such specifications are required to provide suitable quality control of the collected data by requiring that instrumentation meet certain criteria with regard to response time, span stability, and zero stability.

- Plume Color and Plume Opacity

The color and opacity of the incinerator plume can be measured by EPA Method 9 (6). EPA Method 9 involves the visual determination of plume opacity by a qualified observer. Commercially available smoke generators are available which can be used to provide calibration of the observer during the certification procedures defined in EPA Method 9 (6).

- Oxygen Measurement

The oxygen level in the incinerator effluent must be determined to allow correction of the measured particulate loading to a standard excess air level. EPA Method 3 (6) involves the collection of a gas sample, and subsequent analysis of the oxygen level by an Orsat analyzer.

- Hydrogen Halide Measurement

Several wet chemical methods are available for the measurement of hydrogen halides in stack gas effluents. These methods generally involve the collection of the hydrogen halides in impingers containing water or dilute caustic (0.1 N NaOH). A filter is utilized upstream of the impingers to remove particulates.

Analysis for the hydrogen halides by a specific ion electrode method is the preferred analysis method due to potential interferences. Recent research into the suitability of ion chromatography as a reliable tool for analysis of several anions corroborates the suitability of this technique for the analysis of hydrogen halides in stack gas samples. It is recommended that this technique, or the selective electrode technique, be used for the analysis of hydrogen halide in testing incinerator effluents. Both techniques will permit analysis of effluent concentrations as low as 1 ppm.

2. Sampling Methods for Solid and Liquid Effluents

The solid and liquid effluents from a hazardous waste incineration facility, including bottom ash or fly ash/ESP catches, may be sampled by the methods discussed previously for the influent waste streams. Solid effluents will be sampled using scoops, corers, etc., as appropriate. Liquid effluents, primarily scrubber water, may be sampled by a variety of grab techniques including Coliwasa, dipper, and tap samplers.

D. HEALTH AND SAFETY PRECAUTIONS

Proper safety precautions to protect the field crew from general and specific hazards of sampling hazardous wastes should be a major focus of any site-specific sampling plan. Proper safety precautions must be observed when sampling any hazardous wastes.

In all cases, the field crew collecting a sample should be aware that wastes can be corrosive, flammable, explosive, toxic and/or capable of releasing acutely poisonous gases. Background information about the waste is necessary in deciding the extent of safety precautions to be observed in the choice of protective equipment to be used during sampling.

If full protection is indicated, the person collecting the sample should use a self-contained breathing apparatus, protective clothing, hard hat, neoprene rubber gloves, goggles, and rubber boots. The self-contained breathing apparatus should consist of an air-tight face mask and a supply of air in a pressure tank which is equipped with a pressure regulator. Protective clothing should consist of a long-sleeved neoprene rubber coat and pants or long-sleeved coverall and an oil and acid proof apron (5).

Once work begins at a field location, the sampling team leader, or an individual designated by him and approved by the Safety Officer, should have authority and responsibility for the implementation of the safety regulations.

The following precautions should be employed by all field crew members:

- Steel-toed safety shoes or boots should be worn.
- Eye protection should be worn at all times.
- Hard hats should be worn.
- Adequate protective clothing should be worn to prevent burns from heat or chemicals or exposure to severe environmental conditions. As necessary, a supply of gloves (both rubber and cotton), shirts, pants, lab coats, aprons, jackets, rain slickers, and parkas should be available for use.
- In general, all field work should be performed within the view (or hearing) of at least one other individual. At remote locations, this means that there should be at least two field crew members.
- Upon arrival at the field site, the team leader or his designated alternate should become familiar with the locations of all the safety equipment offered at the facility. If any equipment is unfamiliar to him, he should ask for instructions on its use and transmit all information regarding these safety items to each member of the field crew.
- Either prior to departure for the field site, or immediately upon arriving there, the field leader should identify all local emergency assistance facilities and record their telephone numbers for future reference, including fire departments, rescue squads, poison information centers, and hospital emergency facilities. Home telephone numbers for all team members should also be recorded by the team leader in case of need for emergency notification of relatives.

E. COLLECTION OF REPRESENTATIVE SAMPLES

1. Gases

The representativeness of all gas samples is ensured by the integrated sampling approaches presented previously. Stack gas samples taken by MM5, SASS, or VOST represent collections obtained over a period of several hours at or near the isokinetic sampling point. Hence, these stack gas samples contain the average composition of the stack gas during the time period sampled. Bag samples are also collected over a period of several hours and thus any fluctuations in the levels of specific components are integrated, yielding an average composition sample.

2. Liquids

Each sample collected should be prepared in strict accordance with a specified procedure. When sampling nonvolatile liquid products, the sampling apparatus should be filled and allowed to drain before drawing the actual sample. If the actual sample is to be transferred to another container, the sample container should be rinsed with some of the product to be sampled and drained before it is filled with the actual sample.

3. Solids

The sampling procedure for solids should allow for some element of randomness in the selection of subsamples since a variation in the quality of the material is possible. Generally, where segregation is known to exist and random variation of quality is not possible, the sampling should be designed to allow for this status. The sampler should always be on the alert for possible biases arising from the use of a particular sampling device, or from unexpected segregation in the material. Procedures for avoiding bias in the sampling of solid materials, including pattern sampling of bulk materials and procedures for blending and reducing samples to uniform subsamples given in EPA manuals (4,5) should be used to ensure adequately representative samples.

4. Slurries

The sampling of slurries with any degree of accuracy is difficult. This is particularly true when sampling a normally static system such as a storage tank or vat. Thus, arrangements should be made to agitate thoroughly the contents of such storage units prior to sampling. The most desirable and convenient place to sample a slurry is from a pipeline as the material moves through the line. Even in a pipe, it is difficult to obtain a representative sample since slurries subjected to shearing will tend to change in composition due to loss of liquid.

If only a portion of a slurry sample is needed for analysis, the sample should be shaken and a portion more than adequate for analysis dumped out. Attempts to pour a predetermined volume of a heterogeneous sample for analysis are unsatisfactory, since the solids have time to separate during pouring. The more frequently subsamples are taken, the more accurately will the sample represent the total stream.

5. Sample Handling

After a sample has been transferred into the proper sample container, the container must be tightly capped as quickly as possible to prevent the loss of volatile components and to exclude possible oxidation from the atmosphere.

The use of a preservative or additive is not generally recommended. However, if only one or two components of a waste are of interest and these components are known to rapidly degrade or deteriorate chemically or biochemically, the sample may be refrigerated at 4-6°C and/or treated with preservatives.

To split or withdraw an aliquot of a sample, considerable mixing, homogenization, or quartering is required to ensure that representative or identical portions are obtained. When transferring a sample aliquot, the container should be kept open as briefly as possible.

F. IDENTIFICATION OF SAMPLES

Each sample must be labeled and sealed properly immediately after collection.

1. Sample Labels

Sample labels are necessary to prevent misidentification of samples. Gummed paper labels or tags are adequate. The label must include at least the following information:

Name of Collector (individual and affiliation)
Date and Time of Collection
Place of Collection
Collector's Sample Number which uniquely identifies the sample.

2. Field Log Book

All information pertinent to a field survey and/or sampling must be recorded in a log book. This must be a bound book, with pages numbered consecutively. Entries in the log book should include the following:

Location of Sampling (e.g., hauler, disposal site, etc.) and Address
Name and Address of Field Contact
Producer of Waste and Address
Type of Process Producing Waste (if known)
Type of Waste (e.g., sludge, wastewater, etc.)
Description of Sampling Point
Date and Time of Collection
Collector's Sample Identification Number(s)
Sample Distribution (e.g., laboratory, hauler, etc.).

3. Field Observations

Any field observations should also be incorporated into the log book. Sampling situations vary widely. No general rule can be given as to the extent of information that must be entered in the log book. A good rule, however, is to record sufficient information so that others may consistently reconstruct the sampling situation without reliance on the memory of the sample collector.

G. SAMPLING METHOD SUMMARIES

The sampling methods described in the previous portions of this section are presented in a summary form. Each of the numbered methods is presented as a summary table which includes the method name and number, appropriate sample matrix, the general procedure to be used, and literature references. In each case, the cited reference(s) provide a complete description of the procedure with a level of detail suitable for direct use by the sampling and analysis team.

Method Number: S001

Method Name: Coliwasa

Basic Method: Liquid Grab Sample

Matrix: Liquids

Apparatus: Coliwasa sampler, as described in SW-846 (4).

Sampling Method Parameters:

The Coliwasa sampler will be inserted in the closed position into the liquid. The sampler will then be opened, filled, capped, and removed.

References:

U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

deVera, E.R., B.P. Simmons, R.D. Stephens and D.L. Strom, "Samplers and Sampling Procedures for Hazardous Waste Streams," EPA-600/2-80-018 (January 1980). NTIS No. PB80-135353.

Method Number: S002

Method Name: Dipper (Pond Sampler)

Basic Method: Liquid Grab Sample

Matrix: Liquids

Apparatus: Beaker attached to telescoping pole, as described in SW-846 (4).

Sampling Method Parameters:

The beaker will be inserted into the liquid with the opening downward, until the desired depth is reached. The beaker will then be turned right side up, filled with sample, the dipper raised, and the sample transferred to a storage vessel. A 2-4L sample will be collected.

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

deVera, E.R., B.P. Simmons, R.D. Stephens and D.L. Strom, "Samplers and Sampling Procedures for Hazardous Waste Streams," EPA-600/2-80-018 (January 1980). NTIS No. PB80-135353.

Method Number: S003

Method Name: Weighted Bottle

Basic Method: Liquid Grab Sample

Matrix: Liquids

Apparatus: Weighted bottle, constructed as described in ASTM D-270 (8) and ASTM E-300 (9).

Sampling Method Parameters:

A stoppered bottle will be lowered to the appropriate depth, the stopper removed, and a sample collected. After the bottle is filled, the sample bottle will be capped and wiped off.

References:

U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book of ASTM Standards," Method D-270 (1975).

American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book of ASTM Standards," Method E-300 (1973).

Method Number: S004

Method Name: Tap

Basic Method: Liquid Grab Sample

Matrix: Liquids

Apparatus: Tap Valves
Sample Line (washed teflon)
Collection Bottles

Sampling Method Parameters:

A sample line will be inserted into the collection vessel. The sample line and bottle must be thoroughly rinsed with the liquid waste prior to isolating the sample. (This waste must be disposed of in an appropriate manner.) A 2L (minimum) sample will be collected over a sampling time which exceeds 5 min.

References: Lentzen, D.E., D.E. Wagoner, E.D. Estes and W.F. Gutknecht, "EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," EPA-600/7-78-201 (October 1978). NTIS No. PB293795/AS.

American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book of ASTM Standards," Method D-270 (1975).

Method Number:	S005
Method Name:	Thief (Grain Sampler)
Basic Method:	Solid Grab Sample
Matrix:	Solids
Apparatus:	Thief (available from laboratory supply houses)

Sampling Method Parameters:

The thief will be inserted into the solid to be sampled, the inner tube rotated to open the sampler, and then agitated to encourage flow of the sample. The sampler will be closed, and the sample withdrawn.

Reference: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Method Number:	S006
Method Name:	Trier (Sample Corer/Waste Pile Sampler)
Basic Method:	Solid Grab Sample
Matrices:	Sludges Solids
Apparatus:	Sample corer (trier), fabricated from PVC pipe or sheet metal, as described in SW-846. (The waste pile sampler is a larger scaled version.)

Sampling Method Parameters:

The sampler will be inserted into the solid material at an angle of 0-45°, rotated to cut a core of the solid or sludge, and removed with the concave side upward.

Reference: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Method Number:	S007
Method Name:	Trowel (Scoop)
Basic Method:	Solid Grab Sample
Matrix:	Solids
Apparatus:	Stainless steel or polypropylene laboratory scoop (7 x 15 cm)

Sampling Method Parameters:

Prior to collecting a sample, the top-half inch of the solid must be removed. Kg-sized samples will be obtained by combining subsamples taken at several locations.

References:

U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

deVera, E.R., B.P. Simmons, R.D. Stephens and D.L. Strom, "Samplers and Sampling Procedures for Hazardous Waste Streams," EPA-600/2-80-018 (January 1980). NTIS No. PB80-135353.

Method Number:	S008
Method Name:	MM5 Train
Basic Method:	Comprehensive Sampling Train (filter-sorbent-impinger)
Matrix:	Stack Gas (particulate plus vapor phase material)
Apparatus:	RAC or equivalent sampling train, modified to include sorbent module as shown in Figure 3
	Filter - glass fiber filter
	Sorbent - XAD-2 resin or as necessary for collection of target species (Table 7)
	Impinger reagent - as necessary for collection of target species (Table 7)

Sampling Method Parameters:

The stack will be traversed to determine the point of average velocity and a gas sample collected at isokinetic conditions, as specified in EPA Methods 1-5 (6). A 5 dscm sample will be collected at a sampling rate of approximately 0.75 ft^3/min.

As a check on recovery, the filter/sorbent and/or impinger solutions must be spiked before or immediately after sampling with a known quantity of the deuterated or fluorinated analog(s) of the target compound(s).

References:

Title 40, Code of Federal Regulations, Part 60, Appendix A, Methods 1-5 (1980).

Martin, R.M., "Construction Details for Isokinetic Source Sampling Equipment," EPA-APTD-0581 (1971). NTIS No. PB209060.

Rom, J.J., "Maintenance, Calibration and Operation of Isokinetic Source Sampling Equipment," EPA-APTD-0576 (1972). NTIS No. PB209022.

Method Number:	S009
Method Name:	SASS Train
Basic Method:	Comprehensive Sampling Train (filter-cyclone-sorbent-impinger)
Matrix:	Stack Gas (particulate plus vapor phase material)
Apparatus:	Acurex or equivalent sampling train
	Filter - glass fiber filter
	Sorbent - XAD-2 Resin (or as necessary for collection of target species) (Table 7)
	Impinger reagent - as necessary for collection of target species (Table 7)
	Cyclone cutoffs - 10 μm, 3 μm, 1 μm

Sampling Method Parameters:

The stack will be traversed to determine the point of average velocity and a gas sample collected under isokinetic conditions, as specified in EPA Methods 1-5 (6). A 30 dscm sample will be collected at approximately 4 ft^3/min.

As a check on recovery, the filter/sorbent and/or impinger solutions must be spiked before or immediately after sampling with a known quantity of a deuterated or fluorinated analog(s) of the target compound(s).

References: Lentzen, D.E., D.E. Wagoner, E.D. Estes and W.F. Gutknecht, "EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," EPA-600/7-78-201 (October 1978). NTIS No. PB293795/AS.

Title 40, Code of Federal Regulations, Part 60, Appendix A, Methods 1-5 (1980).

Method Number:	S010
Method Name:	Gas Bulb
Basic Method:	Gas Grab Sample (reactive gases)
Matrix:	Stack Gas
Apparatus:	2L glass bulb in styrofoam package Glass wool for particulate removal Side bleed gas control mounted perpendicular to duct

Sampling Method Parameters:

A gas bulb will be purged with a 20L gas sample at 0.5 L/min prior to isolating sample. The bulb will then be re-evacuated, the valve opened, a 2L gas sample collected, and the valve closed.

References: Lentzen, D.E., D.E. Wagoner, E.D. Estes and W.F. Gutknecht, "EPA/IERL-RTP Procedures Manual Level 1 Environmental Assessment (Second Edition)," EPA-600/7-78-201 (October 1978). NTIS No. PB293795/AS.

Title 40, Code of Federal Regulations, Part 60, Appendix A, Method 7 (1980).

Method Number:	S011
Method Name:	Gas Bag
Basic Method:	Gas Grab Sample (unreactive gases)
Matrix:	Stack Gas
Apparatus:	Integrated gas sampling train (including probe with filter, condenser, flow controllers, meters, and pumps)

Sampling Method Parameters:

The probe will be inserted into the center of the stack, and a 30L gas sample collected at a sampling rate of 0.5 L/min.

References:

Lentzen, D.E., D.E. Wagoner, E.D. Estes and W.F. Gutknecht, "EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," EPA-600/7-78-201 (October 1978). NTIS No. PB293795/AS.

Title 40, Code of Federal Regulations, Part 60, Appendix A, Method 3 (1980).

Method Number:	S012
Method Name:	VOST
Basic Method:	Sampling Train
Matrix:	Stack Gas
Apparatus:	Integrated gas sampling train including probe with condensers Tenax trap Tenax/charcoal trap Condensate trap impingers

Sampling Method Parameters:

A 20L gas sample will be collected through a sorbent tube at a flow rate of 1 L/min. Sorbent traps will be changed every 20 min over a 2 h sampling period.

Reference: Appendix F.

V. SAMPLE PREPARATION PROCEDURES

A. OVERVIEW

The sample preparation procedures for use with hazardous waste influents and effluents involve a number of steps. The collected sample, whether gaseous, liquid, or solid, must be converted into a matrix which is compatible with the final analysis methods needed for measurement of the designated POHC(s). The sample preparation scheme for analysis of organic components may require extraction of the sample, concentration of an extract, and cleanup of the sample extract to remove potential interferences. Surrogate and standard addition methods are required for better precision in assessing the POHC level(s) by determining recoveries for the POHC(s) of interest. Digestion of a sample is necessary prior to analysis of inorganic constituents.

This section describes the sample preparation steps appropriate for the hazardous constituents identified in 40 C.F.R. Appendix VIII (May 20, 1981). The sample preparation methods were chosen to be as widely applicable as possible. Preparation methods (e.g., extraction and concentration for organics and digestion for inorganic species) are not necessarily optimized for each specific POHC. Rather, they have been generalized to encompass a large number of compounds. (Method description summaries are compiled at the end of the chapter.)

The types of samples which could be collected during the evaluation of a hazardous waste incinerator include:

- Permanent gases (reactive and nonreactive) and stack gas samples collected as comprehensive sampling train components (particulate catch, sorbent, impinger reagents);
- Aqueous liquids (including process waters, scrubber waters, etc.) and organic liquids;
- Sludges, including suspensions, slurries, and gels; and
- Solids, including particulates on filters, solid residues, and sorbents.

B. REPRESENTATIVE ALIQUOTS FROM FIELD SAMPLES (Methods P001-P003)

Combination and preparation of representative aliquots (composites) of collected samples are appropriate for all solid and liquid grab samples. Samples of gases collected with the bag sampling approach and stack gas samples collected via the MM5 or SASS train and VOST already represent time-averaged sample collections. In effect, the sampling approach has composited the gas sample on a time-averaged basis. Other

grab samples (liquids and solids) will be homogenized prior to withdrawal of aliquots for analysis. Individual aliquots are composited to form a single sample for subsequent preparation and analysis procedures. The procedures appropriate for aliquoting and compositing samples are summarized in Table 8.

The aliquot sizes that are taken from each type of field sample for the various analytical procedures are specified in Table 9. These are default values which may be increased or decreased in specific instances, depending on target detection limits and/or suspected concentrations based on professional judgment.

All sample aliquots removed for organic analysis are stored in glass containers with teflon-lined screw caps, and the sample aliquots for volatile organic analysis are stored so that there is no headspace above the sample. Sample aliquots for inorganic analysis are stored in high-density, linear, polyethylene containers.

C. RECOVERY MEASUREMENTS (Methods P011-P014)

It is important to monitor the recovery of the POHC(s) during sample preparation as an estimate of the accuracy of the analytical measurement and an assessment of the overall efficiency of the analytical procedures. Two methods are used for these purposes: (1) the addition of surrogate compounds which are chemically similar to the POHCs of interest, and (2) the addition of POHCs themselves in their stable isotopically labeled forms. These compounds are added to the various samples immediately after return to the analytical laboratory.* Table 10 lists some potential compounds for use as surrogates. For stack gas samples, injection of the surrogate compounds directly into the bulb or bag or onto the filter or sorbent from the MM5 or SASS train, is appropriate.

The spiking levels used in each instance are selected after consideration of the target detection limits for potential hazardous constituents, and the expected concentrations of organic components, based on professional judgment. Concentrations for surrogate standards on the order of 50-1000 ppm are expected to be added to waste samples, depending on the total organic content of the waste. For incinerator effluent samples, spiking levels for surrogate standards are chosen to correspond to 2 to 10 times the detection limit required to measure 99.99 percent DRE of the designated POHC(s).

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*To avoid interferences with conventional detectors, it is important that the deuterated and ^{13}C-surrogates are added only to those samples that are to be taken for mass spectrometric analysis.

TABLE 8

SUMMARY OF PROCEDURES FOR COMPOSITING SAMPLES

Method	Physical Form	Proportioning Method	Compositing Method
P001	Liquids	Homogenize and pour aliquot.	Combine aliquots in container and shake.
P002	Sludges	Homogenize and use dipper to take three portions.	Combine aliquots in container and mix.
P003	Solids	Grind, if necessary, to reduce particle size (20 mesh screen), using agate or alumina equipment, and riffle through steel or aluminum riffler.	Combine aliquots, cone-blend three times, roll-blend, and cone and quarter.

Sources: American Society for Testing and Materials, Philadelphia, Pennsylvania, Annual Book of ASTM Standards, Method No. E-300-73, Parts 29 and 30 (1973).

Berl, W.G. (ed.), Physical Methods in Chemical Analysis, Academic Press, New York, Vol. III, pp. 183-217 (1956).

Kennedy, W.R., and J.F. Woodruff (eds.), Symposium on Sampling Standards and Homogeneity, Los Angeles, California, June 25-30, 1972, American Society for Testing and Materials, Philadelphia, Pennsylvania (1973).

TABLE 9

ESTIMATED QUANTITIES OF SAMPLE REQUIRED FOR ANALYSIS*

Analysis/Sample Type	Aqueous Liquids	Sludges	Organic Liquids	Solids
PROXIMATE ANALYSIS				
Moisture, Solid and Ash Content				
Macroscale Technique	100 mL	25 g	2 mL	10 g
Microscale Technique	NA	50 mg	50 mg	50 mg
Elemental Composition	50-300 mg (solid content)	50-300 mg (solid content)	50-300 mg (solid content)	50-300 mg (solid content)
TOC, TOX	≤100 mL	20 mL	NA	NA
SURVEY ANALYSIS				
Inorganics	50-300 mg (solid content)	50-300 mg (solid content)	50-300 mg (solid content)	50-300 mg (solid content)
Organics	1 L	100 mL	1 mL	20 g
DIRECTED ANALYSIS				
Inorganics	1 L	100 g	100 mL	100 g
Organics	1 L	100 mL	1 mL	50 g

*Minimum quantity for a single analysis.
NA = Not Applicable.

TABLE 10

POTENTIAL COMPOUNDS FOR USE AS SURROGATES

Volatile Organics (Method P011)

Chloroform-^{13}C

Diethylether-d_{10}

1,2-Dichloroethane-d_4

Benzene-d_6

Bromoform-^{13}C

Bromomethane-d_3

Ethylbenzene-d_{10}

Basic Extractable Organics (Method P012)

m-Fluoroaniline

Acridine-d_9

Acidic Extractable Organics (Method P013)

2-Chlorophenol-3,4,5,6-d_4

Pentachlorophenol-$^{13}C_6$

Phenol-d_5

Bromophenol

2,4,-Dinitrophenol-3,5,6-d_3

Benzoic acid-d_5

Benzoic acid-^{13}C

Neutral Extractable Organics (Method P014)

Hexachlorobutadiene-1-^{13}C

Octafluorobiphenyl

Naphthalene-d_8

1-Fluoronaphthalene

2,6-Dinitrotoluene-α-α-α-d_3

1,2-Dichlorobenzene-d_4

Di-n-butylphthalate-3,4,5,6-d_4

Hexachlorobenzene-$^{13}C_6$

Benz(a)anthracene-d_{12}

9-Phenylanthracene

D. SOLVENT EXTRACTION OF ORGANIC COMPOUNDS (Methods P021-P024)

Solid and liquid samples are extracted at acidic and basic conditions (except for extractions using a Soxhlet apparatus). The extracts are generally combined prior to analysis, unless information from the engineering study suggests that species from the acid and base/neutral fractions will react. In this case, the acidic and basic extracts will be analyzed separately.

1. Aqueous Liquids (Method P021)

Method P021 procedures apply to (a) spent scrubber liquor or other wastewater from the incineration facility, (b) incinerator influent waste streams that are highly aqueous, and (c) aqueous condensate collected from the stack gas effluent in the Modified Method 5 or SASS trains (Figure 2).

a. Semivolatiles (Method P021a)

An aliquot (usually 1L) is taken for liquid/liquid extraction. If the aqueous aliquot is initially neutral or basic, the pH of the sample is adjusted to $\geq$11 using 6N NaOH and the sample extracted with three successive 60-mL portions of methylene chloride. The pH of the aqueous sample is then adjusted to $\leq$2 using 6N H_2SO_4 and the sample again extracted with three 60-mL portions of methylene chloride. If the aqueous aliquot is initially acidic, the sample is extracted first at pH $\leq$2. Subsequently it is adjusted to pH $\geq$11 for the second extraction. All extracts (ca. 360 mL) are combined in a labeled amber glass bottle. If less than 51 mL (85%) of the methylene chloride organic phase is recovered for each individual extraction, the aqueous phase is centrifuged at 3000 rpm for 15 min and the recovered organic phase then added to the combined extracts in the bottle.

b. Volatiles (Method P021b)

An aliquot (20 mL) of an aqueous liquid sample is placed in a 125-mL separatory funnel with carbon disulfide (2 mL) and methanol (20 µL) containing 1,2-dichloropropene (200 µg) as an internal standard. The contents are shaken for 2 minutes and the layers are then allowed to settle. The sample extract is transferred to a labeled container (the transfer need not be quantitative).

2. Sludges (Method P022)

The Method P022 procedures apply to incinerator influent waste streams that are sludges, slurries, or gels. They could also be applied to any sludges or slurries produced by stack gas pollution control devices.

a. Semivolatiles (Method P022a)

An aliquot (100 mL) is taken for liquid/liquid extraction using homogenization and methylene chloride (100 mL) is added to the sample in a glass container. If the sludge is known or expected to contain $\geq$1% by weight of extractable organics, 200 mL of methylene chloride are used for each extraction. The mixture is homogenized using a blender or impeller for 45 to 60 seconds (maximum). The homogenized mixture is transferred with a 100-mL pipette to a labeled amber glass bottle. The extraction/homogenization/centrifugation is repeated twice.

For sludge/slurry samples suspected of containing >80% water (based on professional judgment), the pH is adjusted to $\geq$11 with 6N NaOH prior to extraction. (Note: if precipitation is observed when NaOH is added, the sample will be made slightly acidic with 6N H_2SO_4, and CO_2 evolution allowed to cease before adjusting the pH to $\geq$11.) If the sludge/slurry aliquot is initially acidic, the sample is extracted first at pH $\leq$2, and subsequently it is adjusted to pH $\geq$11 for the second extraction.

After extraction with three 100-mL volumes of methylene chloride, the pH is adjusted to $\leq$2 with 6N H_2SO_4 and the extraction repeated with three additional 100-mL portions of methylene chloride. All extracts are combined in a labeled amber glass bottle.

b. Volatiles (Method P022b)

An aliquot (2g, wet weight) is placed in a 50-mL centrifuge tube. Water (20 mL), carbon disulfide (2 mL), and methanol (20 µL) containing 200 µg of 1,2-dichloropropene internal standard is added. If the sludge is known, or expected, to contain >20 mg/g by weight of extractable organics, the sample is placed in a 100-mL centrifuge tube and the volumes of carbon disulfide are increased to 20 mL (or more). The tube is capped and the contents agitated for 1 minute using a vortex mixer. The mixture is then centrifuged at 3000 rpm for 15 minutes and the extract transferred to a labeled container.

3. Organic Liquids (Method P023)

The Method P023 procedure applies to incinerator influent waste streams that consist of organic liquids. An aliquot (1 mL) is diluted to 100 mL with methylene chloride. If it is apparent that a portion of the sample is insoluble in methylene chloride, a separate 100-mL aliquot is taken and treated as a sludge sample.

4. Solids (Method P024)

The Method P024 procedures apply to (a) incinerator waste influent streams that are solid, (b) ash collected from flue gas cleaning systems, or from the incinerator itself, and (c) particulate material and solid sorbent samples collected from either (MM5/SASS) stack gas sampling train.

a. Semivolatiles (Method P024a,b)

Two procedures are used for extraction of solid samples. Homogenization (for non-abrasive materials) is used for most wastes. Extraction using a Soxhlet apparatus is used for abrasive samples and for the particulate material and solid sorbent portions of the comprehensive stack gas sampling systems.

- Semivolatiles by Homogenization (Method P024a)

A 40g aliquot is weighed into a 250-mL centrifuge tube, and 40 mL of 10% sodium chloride in reagent water (deionized, distilled water with organics removed by carbon adsorption) is added and the pH adjusted to $\geq$11. Methylene chloride (60 mL) is added and a probe device (SDT tissue mixer) used to disperse the sample for a total of 1 minute. Then the mixture is centrifuged for 15 minutes at 1400 rpm, and the methylene chloride phase is withdrawn with a 50-mL syringe. If the emulsion interface between layers is more than one-half the volume of the solvent layer, a 120-mL portion of methylene chloride is used for the extraction. The extraction and dispersion are repeated for a total of three extractions, using 60-mL aliquots of methylene chloride each time.

The pH of the aqueous/solid mixture is then adjusted to $\leq$2 with 6N H_2SO_4 (added slowly to prevent foaming). The contents of the centrifuge bottle are extracted and centrifuged with three additional 60-mL portions of methylene chloride. The extracts (ca. 360 mL) are then combined in a labeled sample container.

- Semivolatiles by Soxhlet Extraction (Method P024b)

The MM5/SASS particulate materials or solid adsorbent (XAD-2), or a 20-g aliquot of a solid waste sample, combined with 20g of anhydrous sodium sulfate are placed in a glass or ceramic extraction thimble. (If high levels of water are present in the waste sample and the temperature of the sample rises when sodium sulfate is added, the sample is suspended in methylene chloride prior to adding the sodium sulfate.) Sorbent or particulate samples on filters are placed directly in the thimble after weighing. A pre-extracted glass wool plug is placed on top of the sample. A 200-mL portion of methylene chloride is placed in the 500-mL round bottom flask containing a teflon boiling chip. The flask is attached to the extractor and the solids are extracted for 16 hours (3-4 turnovers per hour). The extract is finally transferred to a labeled amber glass bottle.

b. Volatiles (Method P024c)

A 2g (wet weight) aliquot of solid waste sample is placed in a 50-mL centrifuge tube. Water (20 mL), carbon disulfide (2 mL), and methanol (20 µL) containing 200 µg of 1,2-dichloropropene internal standard, is added. If the solid is known to contain >20 mg/g by weight extractable organics, the sample is placed in a 100-mL centrifuge tube, and the volume of carbon disulfide is increased to 20 mL (or more). The tube is then capped, and the contents agitated for 1 minute using a vortex mixer. The mixture is then centrifuged at 3000 rpm for 15 minutes and the extract transferred to a labeled container. (This procedure does not apply to MM5/SASS particulate or sorbent.)

E. DRYING AND CONCENTRATING OF SOLVENT EXTRACTS (Method P031)

Aliquots of each methylene chloride sample extract are taken for analysis of the total chromatographicable content (TCO) (Method A011) prior to concentration. Sample extracts are passed through a short column of anhydrous sodium sulfate which has been prerinsed with the extracting solvent (methylene chloride) into a 500-mL Kuderna-Danish (K-D) flask fitted with a 10-mL calibrated receiving tube containing a teflon boiling chip. The extract is evaporated rapidly to 5 to 10 mL in the 500-mL K-D apparatus fitted with a three-ball Snyder column. The K-D apparatus is allowed to cool, and the column and receiver are rinsed with solvent. The three-ball Snyder column and 500 mL-K-D receiver are removed and the boiling chip replaced. A microSynder column is then attached to the 10-mL receiver tube and the extract is evaporated to less than 1 mL. (The sample extract is not allowed to go to dryness.) The final extract volume is adjusted to 1 mL (if possible), or to a volume such that the extract contains 1% to 5% total extractable organics, based on the TCO analysis (Method A011).

F. DIGESTION (Method P032)

The preparation procedures for all samples which contain metals include a digestion step. Its purpose is to convert all of the metal-containing species into an inorganic form for subsequent metals analysis. There are numerous digestion procedures which may be applied to different types of samples to convert metals in organic and bound compounds to a readily analyzable inorganic form. For illustration, nitric acid digestion procedure is outlined below as the typical digestion method.

An aliquot from a well-mixed field sample, such as an aqueous liquid, sludge, or solid, is prepared for metals analysis. The sample is placed in a beaker and concentrated nitric acid added to the beaker. The sample is then heated on a hotplate and evaporated without boiling to near dryness. A second addition of nitric acid is made to the beaker upon cooling. The beaker is covered and heated with additions of nitric

acid until the material becomes light in color. This completes the digestion of the sample. The sample may then be transferred quantitatively to volumetric glassware for analysis of the metal of interest.

G. SAMPLE CLEANUP PROCEDURES (Methods P041-P045)

For some samples, the level of interfering compounds is sufficiently high to preclude successful analysis for the POHCs of interest. For such samples, one or more cleanup steps have to be included in the sample preparation procedures. Because of the wide variation in the physical and chemical properties of the listed POHCs, no single sample cleanup method has been demonstrated to be appropriate for all of the listed POHCs. A number of different cleanup methods, such as size exclusion chromatography, liquid column chromatography using columns filled with silica gel, Florisil, activated alumina, etc., solvent partitioning, and filtration may be used alone, or in combination, to cleanup samples for analysis.

Florisil column chromatography is generally the method chosen for preparing a sample that requires cleanup prior to analysis. Additional cleanup procedures may be necessary if high background levels of interferences remain after Florisil chromatography. These include BioBeads SX-3 (Sephadex LH-20), silica gel, or alumina column chromatography or liquid/liquid extraction.

Separation of the components in a sample using BioBeads SX-3 column chromatography is based on size exclusion. High molecular weight compounds elute first from the column and, subsequently, lower molecular weight compounds are eluted. If necessary, this cleanup procedure is used following elution of the sample from a Florisil column.

If BioBeads SX-3 fraction is not adequate to improve the detection of the constituents of concern in the sample matrix, then silica gel or alumina column chromatography is employed. These sorbents allow fractionation of the sample constituents based upon their molecular activity (polarity, functional groups). The less active constituents elute first and the more active constituents are retained and eluted in a later fraction. Again, these cleanup methods are used, if necessary, after Florisil and/or BioBeads SX-3 column chromatography.

If the sample matrix still prevents the components of interest from being detected, then the EPA permit assistance team should be consulted for alternative modes of sample preparation.

H. SAMPLE PREPARATION METHOD SUMMARIES

The preparation procedures (designated with a P) appropriate to the hazardous constituents from Appendix VIII are summarized in tabular form on the following pages.

Method Numbers: P001-P003

Method Name: Representative Aliquots from Field Samples

Matrices: Aqueous Liquids (P001)
Organic Liquids (P001)
Sludges (P002)
Solids (P003)

Method Parameters:

P001 - Liquids (aqueous and organic)

Samples will be homogenized and an aliquot removed. Appropriate aliquots will be combined in a container and shaken.

P002 - Sludges

Samples will be homogenized and aliquots removed. Aliquots will then be combined and mixed.

P003 - Solids

If necessary, the sample will be ground to reduce the particle size (20 mesh screen) using agate or alumina equipment. The sample will then be riffled through a steel or aluminum riffler; appropriate aliquots combined, cone-blended three times, roll-blended, and coned and quartered.

References:

American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book of ASTM Standards," Method No. E-300-37, Parts 29 and 30 (1973).

Berl, W.G. (ed.), Physical Methods in Chemical Analysis, Academic Press, New York, Vol. III, 183-217 (1956).

Kennedy, W.R. and Woodruff, J.F. (eds.), Symposium on Sampling Standards and Homogeneity, Los Angeles, California, June 25-30, 1972, American Society for Testing and Materials, Philadelphia, Pennsylvania (1973).

Method Numbers: P011-P014

Method Name: Surrogate Addition to Sample Aliquots for Organic Analysis

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Method Parameters:

Surrogate compounds will be added to sample aliquots taken for the analysis of volatile and nonvolatile organic compounds in order to assess the overall recovery of the analytical procedures. To avoid interferences with conventional detectors, it is important that the isotopically-labeled surrogates are only added to those samples that are taken for mass spectrometric analysis. The surrogate compounds will include, but not necessarily be limited to, the following:

Volatile Organics (Method P011)

Chloroform-^{13}C
Diethylether-d_{10}
1,2-Dichloroethane-d_4
Bromomethane-d_3
Benzene-d_6
Ethylbenzene-d_{10}
Bromoform-^{13}C

Basic Extractable Organics (Method P012)

m-Fluoroaniline
Acridine-d_9

Acidic Extractable Organics (Method P013)

2-Chlorophenol-3,4,5,6-d_4
Benzoic Acid-d_5
Phenol-d_6
2,4-Dinitrophenol-3,5,6-d_3
Bromophenol
Benzoic Acid-^{13}C

Neutral Extractable Organics (Method P014)

Hexachlorobutadiene-1-^{13}C
Octafluorobiphenyl
Naphthalene-d_8
1-Fluoronaphthalene
2,6-Dinitrotoluene-2,2,2-d_3
Di-n-butylphthalate-3,4,5,6-d_4
Benz(a)anthracene-d_{12}
9-Phenylanthracene

The spiking levels used in each instance will be selected after consideration of target detection limits for potential hazardous constituents, and expected concentrations of organic components based on professional judgment. It is expected that surrogate concentrations on the order of 50-1000 ppm will be added to the waste samples, depending on the total organic content of the waste. For incinerator effluent samples, spiking levels for surrogate standards will be chosen to correspond to 2 to 10 times the detection limits required to measure 99.99% DRE of the designated POHC(s).

Method Number: P021a

Method Name: Extraction of Semivolatiles from Aqueous Liquids

Basic Method: Liquid/Liquid Extraction

Matrix: Aqueous Liquids

Method Parameters:

A 1L aliquot will be taken for liquid/liquid extraction. If the aqueous aliquot is initially neutral or basic, the pH will be adjusted to $\geq$ 11 using 6N NaOH and the sample extracted with three successive 60-mL portions of methylene chloride. The pH of the aqueous sample will then be adjusted to $\leq$ 2 using 6N H_2SO_4 and the sample again extracted with three 60-mL portions of methylene chloride. All extracts (ca. 360 mL total) will be combined in a labeled amber glass bottle. If < 300 mL (85%) of methylene chloride is recovered, the aqueous phase will be centrifuged at 3000 rpm for 15 min and the recovered organic phase added to the combined extracts in the bottle.

If the aqueous aliquot is initially acidic, the sample will be extracted first at pH $\leq$ 2 and subsequently adjusted to pH $\geq$ 11 for the second extraction.

Reference: U.S. Environmental Protection Agency, Federal Register, 44, 69464-69575 (December 3, 1979).

Method Number: P021b

Method Name: Extraction of Volatiles from Aqueous Liquids

Basic Method: Liquid/Liquid Extraction

Matrix: Aqueous Liquids

Method Parameters:

A 20-mL aliquot of an aqueous liquid sample will be placed in a 125-mL separatory funnel with carbon disulfide (2 mL) and methanol (20 µL) containing 200 µg of 1,2-dichloropropene internal standard. The contents will be shaken for 2 min and the layers allowed to settle. The sample extract will be transferred to a labeled container (the transfer need not be quantitative).

Reference: McKown, M.M., J.S. Warner, R.M. Riggin, M.P. Miller, R.E. Heffelfinger, B.C. Garrett, G.A. Jungclaus and T.A. Bishop, "Development of Methodology for the Evaluation of Solid Wastes," Report prepared for U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, D.C., by Battelle Columbus Laboratories, Columbus, Ohio under Contract No. 68-03-2552 (January 1981).

Method Number: P022a

Method Name: Extraction of Semivolatiles from Sludges

Basic Method: Liquid/Liquid Extraction

Matrix: Sludges (including gels and slurries)

Method Parameters:

A 100-mL aliquot will be taken for liquid/liquid extraction with homogenization. A 100-mL portion of methylene chloride will be added to the waste sample in a glass container. If the sludge is known or expected to contain > 1% by weight of extractable organics, a 200-mL portion of methylene chloride will be used for each extraction. The mixture will be homogenized using a blender or impeller for 45 to 60 s (maximum). The homogenized mixture will be centrifuged for 30 min at 3000 rpm. The organic phase will be transferred with a 100-mL pipette to a labeled amber glass bottle. The extraction/homogenization/centrifugation will be repeated two more times.

For sludge/slurry samples suspected to contain > 80% water (based on professional judgment), the pH will be adjusted to $\geq$ 11 with 6N NaOH prior to extraction. (Note: if precipitation is observed when NaOH is added, the sample will be made slightly acidic with 6N H_2SO_4 and CO_2 evolution allowed to cease before adjusting the pH to $\geq$ 11.)

After extraction with 3 x 100 mL of methylene chloride, the pH will be adjusted to $\leq$ 2 with 6N H_2SO_4 and the extraction repeated with 3 additional 100-mL portions of solvent. All extracts will be combined in a labeled amber glass bottle.

If the sludge/slurry aliquot is initially acidic, the sample will be extracted first at pH $\leq$ 2 and subsequently adjusted to pH $\geq$ 11 for the second extraction.

Reference: McKown, M.M., J.S. Warner, R.M. Riggen, M.P. Miller, R.E. Heffelfinger, B.C. Garrett, G.A. Jungclaus and T.A. Bishop, "Development of Methodology for the Evaluation of Solid Wastes," Report prepared for U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, D.C., by Battelle Columbus Laboratories, Columbus, Ohio under Contract No. 68-03-2552 (January 1981).

Method Number: P022b

Method Name: Extraction of Volatiles from Sludges

Basic Method: Liquid/Liquid Extraction

Matrix: Sludges (including gels and slurries)

Method Parameters:

A 2g (wet weight) aliquot will be placed in a 50-mL centrifuge tube. Water (20 mL), carbon disulfide (2 mL), and methanol (20 µL) containing 200 µg of 1,2-dichloropropene internal standard will be added. If the sludge is known or expected to contain > 20 mg/g by weight extractable organics, the sample will be placed in a 100-mL centrifuge tube and the volume of carbon disulfide increased to 20 mL (or more). The tube will be capped and the contents agitated for 1 min using a vortex mixer. The mixture will then be centrifuged at 3000 rpm for 15 min and the extract transferred to a labeled container.

Reference: McKown, M.M., J.S. Warner, R.M. Riggen, M.P. Miller, R.E. Heffelfinger, B.C. Garrett, G.A. Jungclaus and T.A. Bishop, "Development of Methodology for the Evaluation of Solid Wastes," Report prepared for U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, D.C., by Battelle Columbus Laboratories, Columbus, Ohio under Contract No. 68-03-2552 (January 1981).

Method Number: P023

Method Name: Semivolatiles from Organic Liquids

Basic Method: Solvent Dilution

Matrix: Organic Liquids

Method Parameters:

A 1-mL aliquot will be diluted to 100 mL with methylene chloride. If it is apparent that a significant portion of the sample is insoluble in methylene chloride, a separate 100-mL aliquot will be taken and treated as a sludge sample (Method P022a).

Reference: McKown, M.M., J.S. Warner, R.M. Riggen, M.P. Miller, R.E. Heffelfinger, B.C. Garrett, G.A. Jungclaus and T.A. Bishop, "Development of Methodology for the Evaluation of Solid Wastes," Report prepared for U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, D.C., by Battelle Columbus Laboratories, Columbus, Ohio under Contract No. 68-03-2552 (January 1981).

Method Number: P024a

Method Name: Extraction of Semivolatiles from Solids

Basic Method: Liquid/Solid Extraction
Homogenization

Matrix: Solids (nonabrasive materials)

Method Parameters:

A 40g aliquot will be weighed into a 250-mL centrifuge tube. A 40-mL portion of 10% sodium chloride in deionized, distilled water with organics removed by carbon adsorption will be added and the pH adjusted to $\geq$ 11. A 60-mL portion of methylene chloride will be added and a probe device (SDT tissue mixer) used to disperse the sample for a total of 1 min. The mixture will then be centrifuged for 15 min at 1400 rpm and the methylene chloride phase withdrawn with a 50-mL syringe. If the emulsion interface between layers is more than one-half the volume of the solvent layer, a 120-mL aliquot of methylene chloride will be used for the extraction. The extraction and dispersion will be repeated a total of three times, with a 60-mL aliquot of methylene chloride used each time.

The pH of the aqueous/solid mixture will then be adjusted to pH $\leq$ 2 with 6N H_2SO_4 (added slowly to prevent foaming). The contents of the centrifuge bottle will be extracted and centrifuged with three additional 60-mL portions of methylene chloride.

The extracts (ca. 360 mL) will be combined in a labeled sample container.

Reference: Miller, H.C., R.H. James and W.R. Dickson, "Evaluated Methodology for the Analysis of Residual Wastes," Report prepared for U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, D.C., by Southern Research Institute, Birmingham, Alabama under Contract No. 68-02-2685 (December 1980).

Method Number: P024b

Method Name: Extraction of Semivolatiles from Solids

Basic Method: Liquid/Solid Extraction
Soxhlet Apparatus

Matrix: Solids (abrasive materials)
XAD-2 Resin from sorbent module

Method Parameters:

A 20g aliquot (or the entire contents of sorbent module) will be combined with 20g anhydrous sodium sulfate and placed in a glass or ceramic extraction thimble. (Small quantities of solid sample on filters may be placed directly in the thimble after weighing.) A pre-extracted glass wool plug will be placed on top of the sample. A 300-mL portion of methylene chloride will be placed in the 500-mL round bottom flask containing a teflon boiling chip. The flask will be attached to the extractor and the solids extracted for 16 h (3-4 turnovers per h). The extract will be transferred to a labeled amber glass bottle.

Reference: Miller, H.C., R.H. James and W.R. Dickson, "Evaluated Methodology for the Analysis of Residual Wastes," Report prepared for U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, D.C., by Southern Research Institute, Birmingham, Alabama under Contract No. 68-02-2685 (December 1980).

Method Number: P024c

Method Name: Extraction of Volatiles from Solids

Basic Method: Liquid/Liquid Extraction

Matrix: Solids

Method Parameters:

A 2g (wet weight) aliquot will be placed in a 50-mL centrifuge tube. Water (20 mL), carbon disulfide (2 mL), and methanol (20 µL) containing 200 µg of 1,2-dichloropropene internal standard will be added. If the solid is known to contain > 20 mg/g by weight of extractable organics, the sample will be placed in a 100-mL centrifuge tube, and the volume of carbon disulfide increased to 20 mL (or more). The tube will be capped and the contents agitated for 1 min using a vortex mixer. The mixture will then be centrifuged at 3000 rpm for 15 min and the extract transferred to a labeled container.

Reference: McKown, M.M., J.S. Warner, R.M. Riggin, M.P. Miller, R.E. Heffelfinger, B.C. Garrett, G.A. Jungclaus and T.A. Bishop, "Development of Methodology for the Evaluation of Solid Wastes," Report prepared for U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, D.C., by Battelle Columbus Laboratories, Columbus, Ohio under Contract No. 68-03-2552 (January 1981).

Method Number: P031

Method Name: Drying and Concentrating Solvent Extracts

Basic Method: Kuderna-Danish Concentration

Matrix: Sample Extracts

Method Parameters:

Aliquots of all sample extracts will be taken for TCO analysis (Method A001) prior to concentration.

Sample extracts will be passed through a short column of anhydrous sodium sulfate, prerinsed with extracting solvent (methylene chloride) into a 500-mL Kuderna-Danish (K-D) flask fitted with a 10-mL calibrated receiver tube containing a teflon boiling chip.

The extract will be evaporated rapidly to 5-10 mL in the 500-mL K-D apparatus fitted with a 3-ball Snyder column. The K-D apparatus will be allowed to cool and the column and receiver rinsed with the solvent.

The 3-ball Snyder column and 500-mL K-D receiver will be removed and the boiling chip replaced. A micro-Snyder column will be attached to the 10-mL receiver tube and the extract evaporated to less than 1 mL. (The sample extract will not be allowed to go to dryness.) The final extract volume will be adjusted to 1 mL (if possible) or to a volume such that the extract contains 1-2% total extractable organics as determined by the TCO analysis (Method A001).

Reference: U.S. Environmental Protection Agency, Federal Register, 44, 69464-69575 (December 3, 1979).

Method Number: P032

Method Name: Digestion Procedures for Metals

Basic Method: Acid Digestion

Matrices:
Aqueous Liquids
Organic Liquids
Sludges
Solids

Inorganic Species from Appendix VIII to which the method may be applied:

Antimony (Sb)
Arsenic (As)
Barium (Ba)
Beryllium (Be)*
Cadmium (Cd)
Chromium (Cr)
Lead (Pb)
Mercury (Hg)
Nickel (Ni)
Osmium (Os)*
Selenium (Se)
Silver (Ag)
Strontium (Sr)*
Thallium (Th)*
Vanadium (V)*

Method Parameters:

Aliquots (100 g (5-10g if sample is primarily solid) or 100 mL) from well- mixed field samples (Methods P001-P003), will be used for the analysis of metals.

Most samples will be prepared for analysis by general HNO_3 digestion procedures as specified in the methods for Sb, Ba, Cd, Cr, Pb, Hg, Ni, and Ag in SW-846, Section 8, Methods 8.50 to 8.60 and by HNO_3-H_2O_2 for As and Se. Waste samples containing high levels of organic materials, such as oil, greases, or waxes, will be prepared by dissolving the sample in an appropriate organic solvent or digesting the sample in nitric acid, sulfuric acid, hydrogen peroxide, and hydrochloric acid as specified in SW-846, Section 8, Pages 8.49-7 to 8.49-11. Special precautions, however, should be taken if $BaSO_4$, $PbSO_4$, or AgCl precipitate.

*These elements are not included in the SW-846 reference; it is believed that this digestion procedure would also be applicable to them.

References:

U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980), and SW-846, Revision A (August 8, 1980), and SW-846, Revision B (July 1981).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB 297686/AS.

Bock, R., A Handbook of Decomposition Methods in Analytical Chemistry. International Textbook Company, London (1979).

Dolezal, J., Povondra P., and Svick, Z., Decomposition Techniques in Inorganic Analysis, Iliffe Books Ltd., London (1968).

Gorsuch, T.T., The Destruction of Organic Matter, Pergamon Press, Oxford (1970).

Method Number: P041

Method Name: Florisil Column Chromatography

Matrix: Sample Extracts

Method Parameters:

Florisil (60/100 mesh PR grade) will be used. Due to the fact that the adsorption capacity of Florisil may vary, the lauric acid value of each manufactured lot of Florisil should be determined. The amount of Florisil to be used for each column will be calculated by the formula:

100 ÷ lauric acid value x 20g Florisil per column.

This amount of Florisil will be weighed out and each preweighed portion will be heated for more than 5 h at 130°C. The warm Florisil will be added directly to a glass chromatography column and allowed to cool with tapping to settle the adsorbent bed.

A one-half inch of dried, cleaned sodium sulfate will be added to the top of the Florisil. The column will be pre-eluted with the initial solvent to be used for chromatographing the sample extract. This eluent will be discarded. An aliquot of the sample extract (P021-P030) will be added to the top of the column.

Reference: U.S. Environmental Protection Agency, Federal Register, 44, 69464-69575 (December 3, 1979).

Method Number: P042

Method Name: BioBeads SX-3

Matrix: Sample Extracts

Method Parameters:

A 20-25g aliquot of BioBeads SX-3 (200/400 mesh, BioRad Laboratories 152-2750) will be placed in a 200-mL beaker covered with methylene chloride and allowed to swell overnight. The swelled beads will be placed into a 500 mm x 10 mm I.D. chromatographic column, containing a glass wool plug at the bottom. The column will then be rinsed with methylene chloride. A glass wool plug followed by a layer of glass beads will be placed on top of the BioBeads, and the column pre-eluted with an additional 200 mL of methylene chloride.

A 5-mL portion of the GPC calibration solution (100 mg corn oil, 2 mg bis(2-ethylhexyl)phthalate, 2 mg pentachlorophenol in 1 mL methylene chloride) will be transferred to the BioBeads SX-3 column. The column will be drained into a 12-mL graduated cylinder tube until the liquid is just above the surface of the GPC packing, and eluted with 200 mL methylene chloride. 10-mL fractions will be collected. Aliquots of these fractions will be analyzed for bis(2-ethylhexyl)phthalate and pentachlorophenol by GC/FID on a 1% SP1240 DA GC column. The corn oil elution pattern will be determined by evaporating an aliquot of each of the fractions to dryness and determining the weight of the residue. The concentration of each component in each fraction will be plotted versus the total eluent volume. From this plot, the range of eluent volumes to be collected will be determined as follows:

Initial Volume =

Eluent Volume at which $\geq$ 85% of the corn oil is eluted.

Final Volume =

Eluent Volume at which 100% of the phenol and phthalate is eluted + 50 mL.

For a typical calibration, the first 60 mL (85% corn oil) will be discarded and the next 110 mL retained for sample analysis.

An aliquot volume of the sample extract (P021-P030) equivalent to 200 mg (determined by Method A012-GRAV) will be transferred to the calibrated GPC column. A 200-mL portion of methylene chloride will be used to elute the column. The eluent volume determined above will be collected and concentrated as described in Method P031.

Reference: Miller, H.C., R.H. James and W.R. Dickson, "Evaluated Methodology for the Analysis of Residual Wastes," Report prepared for the U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, D.C., by Southern Research Institute, Birmingham, Alabama, under Contract No. 68-02-2685 (December 1980).

Method Number: P043

Method Name: Silica Gel Chromatography

Matrix: Sample Extracts

Method Parameters:

Silica gel is typically used as a secondary cleanup procedure to other preparation techniques such as derivatization. The procedure described below follows the Level 1 approach. Other procedures are described in the Federal Register, as referenced below.

Silica gel (Davison, 60-200 mesh, Grade 950) which has been activated at 130°C for > 5 h will be stored in a dessicator until used. A 10 mm I.D. chromatographic column will be slurry packed with 6.0g activated silica gel in n-pentane. Approximately 3 ± 0.2g clean, anhydrous sodium sulfate will be added to the top of the silica gel layer. The column will be pre-eluted with 20 mL n-pentane (pesticide grade) and the eluent discarded just prior to exposure of the sodium sulfate layer to air. 2 mL of sample in cyclopentane will be pipetted onto the column. The following solvents will be used to elute the constituents in the sample from the silica gel:

Fraction 1	pentane (25 mL)
Fraction 2	20% methylene chloride in pentane (10 mL)
Fraction 3	50% methylene chloride in pentane (10 mL)
Fraction 4	methylene chloride (10 mL)
Fraction 5	5% methanol in methylene chloride (10 mL)
Fraction 6	20% methanol in methylene chloride (10 mL)
Fraction 7	50% methanol in methylene chloride (10 mL).

References:

Lentzen, D.E., D.E. Wagoner, E.D. Estes and W.F. Gutknecht, "EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," EPA-600/7-78-201 (October 1978). NTIS No. PB293795/AS.

U.S. Environmental Protection Agency, Federal Register, 44, 69464-69575 (December 3, 1979).

Method Number: P044

Method Name: Alumina Column Chromatography

Matrix: Sample Extracts

Method Parameters:

Chromatography on alumina is typically used after sample extraction and Florisil chromatography.

A previously-prepared extract which has, in most cases, already been subjected to Florisil column separation will be evaporated to dryness and redissolved in $\leq$ 10 mL of chloroform (pesticide grade). An alumina column will be prepared by adding 3 inches of activated alumina (Woelm neutral, Alupharm Chemicals, New Orleans, Louisiana, or equivalent, deactivated to 3% water) to a liquid chromatography column, 100 x 20 mm with a teflon stopcock.

The chloroform solution containing the organic(s) of interest will be transferred to the column. The column will be eluted with the appropriate solvents, as given in the reference below.

Reference: U.S. Environmental Protection Agency, Federal Register, 44, 69464-69575 (December 3, 1979).

Method Number: P045

Method Name: Liquid/Liquid Extraction

Matrix: Sample Extracts

Method Parameters:

A 10g aliquot of the sample extract (Methods P021-P030) or an organic liquid sample will be diluted in 20 mL of an appropriate solvent. A 20-mL portion of distilled water, adjusted to pH 12-13 with 6N NaOH, will be added. This sample/aqueous mixture will be shaken in a 125-mL separatory funnel for 1 min. The phases will be allowed to settle for 10 min and the aqueous phase removed. The organic solvent layer will be extracted two additional times with distilled water at pH 12-13.

Reference: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

VI. ANALYSIS PROCEDURES

A. OVERVIEW

The overall strategy for analyzing hazardous wastes includes both test procedures to determine the characteristics of the waste, and analysis procedures to determine the composition of the waste. This section summarizes the test procedures for determining the characteristics of the waste. It also describes analysis methods appropriate to the various hazardous constituents of interest in waste, stack gas effluents, and other effluents during a trial burn. Both the preparation and analysis methods were chosen to be as widely applicable as possible. Analysis procedures, both specific and survey, were selected on the basis of their appropriateness to a large number of compounds, and were not necessarily optimized for each individual constituent. The primary rationale behind this approach was to minimize the cost of providing assessments of the levels of POHCs, while still meeting the constraints of the permitting process.

The test procedures used to determine the characteristics of the waste and the steps involved in the proximate analysis of the waste are performed on a waste sample prior to any sample preparation procedures. Both the survey and directed analysis procedures will involve at least some of the sample preparation steps outlined in the preceding chapter. These analyses generally require either a sample extract for organic analysis or a digested sample for inorganic analysis.

B. WASTE CHARACTERISTICS

The characteristics of the waste are defined in terms of Ignitability (I), Corrosovity (C), Reactivity (R), and Extraction Procedure Toxicity (E). The test procedures specified in "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980), SW-846 Revision A (August 8, 1980), and SW-846 Revision B (July 1981), are used to determine whether the wastes exhibit the characteristics of a hazardous waste, as defined by Section 3001 of RCRA.

1. Ignitability (Method C001)

The objective in determining the ignitability characteristic is to (a) identify wastes which present fire hazards due to being ignitable under routine storage, disposal, and transportation procedures, and (b) identify wastes capable of severely exacerbating a fire once it is started.

A solid waste is considered to exhibit the characteristic of ignitability if a representative sample of the waste has any of the following properties:

- it is a liquid, other than an aqueous solution, containing less than 24 percent alcohol by volume, and has a flash point of less than 60°C;

- it is not a liquid but is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture or spontaneous chemical changes and, when ignited, burns vigorously;

- it is an ignitable compressed gas; or

- it is an oxidizer.

2. Corrosivity (Method C002)

The objective in determining the corrosivity characteristic, as defined in 40 C.F.R. Part 261.22, is to identify wastes which might pose a hazard to human health or the environment due to their ability to mobilize toxic metals if discharged into a landfill environment. In addition, a secondary objective is to identify wastes that would require handling, storage, transportation, and management equipment to be fabricated of specially selected materials of construction. Also, corrosivity tests identify wastes that might destroy human or animal tissue in the event of inadvertent contact.

A solid waste is considered to exhibit the characteristic of corrosivity if a representative sample has either of the following properties:

- it is aqueous and has a pH $\leq$ 2 or $\geq$ 12.5; or

- it is liquid and corrodes steel at a rate > 6.35 mm per year at a test temperature of 55°C.

3. Reactivity (Method C003)

The definition of a waste as "reactive" is intended to identify wastes which, because of their extreme instability and tendency to react violently or explode, would pose a problem at all stages of the waste management process. This definition is a paraphrase of the narrative definition used by the National Fire Protection Association.

A solid waste is considered to exhibit the characteristic of reactivity if it shows any of the following properties:

- it readily undergoes violent chemical changes;

- it reacts violently or forms potentially explosive mixtures with water;

- it generates toxic fumes when mixed with water or, in the case of cyanide or sulfide bearing wastes, when exposed to mildly acidic or basic conditions;

- it explodes when subjected to a strong initiating force; or
- it fits within the Department of Transportation's forbidden explosives, Class A explosives, or Class B explosives classification.

Reactivity is determined by applying best professional judgment to the available data. There are no explicit experimental test procedures for determining this characteristic.

4. Extraction Procedure Toxicity (Method C004)

The Extraction Procedure Toxicity Test (E) is designed to simulate the leaching a waste would undergo if it were disposed in an improperly designed sanitary landfill. It is a laboratory test in which a representative sample of a waste is extracted with distilled water maintained at a pH of 5 with acetic acid. The extract obtained, the "EP extract," is then analyzed to determine if any of the thresholds established for eight elements (viz., arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver), four pesticides (viz., endrin, lindane, methoxychlor, and toxaphene), and two herbicides (viz., 2,4,5-trichlorophenoxypropionic acid (2,4,5-T), and 2,4-dichlorophenoxyacetic acid (2,4,-D)) have been exceeded.

A solid waste is considered "EP toxic" if the threshold levels (Table 11) designated in 40 C.F.R. Part 261.24, are exceeded in the "EP extract."

C. PROXIMATE ANALYSIS

The initial analysis of all waste samples will involve an analysis of the approximate composition of the sample. Such an analysis includes determination of physical properties, such as moisture, solid, and ash content, as well as determination of such chemical properties as the amount of total organic carbon, total organic halogen, elemental composition, viscosity, and heating value of the waste. A description of each method follows:

The type of data generated by the proximate analysis is indicated on the Proximate Analysis Reporting Form, shown as Table 12.

1. Moisture, Solid and Ash Content (Methods A001-A002)

a. Macro-scale Technique (Method A001)

- Loss on Drying--LOD (Method A001a)

An aliquot (Table 9) of a well mixed sample is transferred to a tared porcelain, platinum, or Vycor evaporating dish (previously ignited at 600°C for 1 hour and cooled in a desiccator). The sample and dish are weighed and then heated on a hot plate to evaporate the sample without

TABLE 11

THRESHOLD LEVELS OF CONTAMINANTS IN THE EXTRACTION PROCEDURE TOXICITY TEST

Contaminant	Threshold Level (mg/L)
Metals	
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium (Cr + 6)	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0
Pesticides	
Endrin	0.02
Lindane	0.4
Methoxychlor	10.0
Toxaphene	0.5
Herbicides	
2,4-Dichlorophenoxyacetic acid	10.0
2,4,5-Trichlorophenoxypropionic acid	1.0

TABLE 12

PROXIMATE ANALYSIS REPORTING FORM

Sample_____

Moisture, Solid, and Ash Content

Analyst and/or Laboratory

Date

% Moisture
% Solids
% Ash

Elemental Composition

% Carbon
% Nitrogen
% Sulfur
% Phosphorus
% Fluorine
% Chlorine
% Bromine
% Iodine

Total Organic Carbon

Total Organic Halogens

Heating Value of Waste

Viscosity

boiling, to near dryness. The sample and dish are then transferred to a 103°C oven to complete the evaporation. Periodically (at intervals usually greater than or equal to 1 hour), the sample is removed from the oven, cooled in a desiccator and weighed. The drying is considered complete when the loss of weight in a given interval is less than 4 percent of the previous weight.

The percent solids are calculated as follows:

$$\text{Solids (\%)} = \frac{\text{Final Weight--Tare}}{\text{Initial Weight--Tare}} \times 100.$$

The percent moisture is calculated as follows:

$$\text{Moisture (\%)} = 100 - \text{\% Solids.}$$

It should be noted here that the moisture content determination involves heating a sample at 103°C for a prolonged time period, and it is probable that the volatile organic content would be lost along with the moisture content. The loss of volatile organic components would also be applicable to the micro-scale moisture content determination.

- Loss on Ignition--LOI (Method A001b)

After removal of an aliquot (<10% of the solid residue) for elemental analysis, the weighed solids in the evaporating dish are ignited for 30 minutes at approximately 600°C. The ash is then cooled in a desiccator, and weighed.

The ash content is calculated as follows:

$$\text{Ash (\%)} = \frac{\text{Weight of Solid after Ignition}}{\text{Weight of Sample before Drying}} \times 100.$$

If ash content is <0.1%, the result will be reported as ppm ash:

$$\text{Ash (ppm)} = 10^4 \times \text{\% Ash.}$$

b. Micro-scale Technique (Method A002)

Thermogravimetric analysis (TGA) may also be used for micro-scale determination of moisture, solid, and ash content of non-aqueous liquid samples and solid samples when insufficient sample is available for the macro-scale analysis of these parameters.

A sample aliquot ($\leq$50 mg) is placed in the sample boat of the TGA instrument and heated at the rate of 10°C/min in air to 500°C. The results of the TGA analysis are reported as a plot of weight (mg) vs. temperature (°C). The moisture, solid, and ash content are estimated from the curve as follows:

$$\text{Solids (\%)} = \frac{\text{Weight at 125°C}}{\text{Initial Weight}} \times 100$$

$$\text{Moisture (\%)} = 100 - \text{\% Solids}$$

$$\text{Ash (\%)} = \frac{\text{Final Weight at 500°C}}{\text{Initial Weight}} \times 100.$$

It is preferable that the thermal instrument be capable of presenting weight loss directly in percent. The values can then be determined directly from the curve as follows:

Moisture (%) = Value at 125°C
Solids (%) = 100 - Value at 125°C
Ash (%) = 100 - Value at 500°C

A faster method involves two isothermal measurements, one at 125°C and another one at 500°C. Instrument recordings may be made by either of the two methods above. A 2-min equilibration period is allowed at each isothermal temperature.

2. Elemental Composition (Method A003)

Aliquots of organic liquid wastes, solid wastes, or of the dried solids (from the LOD determination of aqueous wastes or sludges) are analyzed to determine the concentration (%) of the following elements: carbon, nitrogen, phosphorus, sulfur and halogens (i.e., iodine, chlorine, fluorine, bromine). A number of service laboratories perform these analyses on a routine basis.

3. Total Organic Carbon and Total Organic Halogen (Method A004)

The levels of total organic carbon (TOC) and total organic halogen (TOX) are measured in much the same way as carbon and halogens are measured in Method A003. The total organic carbon is measured by combustion of the sample to form CO_2 (with or without subsequent conversion to CH_4) and measurement of the CO_2 and CH_4 formed during combustion. For organic halogens, the sample is combusted to form the halide which is trapped in solution. Potentiometric titration against silver is then performed to determine a total halogen concentration (except fluorine).

Determination of the total organic carbon and total organic halogens is more useful than the elemental composition determination if the sample is primarily an aqueous liquid.

4. Viscosity (Method A005)

The viscosity of liquid wastes affects the feasibility of destroying those wastes at a particular incineration facility. This fact can be attributed, in part, to the limits on the feed rate of the waste imposed by the viscosity of the waste. The viscosity of the waste is determined by measuring the time (in seconds) it takes for a fixed volume of the liquid waste to flow through the capillary of a calibrated viscometer. Both the head pressure on the waste and the temperature of the viscometer are controlled. The kinematic viscosity is the product of the flow time and the calibration constant of the viscometer. The dynamic viscosity--the value of interest for incineration processes--is obtained by multiplication of the measured kinematic viscosity by the density of the liquid waste.

5. Heating Value of the Waste (Method A006)

The heating value of a waste corresponds to the quantity of heat released when the waste is burned (commonly expressed in Btu/lb). Since combustion reactions are exothermic, all organic wastes have some finite heating value. However, the magnitude of this heating value must be considered in establishing an energy balance for the combustion chamber and in assessing the need for auxiliary fuel firing. To maintain combustion, the amount of heat released by burning the waste must be sufficient to heat the incoming waste to its ignition temperature and to provide the necessary activation energy for the combustion reactions to occur. Activation energy (expressed as Btu/lb or the equivalent) is the quantity of heat needed to destabilize molecular bonds and create reactive intermediates so that the exothermic reaction with oxygen will then proceed. The experimental determination of the heating value for the waste influents is measured by calorimetry.

D. SURVEY ANALYSIS

The survey analysis methods are designed to provide an overall description of the chemistry of a sample during a trial burn in terms of both the major types of organic compounds and the inorganic elements that are present. The additional characterization of the waste influent stream or the effluent streams by survey methods during a trial burn provides a check on the manifest listing of components in the waste, permits identification of high priority POHCs in the wastes or in the effluents which may be unexpected, and supplements the chemical information obtained during the directed analysis of those POHCs specified in the facility permit.

A survey analysis approach, which is compatible with the preparation procedures presented and is consistent with the environmental goals described previously, is an adaptation of the Level 1 Environmental Assessment procedures (7) developed by the EPA's Process Measurements Branch as part of a phased approach to environmental assessment. For POHCs, the survey analysis methods include determination of:

- organic content by chromatographic (TCO) and gravimetric (GRAV) procedures,

- organic compound class type by infrared (IR) and probe mass spectrometric procedures (LRMS), and

- specific major organic components by gas chromatography/ mass spectrometric (GC/MS) analysis.

For inorganic-containing species in Appendix VIII, the survey analysis methods include determination of the elemental composition of the sample.

1. Survey Analysis of Organic Content (Methods A011-A017)

The survey analysis methods for organic components provide information for identifying the major classes of organic compounds present in the waste, the facility process streams, and the stack gas. There is also sufficient information for estimating the concentrations of the compound classes in the various streams. An example of the information obtained from a survey analysis of an integrated stack gas sample collected by the SASS sampling method is presented in Table 13. The concentration estimates are intended to be accurate to within a factor of 2 or 3 and are generally reported to one significant figure.

a. Organic Content by TCO (Method A011)

The chromatographable organics (TCO) value provides a quantitative measure of the amount of organic material in the sample which have boiling points between 100 and 300°C. This method is based on gas chromatography.

An aliquot (1-5 µL) of the organic extract prepared according to the procedures in Methods P021 to P030 of this manual is taken for gas chromatographic TCO analysis. The analysis is made using the Level 1 GC conditions (10% OV-101 on 100/120 mesh support; 30°C (6 min) → @ 20°C/min → 250°C (hold); FID). Normal hydrocarbons are used for qualitative retention time and for quantitative detector response calibration. The TCO results are reported as mg of TCO range organics (b.p. 100-300°C) per mL of extract and also per L (kg) of waste. The chromatograms, which contain "fingerprint" data beyond the TCO values, should be retained.

Data from the TCO analysis are reported on a form such as delineated below:

TABLE 13

SUMMARY OF RESULTS FOR ORGANIC EXTRACTS OF A SASS TRAIN SAMPLE

Σ (mg/m^3)

Categories	Particulate Module			Sorbent Module			
	Rinses*	>3 μm	<3 μm	Resin	Rinse	Condensate**	Total***
Aliphatic hydrocarbons		<0.06	0.04	0.3	0.8		1.1
Aromatic hydrocarbons--benzenes							0.6
Fused aromatics, MW <216		0.25	0.15	6.3	22.0		29.0
Fused aromatics, MW >216		0.25	0.15	4.2	21.0		26.0
Heterocyclic N		0.31	0.19	0.6	19.0		20.0
Heterocyclic S		<0.06	<0.04	0.4	2.0		2.4
Heterocyclic O		<0.06	<0.04	0.2	2.0		2.2
Phenols		0.06	0.04	0.1			0.2
Esters		0.18	0.11	0.1	0.1		0.5
Carboxylic acids		<0.60	<0.04	0.3	0.3		0.6
Sulfur					0.2		0.2
Inorganics				0.1			0.1
Unclassified		0.06	<0.04	0.2			0.3
Silicones		0.06	0.04				0.1

* Rinses corresponded to 0.03 mg/m^3 of organics and were not subjected to LC-IR-LRMS analysis.

** No condensate was collected for this sample.

*** Rounded results.

Source: Reference 7.

Sample Number	TCO in Extract (mg/mL)	TCO in Waste (mg/L or mg/kg)

b. Organic Content by GRAV (Method A012)

The gravimetric (GRAV) value provides a quantitative measure of the amount of organic material in the sample which have boiling points in excess of 300°C.

An aliquot corresponding to one-tenth of the concentrated sample extract is taken for gravimetric analysis. The aliquot is then transferred to a clean, tared aluminum weighing dish and evaporated in a desiccator at room temperature to constant weight (±0.1 mg). The GRAV results are reported as mg of GRAV range organics (b.p. >300°C) per mL of extract and also per L (kg) of waste.

Data from the GRAV analysis are reported on a form such as that delineated below:

Sample Number	GRAV in Extract (mg/mL)	GRAV in Waste (mg/L or mg/kg)

c. Organic Content--Volatiles (Method A013)

The volatile organic content value provides an estimate of the level of volatile materials present in the sample with boiling points below 100°C. An aliquot (0.5 µL) of the carbon disulfide extract prepared according to Methods P021b, P022b, or P024c, or of the waste iself if it is an organic liquid, is taken for survey analysis of the volatile organic content by gas chromatography with flame ionization detection (GC/FID). A packed column, 0.2% Carbowax 1500/Carbopack C 60/80 mesh, is used with a

temperature program of 47°C (3 min) → @ 8°C/min → 220°C (15 min). If the GC/FID analysis reveals the presence of peaks from volatile sample components at levels higher than the internal standard (i.e., concentrations of $\geq$ 10 ppm in liquid samples, or $\geq$ 100 ppm in solid samples), a separate aliquot of the sample should be taken for GC/MS analysis, according to the procedures presented in Method A016. The total FID intensity is used to guide selection of an appropriate sample size for the GC/MS analysis. If GC/FID analysis shows no peaks higher than that of the internal standard, the results are reported as:

Estimated volatile organic content < 10 ppm (for liquids), and
<100 ppm (for solids).

d. Compound Class Type by Infrared Analysis (Method A014)

The infrared analysis provides information on the functional groups present in the samples. The identified functional groups provide a description of the chemistry of the sample and the major chemical classes present.

An aliquot corresponding to 2-5 mg of the total organic content (TCO and GRAV) of a sample extract (Methods A011, P021-P030), or neat organic liquid waste, is analyzed by infrared (IR) spectrometry. IR spectra are obtained on samples held between two NaCl plates or on KBr pellets. Sample size is adjusted, so that the signal of the strongest sample peak is less than 1.0 absorbance unit. IR instrument conditions used for most samples are given below. Variations, if necessary, should be documented. The recommended conditions are as follows:

1) Dispersive Instrument:

- Resolution: The width of the spectral slit should not exceed 4 cm^{-1} through at least 80 percent of the wave number range.
- Wave number accuracy: ±4 cm^{-1} below 2000 cm^{-1} and ±15 cm^{-1} above 2000 cm^{-1}.
- Noise level: No more than 2 percent peak to peak.
- Baseline flatness: The I_o or 100% line must be flat to within 5 percent across the recorded spectrum.
- Energy: The instrument should be purged with dry gas or evacuated so that atmospheric water bands do not exceed the allowable noise level (2 percent) when the instrument is used in a double beam mode.
- Spectral range: Spectra should be recorded, without gaps, over the spectral range (3800-600 cm^{-1}).
- False radiation: Not to exceed 2 percent.

2) Fourier Transform (FT) Instrument:

The Fourier Transform instrument conditions are generally designed to meet the criteria stated above for dispersive instruments. In an FT-IR analysis, 64 scans average, or the number necessary to achieve a signal-to-noise ratio on the order of 0.5 percent T average, are accumulated. All spectra in a related sample set should be acquired using the same apodization function to allow spectral subtraction. FT-IR spectra are plotted in the transmission mode to facilitate comparison with standard spectra.

A report such as that shown in Table 14 provides a convenient format for reporting the functional groups identified by the infrared analysis. These data are combined with the mass spectral data (Methods A015 and A016) to characterize the sample in terms of the major chemical classes present.

e. Mass Spectrometric Analysis (Method A015)

The low resolution mass spectrometric (LRMS) analysis provides specific compound identifications (non-isomer specific) which may be integrated with other survey analysis information to identify the major chemical classes which are present/not present in the sample in terms of the major chemical components identified.

A sample aliquot (100 µL) of the organic extract (Method P021 to P030) or neat sample is dried at room temperature on the direct insertion probe of the mass spectrometer. Spectra are then acquired over a probe temperature range of 50°C to 400°C.

The ionization mode used for the direct LRMS analysis is the same as that used for the GC/MS analysis to facilitate comparison of the spectra. The mode may be either electron impact (EI) or chemical ionization (18). In the EI mode, an ionization voltage of 70 eV is used to obtain spectra for comparison with standard reference spectra ionization. Voltages of 8-20 eV are used to obtain spectra with reduced fragmentation. A mass spectrometer capable of attaining a true resolution of 1 part in 600 minimum should be used to ensure that it is possible to identify heteroelement compositions.

Spectra are interpreted according to the procedures described by Stauffer (18). The results are reported as a list of the compound types that appear to be present in the sample. The Level 1 list of reporting categories (Table 15) will be used and supplemented as necessary to incorporate multifunctional organics and other specific categories of interest. For each category, the molecular weight range is specified. The relative abundance of each category is indicated on a three-point logarithmic scale:

100 = major component
10 = minor component
1 = trace component

TABLE 14

IR ANALYSIS REPORT FORM

Contractor_____

Sample ID Number_____

Sample Description_____

Analyst Responsible_____Date Analyzed_____Time_____

Instrument_____Sample Cell Type_____

Observations_____

_____

Results

Major Functional Groups	Frequencies on which Assignments are Based

TABLE 15

CATEGORIES FOR REPORTING LRMS DATA

Category (Subcategory)
Aliphatic hydrocarbons
(Alkanes)
(Alkenes)
(Alkynes)
Halogenated aliphatics
(Saturated)
(Unsaturated)
Aromatic hydrocarbons
(Benzenes)
Halogenated aromatic hydrocarbons
Nitro aromatic hydrocarbons
Fused alternate, nonalternate hydrocarbons
MW < 216 (methyl pyrene)
MW > 216
Ethers
(Halogenated ethers)
Epoxides
Aldehydes
Heterocyclic oxygen compounds
Nitriles
(Aliphatic)
(Aromatic)
Alcohols
(Primary, secondary, tertiary)
(Glycols)

Category (Subcategory)
Phenols
(Alkyl, etc.)
(Halogenated phenols)
(Nitrophenols)
Esters
(Phthalates)
Ketones
Amines
(Primary, secondary, tertiary)
(Hydrazines, azo compounds)
(Nitrosoamines)
Heterocyclic nitrogen compounds
(Indoles, carbazoles)
(Quinolines, acridines)
Alkyl sulfur compounds
(Mercaptans)
(Sulfides, disulfides)
Heterocyclic sulfur compounds
(Benzothiophenes)
Sulfonic acids, sulfoxides
Amides
Carboxylic acids
Silicones
Phosphates

Specific notation is made of any compound categories which make their first appearance at elevated probe temperatures (>200°C) since these low volatility materials are less likely to be detected in the complementary GC/MS analysis. An estimate is made and reported as to the percentage of any of the sample that did not vaporize into the MS from the direct insertion probe.

Table 16 shows an example of a LRMS analysis report form.

f. Specific Major Components by GC/MS (Method A016)

In addition to being the primary analytical tool for the directed analysis of organic POHCs, gas chromatography/mass spectrometry (GC/MS) may be used as a survey analysis technique. For a survey analysis, the GC/MS is operated in the full mass range scanning mode with electron impact ionization. The concentrated extract (Method P031), with or without additional cleanup procedures (Methods P041 to P045) of the semivolatile fraction of the sample, is spiked with a retention time standard, such as d_{10}-phenanthrene. The total ion chromatogram for the sample is examined for the 20 most intense peaks, or for all peaks with an intensity of more than 1 percent of the total ion intensity (after eliminating background due to the GC column). Qualitative identification is attempted for all of the designated peaks by either computerized library searching or manual spectral interpretation. Qualitative identification and quantification protocols are detailed later in this chapter.

The results of this analysis are reported as a list of specific compounds identified, the relative retention time (vs. d_{10}-phenanthrene) and relative intensity of the peak, and an indication of the goodness of fit of the sample spectrum to a standard spectrum. The latter is indicated by P=xxx for a purity criterion, F=xxx for a fit criterion, RF=xxx for a reverse fit criterion when computerized matching procedures are employed, and M=strong or M=tentative for a manual identification or confirmation. Table 17 shows an example report form.

g. Specific Major Components by HPLC/IR or HPLC/LRMS (Method A017)

Samples known or suspected to contain substantial quantities of non-volatile organic components (i.e., GRAV:TCO ratio $\geq$20:1) and/or to contain organic compound categories not amenable to gas chromatography are analyzed by HPLC in a survey mode. A reversed phase C_{18}-HPLC column is used with an acetonitrile/water or a methanol/water solvent system. Fractions of the eluent corresponding to the ten most intense peaks as recorded by a 254-nm UV detector, are collected and analyzed by IR (Method A014) or probe LRMS (Method A015) after evaporation of solvent.

The results of this analysis are reported as a list of specific compounds, functional groups, and/or compound classes identified in the HPLC fractions. An indication of the confidence of the assignment(s) is provided by the designations "M=strong" or "M=tentative" for manual identification or confirmation. Table 18 shows an example report form.

TABLE 16

LRMS ANALYSIS REPORT FORM

Contractor_____

Sample ID Number_____

Sample Description_____

Analyst Responsible_____Date Analyzed_____Time_____

Instrument_____

Observations_____

_____

Results

Major Categories, Subcategories, Specific Compounds:

Intensity	Category	MW Range

TABLE 17

GC/MS SURVEY REPORT FORM

Contractor_____

Sample ID Number_____

Sample Description_____

Analyst Responsible_____ Date Analyzed_____ Time_____

Instrument_____

Column_____

GC Temperature Program_____

Observations_____

_____

Results:

Compound Identified	Peak		Goodness of Fit Criterion
	RRT (min)	Relative Intensity (%)	

TABLE 18

HPLC/IR OR HPLC/LRMS SURVEY REPORT FORM

Contractor_____

Sample ID Number_____

Sample Description_____

Analyst Responsible_____Date Analyzed_____Time_____

HPLC Column_____Detector Sensitivity_____

HPLC Solvent System_____

IR Instrument Used_____

LRMS Instrument Used_____

Observations_____

_____

_____

Results

Compound Functional Group or Class Identified	HPLC DATA		Identified by:		Confidence Rating
	Retention Time Window	AUFS at 254 nm	IR	LRMS	

2. Survey Analysis of Inorganics (Method A021)

A survey analysis is conducted to determine the possible presence in the waste of ppm levels of the metals listed in Table 19. This list includes the metals for which primary and secondary drinking water criteria exist, the priority pollutant metals, and the additional metals that can be determined at no incremental cost in the survey analysis by inductively coupled argon plasma (ICAP) emission spectroscopy. The ICAP analysis can provide survey data on 26 metals; additional metals are determined by atomic absorption spectroscopy (AAS), since ICAP is insufficiently sensitive for their determination.

A portion of the waste sample corresponding to 50-300 mg of solid content (as determined by Method A001a or A002) is taken for survey analysis by ICAP. Separate aliquots are taken for the AAS determinations of antimony, arsenic, lead, mercury, and selenium. Samples are digested, using the procedures indicated in Method P032, prior to analysis. The AAS analyses of digested samples are performed, as described in Method A221 to A235 of this report.

The results of the survey analysis for metals are reported as a table of metals found in the digested sample and their concentrations in the digested solution as analyzed and in the original sample. It is anticipated that detection limits for the metals would be on the order of 10-100 ppm in the waste for this survey analysis. Accuracy, precision, and recovery data are not generally obtained for the survey analysis of metals.

E. DIRECTED ANALYSIS

The directed analysis methods presented here allow the measurement of the levels of permit-designated POHCs in samples collected during a trial burn. The compounds listed in Appendix VIII of 40 C.F.R. Part 261 have been sorted into groups, the members of which share a common analytical method for their measurement. In part, these groupings are based on similar chemistry. For example, the analysis methods which are appropriate to a single alcohol POHC are appropriate to other alcohol POHCs. By grouping the POHC compounds in this way, the costs incurred during the directed analysis activities may be minimized.

Whenever possible, a fused silica capillary column GC/MS has been specified as the analytical method of choice. This specification is based on the high sensitivity/selectivity of such systems, coupled with their generally good quantification ability. In those instances in which GC/MS is not appropriate, HPLC methods have been designated whenever possible.

Appendix C provides cross-reference information for each hazardous constituent in Appendix VIII and its method number.

TABLE 19

METALS SOUGHT IN A SURVEY ANALYSIS

Metal	Drinking Water Standard	Priority Pollutant	Method		Alternative Method	
			Name	Number	Name	Number
Aluminum			ICAP	A021		
Antimony		✓	AAS	A221		
Arsenic	✓	✓	AAS	A222		
Barium	✓		ICAP	A021	AAS	A223
Beryllium		✓	ICAP	A021	AAS	A224
Boron			ICAP	A021		
Cadmium	✓	✓	ICAP	A021	AAS	A225
Calcium			ICAP	A021		
Cobalt			ICAP	A021		
Chromium	✓	✓	ICAP	A021	AAS	A226
Copper	✓ (2°)	✓	ICAP	A021		
Iron	✓ (2°)		ICAP	A021		
Lead	✓	✓	ICAP	A021	AAS	A227
Magnesium			ICAP	A021		
Manganese	✓ (2°)		ICAP	A021		
Mercury	✓	✓	AAS	A228		
Molybdenum			ICAP	A021		
Nickel		✓	ICAP	A021	AAS	A229
Osmium			ICAP	A021	AAS	A230
Phosphorus			ICAP	A021		
Potassium			ICAP	A021		
Selenium	✓	✓	AAS	A231		
Silicon			ICAP	A021		
Silver	✓	✓	ICAP	A021	AAS	A232
Sodium			ICAP	A021		
Strontium			ICAP	A021	AAS	A233
Thallium		✓	ICAP	A021	AAS	A234
Thorium			ICAP	A021		
Titanium			ICAP	A021		
Vanadium			ICAP	A021	AAS	A235
Zinc	✓ (2°)	✓	ICAP	A021		
Zirconium			ICAP	A021		

1. Organic Constituents (Appendix VIII)

a. Volatiles (Method A101)

The analysis method for volatile organic POHCs is that specified in SW-846 (4) and EPA Method 624 (19). This method utilizes a purge-and-trap procedure to remove the volatile organics from the sample matrix and collect the volatiles on a sorbent cartridge for subsequent analysis. The collected sample is then thermally desorbed from the sorbent cartridge onto a packed GC column with subsequent MS detection of the volatile species. For volatile gases which were collected on special-purpose sorbents, the sorbent cartridge is thermally desorbed onto a packed GC column for analysis. The analytical finish specified in this method is also suitable for direct application to grab samples collected in gas-sampling bulbs.

In addition to the analytical considerations involved in the transmission of the volatile POHCs through the GC/MS instrumentation, the efficiency of the purge-and-trap system at separating the POHCs from the bulk waste or water (for scrubber waters) is crucial to the accurate measurement of the POHC levels. There is a wide range of purge efficiencies for the various volatile POHCs. This disparity in efficiencies is due in part to the solubility characteristics of the individual constituents. To compensate for differing purging efficiencies, recovery checks must be made in order to compensate for incomplete sparging of each POHC.

b. Extractable Species (Method A121)

The analytical method for the extractable POHCs is essentially that found in SW-846 (4) or EPA Method 625 (19), with the substitution of a fused silica SE-54 coated capillary GC column for the SP 2250 DB packed column. This substitution increases the specificity and sensitivity of the analysis procedure due to the higher resolution and inertness of the fused silica capillary GC column. The method for the extractable hazardous constituents is outlined below.

Following extraction, an aliquot of the combined acidic and basic extracts is injected onto a fused silica capillary GC column, using either on-column, splitless, or split injection techniques (the latter only for concentrated extracts or neat liquid organic wastes). The sample is eluted with a temperature program such as that found in Method A121, using either hydrogen (preferred) or helium as the carrier gas. Electron impact (EI) ionization at 70 eV is utilized to produce mass spectra. Alternatively, chemical ionization (CI) conditions may be used to produce mass spectra, although the significant ions for POHC identification are different from those for EI ionization. The qualitative and quantitative criteria for identifying and measuring the POHCs in this category are found later in this chapter. The MS ions and their abundance ratios have been tabulated in Appendix E.

c. Compounds by HPLC (Methods A122, A123)

HPLC analysis procedures (20) were developed by Southern Research Institute for several organic compounds listed in Appendix VIII (40 C.F.R. Part 261) that could not be determined by gas chromatography with mass spectrometric (GC/MS) detection. Several compounds have been included that are amenable to analysis by either HPLC or GC/MS.

The HPLC method was developed for use with reversed-phase C_{18} columns since reversed-phase columns are less apt than normal-phase columns to sorb organic analytes irreversibly. The UV-VIS detector was selected as the detection system for the generalized HPLC method. Since this detector can measure absorbances over a broad range (190 or 600 nm), this detection system offers selectivity and versatility in determining a variety of compound types.

Two reversed-phase columns were used with an acetonitrile/water eluent:

- Perkin-Elmer HC-ODS-Sil-X-1, 10-µm particle size, 25 cm x 2.6 mm I.D.; and
- Waters Associates' µBondapack C_{18}, 10-µm particle size, 30 cm x 3.9 mm I.D.

(The Waters column was employed only after it was found that the chromatography of certain compounds on the Perkin-Elmer column was not optimal.)

Rather than establish a single set of HPLC operating conditions, various procedural options have been developed that will allow determination of a broad range of compound types. Several isocratic and gradient elution programs with an acetonitrile/water mobile phase were investigated. In the determination of several POHCs, the eluent was acidified. The wavelength of UV-VIS detection was also varied as required to optimize sensitivity.

Six procedural options were developed. Three were formulated for a Perkin-Elmer reversed-phase C_{18} column, and three for a Waters reversed-phase C_{18} column. The options for both columns were either variations of the isocratic composition of the mobile phase or variations of the solvent program. The various procedures for the Perkin-Elmer column are as follows:

- Option 1A

  Solvent A: Distilled, deionized water
  Solvent B: Acetonitrile
  Solvent program: 10% B, 5 min; 10 to 100% B in 35 min; 100% B, 10 min
  Solvent flow rate: 1 mL/min

- Option 1B

  Solvent A: 1% (v/v) acetic acid in distilled, deionized water
  Solvent B: Acetonitrile
  Solvent program: 20% B, 10 min; 20 to 50% B in 10 min; 50% B, 5 min
  Solvent flow rate: 2 mL/min

- Option 1C

  Solvent A: 1% (v/v) acetic acid in distilled, deionized water
  Solvent B: Acetonitrile
  Solvent program: 10% B, 2 min; 10 to 100% B in 18 min
  Solvent flow rate: 2 mL/min

The various procedures for the Waters column are as follows:

- Option 2A

  Solvent A: Distilled, deionized water
  Solvent B: Acetonitrile
  Solvent program: 2% B, isocratic
  Solvent flow rate: 1 mL/min

- Option 2B

  Solvent A: Distilled, deionized water
  Solvent B: Acetonitrile
  Solvent program: 10% B, isocratic
  Solvent flow rate: 1 mL/min

- Option 2C

  Solvent A: Distilled, deionized water
  Solvent B: Acetonitrile
  Solvent program: 20 to 100% B in 20 min; 100% B, 10 min
  Solvent flow rate: 1 mL/min

Table 20 summarizes the data of the HPLC/UV determinations for the constituents listed in Appendix VIII. The appropriate procedural option, approximate retention time, and optimum wavelength of detection are listed for each compound.

d. Aldehydes and Acids (Methods A132, A133)

Aldehydes and acids were grouped together because of their chemical similarity.

TABLE 20

SUMMARY OF DETERMINATIONS OF POHCs BY THE GENERALIZED HPLC ANALYSIS METHOD

Compound	Procedural Option[a]	Retention Time (min)	On-Column Detection Limit[b] (ng)	Wavelength of Detection (nm)
Streptozotocin	1A	1.4	2 -	254 230[c]
6-Amino-1,1a,2,8,8a,8b-hexahydro-8-(hydroxymethyl)-8a-methoxy-5-methylcarbamate azirino[2',3':3,4] pyrrolo [1,1a] indole-4,7-dione (ester) (Mitomycin C)	1A	5.0	17	254
Phenol	1A	5.4	78 -	254 280[c]
4-Nitrophenol	1A	9.5	54 6	254 280[c]
2-Chlorophenol	1A	12.4	72 6	254 280[c]
Melphalan	1A	14.0	10	254
5-Nitro-o-toluidine	1A	14.3	1 -	254 253[c]
Thiuram	1A	16.3	1 -	254 280[c]
Chloro-m-cresol	1A	16.8	77 4	254 280[c]
2,4-Dichlorophenol	1A	17.6	100 2	254 280[c]

TABLE 20 (Continued)

SUMMARY OF DETERMINATIONS OF POHCs BY THE GENERALIZED HPLC ANALYSIS METHOD

Compound	Procedural Option[a]	Retention Time (min)	On-Column Detection Limit[b] (ng)	Wavelength of Detection (nm)
3-(alpha-Acetonylbenzyl)-4-hydroxycoumarin and salts [Warfarin]	1A	19.8	2 -	254 280[c]
2,4,6-Trichlorophenol	1A	20.0	53 7	254 280[c]
2,3,4,6-Tetrachlorophenol	1A	21.5	19 17	254 280[c]
Reserpine	1A	22.7	28 -	254 267[c]
Chlorambucil	1A	23.9	1 -	254 258[c]
2,4-Dichlorophenoxyacetic acid	1B	7.6	69 -	254 284[c]
Daunomycin[d]	1B	8.0	75	254
2,4,5-Trichlorophenoxyacetic acid	1B	14.2	55 -	254 287[c]
2,4,5-Trichlorophenoxypropionic acid	1B	16.5	38 -	254 287[c]
2,4-Dinitro-o-cresol (and salts)	1C	7.6	20	378[c]
Azaserine[d]	2A	4.0	2	254
N-Nitroso-N-methylurea	2A	8.4	10 -	254 234[c]

TABLE 20 (Continued)

SUMMARY OF DETERMINATION OF POHCs BY THE GENERALIZED HPLC ANALYSIS METHOD

Compound	Procedural Option[a]	Retention Time (min)	On-Column Detection Limit[b] (ng)	Wavelength of Detection (nm)
Saccharine and salts	2B	3.2	2 -	254 224[c]
Trypan blue[d]	2C	3.0	20	315
Epinephrine[d]	2C	3.0	60	279
Thiosemicarbazide[d]	2C	3.0	5	254
Thiourea[d]	2C	≅3.0[c]	6	254
Thioacetamide[d]	2C	≅4.0[c]	2	254
Ethylene thiourea[d]	2C	≅4.0[c]	8	254
Crotonaldehyde[d]	2C	5.0	1	230
Diethylstilbestrol	2C	14.0	4	240

[a]See text for description of options.

[b]Quantity injected that is required to yield a response twice the magnitude of background signal.

[c]This wavelength was selected from the reference UV spectrum as the optimum wavelength for analysis.

[d]Potential candidates for analysis by HPLC/UV.

Source: Reference 20.

Aldehydes are sufficiently polar that they exhibit poor chromatography unless they are first subjected to a derivatization procedure. This is reflected in the sampling procedure for aldehydes which uses a derivatizing reagent (2,4,-dinitrophenylhydrazine) for trapping the aldehydes. This reagent produces a colored product which can be identified by HPLC techniques with UV detection. This is the preferred method for analysis of aldehydes. An alternative method which uses pentafluorobenzylhydrazine, forms a derivative of the aldehyde which can then be analyzed by gas chromatography with MS or ECD detection.

The carboxylic acid POHCs are prepared for analysis by esterification with diazomethane to form the methyl ester, or with bis(trimethylsilyl)-acetamide to form the trimethylsilyl ester of the acid POHC. Following esterification, these compounds may be analyzed with GC/MS methods.

e. Alcohols (Method A134)

The alcohol POHCs may be analyzed with GC methods if the chromatographic phase is sufficiently polar. Columns coated with polyethyleneglycol phases have been used for these analyses. The most promising GC column packing material for alcohols is a Carbopack C coated with 0.8% tetra-hydroxyethyleneamine. If a capillary GC column is used, a Carbowax 20M column is sufficiently polar to allow analysis of alcohols. If the sample contains significant quantities of water, then a SE-52 capillary column should be used. Either MS or FID techniques may be used for detection of these compounds.

f. Inorganic-containing POHCs

In this edition of the manual, the analytical methods for the inorganic-containing organic materials are based on measurement of the inorganic species. However, analytical methods for the determination of organometallic constituents are currently under development.

g. Others

The analytical methods for the analysis of several POHCs cannot be classified under any of the preceding groups. The analysis methods for these constituents tend to be single-compound methods. The compounds found in this category generally represent fairly difficult analytical problems and, as such, require specialized analysis procedures. The individual methods are found at the end of this chapter. A cross-reference to the method appropriate for each POHC is found in Appendix C.

Although the number of compounds in the "other" category is moderately high, analyses for these species need to be conducted only in those rare instances when professional judgment (or survey analysis) suggests their probable presence in the waste to be incinerated.

2. Inorganic Constituents (Appendix VIII)

The inorganic constituents which may be analyzed during a directed analysis are categorized as metal or metal-containing, anion-containing, or gases. This designation is referenced to the portion of the POHC which is of primary environmental concern. Thus, a series of organometallic constituents all of which contain mercury, or a series of thallium salts, or a series of cyanide-containing salts are analyzed for mercury, thallium, and total cyanides, respectively. This approach permits a minimum number of analysis methods to encompass the range of inorganic constituents and thus, minimizes the analysis method costs. This approach, also, since it focuses on the environmentally active components of the waste, yields the most accurate assessment of the inorganic emissions of the incineration facility.

a. Metals (Methods A221-A235)

The metal-containing constituents from Appendix VIII are analyzed by atomic absorption spectroscopy (AAS), or inductively coupled plasma emission spectroscopy (ICAP) techniques. Two modes of analysis are used for these species; direct analysis from solution, or cold vapor/hydride evolution. The choice of the analysis mode depends upon the specific metal of interest in the directed analysis. The specific analytical methods are well documented in SW-846 (4) and elsewhere. The following discussion summarizes the general details concerning the AAS and ICAP analyses of these samples. Specific details for each element can be found in the method summaries and the included references (Methods A221 to A235).

The samples containing inorganic compounds are prepared for directed analysis by one of the digestion procedures discussed in the previous chapter. These procedures convert the metal-containing compounds into the inorganic form for analysis. For all of the metals, except arsenic, selenium, and mercury, the solution resulting from the digestion procedure may be aspirated directly into the flame for flame AAS, or into the plasma for ICAP, or injected directly into the furnace for flameless AAS analysis. Within the flame, plasma, or furnace, the inorganic compounds are reduced to their atomic state from which either absorption (AAS) or emission (ICAP) occurs at a wavelength which is specific for the element under investigation. The spectrometer is adjusted so that only the specific wavelength(s) of interest are detected at the photomultiplier detector. The amount of absorption or emission which occurs during the AAS or ICAP experiment may be directly related to the concentration of the metals present.

For selenium and arsenic, the solution resulting from the digestion of the sample is treated with stannous chloride to form the trivalent ion. The solution is then treated with zinc metal which converts the trivalent compound to the volatile hydride. The hydride is then detected by the AAS method.

For mercury, the solution resulting from digestion of the sample is treated with stannous sulfate which reduces the ionic mercury in the sample to the atomic species. The volatile atomic mercury is swept from the sample in a closed system through an absorption cell to a scrubber trap. The level of mercury in the sample is obtained from the integrated AAS signal formed during its evolution from the sample.

Table 21 summarizes the analytical wavelengths for each of the metals from the Appendix VIII list of hazardous constituents which are analyzed by AAS and ICAP procedures. Quantification of the levels of the metals listed in Table 21 must be done with direct methods (i.e., either by comparison to an external calibration curve, or by the method of standard additions). Both of these methods are well known, and have been described in numerous references (4).

An external calibration curve is prepared by plotting the absorbance (AAS) or transmittance (ICAP) versus concentration for a series of standards which span the linear working range of the analytical instrument. If the measured absorbance, or transmittance, of the sample analyzed under the same conditions as the standards is compared to the calibration curve, the concentration of the material in the sample can be interpolated.

For many of the samples which will be collected at hazardous waste incinerators, the level of potential interferences will be high enough that the method of standard additions must be used for quantification. With this method, aliquots of the digested sample are spiked with known amounts of the standard reference material and the absorbance for the spiked and unspiked samples measured. The concentration in the original sample is obtained by extrapolation of the calibration curve for the spiked and unspiked samples to zero absorbance.

b. Anions (Methods A251, A252, A253)

A number of the inorganic species listed in 40 C.F.R. Part 261, Appendix VIII are hazardous primarily because of the anionic portion of the compound. These compounds, which contain either cyanide or phosphide, are analyzed by a single method for that anion. A general procedure for the determination of anions in solution employs ion chromatography as an analytical technique (21).

The general procedure for the determination of inorganic cyanides is to acid-treat the sample, which causes the evolution of gaseous hydrocyanic acid (HCN). The HCN formed is trapped in a scrubber containing sodium hydroxide. The scrubber solution is then analyzed for total cyanide by titration with silver (for concentrations exceeding 1 mg/L of cyanide) or by a colorimetric procedure for lower concentrations. Because of the toxicity of HCN, the sample preparation steps for total cyanide measurement must be performed in a closed system placed in a well ventilated hood.

TABLE 21

CHARACTERISTIC DATA FOR METALS LISTED IN APPENDIX VIII

Metal (Element Symbol)	Wavelength (nm) AAS	Wavelength (nm) ICAP	Sample Form
Antimony (Sb)	217.6	206.8, 187.1	Solution
Arsenic (As)	193.7	189.0, 197.2	Hydride
Barium (Ba)	553.6	455.4, 233.5	Solution
Beryllium (Be)	234.9	313.0, 234.9	Solution
Cadmium (Cd)	228.8	226.5, 214.4	Solution
Chromium (Cr)	357.9	267.7, 294.9	Solution
Lead (Pb)	217.0	220.3, 217.0	Solution
Mercury (Hg)	253.7	194.2, 187.1	Cold Vapor
Nickel (Ni)	232.0	231.6, 227.0	Solution
Osmium (Os)	290.8	225.6, 189.8	Solution
Selenium (Se)	196.0	196.1, 204.0	Hydride
Silver (Ag)	328.1	328.1, 224.6	Solution
Strontium (Sr)	460.7	407.8, 346.4	Solution
Thallium (Tl)	276.8	190.9, 351.9	Solution
Vanadium (V)	318.5	309.3, 214.0	Solution

The phosphide-containing inorganic species may be analyzed by the reaction of the sample with either acid or water to form phosphine. For the directed analysis of phosphide, the sample is placed in a sealed volumetric gas flask which has been flushed with high-purity N_2; dilute mineral acid (0.01N HNO_3) is added to the flask and mixed. A second calibrated gas volumetric flask is prepared by placing three to eight quartz glass chips into the flask and flushing with high purity N_2. After the sample equilibrates, an amount of N_2 is removed from the second flask and the same amount of phosphine-containing gas transferred into it. The transfer syringe is pumped several times before removal and the flask swirled to ensure adequate mixing. This gaseous mixture is then analyzed by gas chromatography with a flame photometric detector.

c. Gases

The gaseous inorganic species, for the most part, have standard methods available to define the operational conditions for their analysis. These methods are all based on GC with either selective detectors such as an alkali flame ionization detector (AFID), a flame photometric detector (FPD), an electron capture detector (ECD) or a nonspecific detector, such as the thermal conductivity detector (TCD). An advantage in using TCD detection is that its characteristics are completely compatible with the requirements for field work and hence, may be used to measure gaseous inorganic species in the field. For a particular sampling and analysis program, field analysis of these gaseous species may be highly advantageous, since the gas samples obtained for these compounds would not need to be transported from the field to the laboratory.

Other GC detectors are frequently utilized because of their selectivity. As the selectivity of the detector increases, the separation requirements of the GC and the preliminary cleanup procedures required for sample analysis are reduced. The characteristics of the selective detectors for those species may be summarized as follows: AFID is best for nitrogen-containing compounds, FPD is best for sulfur- and phosphorus-containing compounds, and ECD is best for halogen-containing compounds.

3. Directed Organic Analysis Criteria

The methods for the qualitative and quantitative analysis of POHCs in hazardous waste incinerator streams are similar or identical to those described in SW-846 (4) or Federal Register Methods 624 and 625 (19). The preferred analysis methods for organics involve the detection of chromatographic eluents, either GC or HPLC. The retention time for each POHC serves as one portion of the qualitative identification criteria, while the detector response integrated over the elution of the POHC of interest serves as the primary quantitative measurement. The following discussion describes the criteria for qualitative identification and quantitative measurement of POHC compounds.

a. Instrumental Operating Parameters

The primary analytical tool for the measurement of hazardous waste incinerator process streams is the GC/MS using fused silica capillary GC columns. The second most important analytical tool for measurement of these streams is HPLC with a variety of detection systems depending upon the compounds of interest. The general details for these methods are described below.

The mass spectrometer is operated in a full mass range scanning mode for most of the analyses of hazardous waste incinerator process streams. The range for which data are acquired in a GC/MS run is sufficiently broad to encompass the major ions, as listed in Appendix E of this report, for each of the potential POHCs in a waste characterization analysis, or for each of the designated POHCs in a trial burn incinerator effluent analysis.

For most purposes, electron impact (EI) spectra are collected since a majority of the POHCs listed give reasonable EI spectra. Also, EI spectra are compatible with the NBS Library of Mass Spectra and other mass spectral references, which aid in the identification process for other components in the incinerator process streams.

To clarify some identifications, chemical ionization (CI) spectra using either positive ions or negative ions may be used to elucidate molecular weight information and simplify the fragmentation patterns of some compounds. In no case, however, should CI spectra alone be used for compound identification.

Although the permitting process specifies the high priority POHCs which must be measured at any hazardous waste incineration facility, incomplete characterization of the incinerator influents may result in unexpected occurrence of additional species in the effluent streams which need to be dealt with. Hence, the more general EI mode of ionization is preferred.

In general, the cycle time between collections of complete mass spectra needs to be selected to be compatible with elution of the components in the sample. For capillary column GC separations, the cycle time should be on the order of one second. Longer cycle times may lead to distortion of the spectra. To characterize a GC peak adequately, at least five spectra should be collected across the peak. For low level components in the extract, the elution peak may be less than 3 seconds wide and, consequently it might not be possible to collect enough scans to characterize the GC peak if the scan repetition rate were greater than 1 second.

To ensure consistency with sources of mass spectra, the GC instrumentation must be tuned to meet the spectra criteria for decafluorotriphenylphosphine (when using analysis Methods A011a, A111, A121 or other fused silica glass capillary column methods), or bromofluorobenzene (when using analysis

Method A101 or other analyses of highly volatile organic species). The criteria for meeting the tuning requirements for these analyses are found in EPA Federal Register Methods 624 and 625 (19) and summarized in Tables 22 and 23, respectively.

When a method specifies analysis by HPLC, the HPLC system consists of several components: reservoir(s) for the elution solvent(s) which may or may not include a gradient device; pumps; injection port; columns; detection and readout devices; and thermostats for the column and detector. These components are commercially available as individual modules, or incorporated into complete HPLC systems. The general operating conditions for HPLC analyses are thoroughly specified in the analytical method description for the various POHCs. The most common HPLC detectors utilize either ultraviolet absorption or fluorescence emission at a single wavelength. In general, these detectors are nonspecific and, consequently, multiple analyses are required to provide accurate identity assignments.

b. Qualitative Identification

The identification of organic POHCs is based on both the chromatographic elution of those compounds and on the specificity of the detection system (i.e., MS for GC/MS and ultraviolet, fluorescence, MS, refractive index or electrochemical for HPLC). The relative retention time of a POHC compared to an appropriate internal standard (discussed in the following section) is generally constant to within about ± 0.2 percent, depending upon the compound. For GC/MS, a match in both the relative retention time for the POHCs and the simultaneous elution of multiple analytical ions specific to that POHC will serve to establish the qualitative identification of the components of the sample. For HPLC with nonspecific detectors (e.g., UV, fluorescence, RI), the qualitative identification is confirmed by a match of the relative retention times on multiple columns between the suspect POHC and a corresponding analytical standard.

MS detection may be used in either a directed or a survey mode. The directed analysis mode is intended to track those POHCs designated in the permitting process for determination of compliance with the DRE performance criterion. The survey analysis mode is intended to identify those and other hazardous constituents which may be present due to unexpected reactions, incomplete combustion, and the like. For the most part, features of the directed mode are also present in the survey mode.

For directed analyses, where specific POHCs are to be measured in the sample, the identification criteria to confirm the presence of a POHC by MS are that 1) the GC retention time for the suspect peak relative to some standard match that for the corresponding POHC, and 2) that the characteristic ions of the suspected POHC are present in the unknown sample at approximately the same ratio as is present in the standard and that those ions coelute. For those POHCs which may be analyzed with MS detection, Appendix E lists the characteristic ions for use with electron impact ionization.

TABLE 22

TUNE CRITERIA FOR DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP)

Mass	Ion Abundance Criteria*
51	30 to 60
68	< 2% of mass 69
70	< 2% of mass 69
127	40 to 60
197	< 1
198	100 (base peak)
199	5 to 9
275	10 to 30
365	> 1
441	Present, but less than mass 443
442	>40
443	17% to 23% of mass 442

*All values in percent abundance relative to mass 198, unless otherwise stated.

TABLE 23

TUNE CRITERIA FOR BROMOFLUOROBENZENE

Mass	Ion Abundance Criteria*
50	20 to 40
75	50 to 70
95	100 (base peak)
96	5 to 9
173	< 1
174	70 to 90
175	5 to 9
176	70 to 90**
177	5 to 9

* All values in percent abundance relative to mass 95, unless otherwise stated.

** Abundance at mass 176 should be about 98% of that at mass 174.

For survey analyses, the qualitative identification of POHCs in a sample is based on the individual mass spectrum of the compound of interest. These identifications are performed primarily by comparison with libraries of mass spectra, using both computerized and, if necessary, manual data base search routines. These tentative identifications may be supplemented by chromatographic retention time data, as appropriate. The following discussion explains the use of computer searches for POHC identification.

A key factor in the use of computerized mass spectra search systems is the data base. Ideally, the data base would include spectra of all potential compounds of interest and the data would have been obtained under the same conditions as used in the analysis of the incinerator process samples. As a practical alternative, the NBS data base is used and supplemented with spectra for those POHC compounds which are not in the library, preferably obtained on the instrument to be used for the sample analysis.

A second key factor in the use of computerized mass spectral search systems is the assessment of the confidence to be placed in the qualitative compound identification or "match" with the reference spectrum in the library. The computerized search system typically generates one or more numerical indicators of the "goodness of fit." In the Finnigan 4000/ INCOS data system, for example, goodness of fit is indicated by three values:

- the fit - how well each library entry is represented in the sample spectrum;
- the reverse fit - how well the sample spectrum is represented in each library entry; and
- the purity - how well both the fit and the reverse fit match the sample spectrum and the library entry.

Of these terms, the purity is the most powerful since a high purity value indicates that both the library entry and the sample spectrum match each other closely and either spectrum accounts for virtually all of the other spectrum. When using a Finnigan 4000/INCOS GC/MS/DS system for survey analysis, it is appropriate to base qualitative compound identifications of POHCs on the purity value. For purity values in excess of 900 on a 0 to 1000 scale, the computer search could be regarded as having identified a single component in the GC peak. A list of the top 5 to 9 choices should also be retrieved as output from the search system. If several compounds with purity values that are close to one another are identified, the analyst should retrieve and examine the library spectra and use the elution order data to ascertain the best candidate for the identity of the GC peak of interest. Similarly, if the purity value has decreased below the 900 value threshold, the analyst should retrieve and examine the library spectra, the sample spectrum, and any retention time data to determine the identification of the sample compound.

The algorithms for calculated "goodness of fit" parameters and the numerical values that are associated with specific levels of confidence in the identification vary, depending on the particular software in the GC/MS system employed for analysis. For this reason, and also because the professional judgment of the mass spectrometrist is an essential element in the qualitative compound identification process, it is not appropriate to specify in this document numerical goodness of fit criteria to be applied to all POHC analyses.

It is essential, however, that all compound identifications be reported with an indication of the goodness of fit criteria that were used in making the assignment. These may include numerical values of parameters from the computerized search system and/or the analyst's professional judgment (e.g., "strong," "probable," "tentative"). (See Table 17 for a suggested format.) Of course, both elution order and accordance with the correct or reference spectrum must be utilized to assure correct identification of any and all POHCs in wastes and in samples from hazardous waste incinerators.

For nonspecific detectors such as most of those with HPLC, POHC identification must be made using multiple LC columns whose relative retention behavior is significantly different. The sample is analyzed on two columns and the retention of the suspect peak compared to that of a reference standard. If the retention on both columns match between the suspect peak and the reference peak, then the suspect peak has been tentatively identified. Isolation of the suspect peak and subsequent analysis by MS and IR, as appropriate, serves to confirm the multicolumn identification.

c. Quantitative Measurement

Following the qualitative identification of POHCs in either the influent or effluent streams of a hazardous waste incineration facility, the levels of the identified species need to be measured. Two purposes are served with these measurements. For those POHCs which were designated during the trial burn permitting process, the quantitative measurements of the influents and effluents are used to check that the DRE value is in excess of 99.99 percent for each of the designated POHCs. For other species which are identified in the samples, the measurement can be used, if necessary, to identify any unexpected environmental hazards. Measurements will be based either on direct calibration using authentic standards or on indirect methods.

External calibration methods, using either the raw response of a standard or the relative response of the standard versus an internal standard as a function of the amount of standard, are widely used in analytical chemistry for quantification. For these methods, a series of calibration standards are prepared from reagent material of the compound(s) of interest which span the linear working range of the analytical instrumentation being used. Each of these standards is analyzed using the same

conditions as would be used for the actual samples. The response-concentration data pairs are combined into a calibration curve by regression methods. The level of the compound in the sample is determined by interpolation within the calibration curve. This method is routinely used for GC/MS and HPLC analysis.

For samples analyzed by GC/MS, stable labeled isotope spikes may be used for quantification. The use of stable labeled isotope spikes has a number of advantages. A stable labeled isotope compound which is added to the sample prior to any cleanup steps exhibits essentially the same characteristics as the nonlabeled compound when taken through the various processing steps involved in the sample workup and analysis. As in other calibration methods, it is necessary to prepare a series of standard solutions to establish the linearity of response over the desired concentration range.

Direct quantification procedures are recommended for any species which are identified in the hazardous waste incinerator samples. However, this may not be possible due to a shortage of reference standards, for example, and indirect methods may be necessary in some cases. The most common of the indirect methods is to use the response characteristics of a chemically similar compound to estimate the level of the target constituent of interest (4). Thus, if for example, benzofluoranthenes were unexpectedly found in a sample, but no standard were available, then the level of benzofluoranthenes present in the sample might be estimated from the response curve of benzo(a)pyrene, benzo(e)pyrene, or perylene. Chemical similarity includes similar functionalities, isomeric structures, and homologous series of compounds. The quantitative estimates by this method are of increasing accuracy as the chemical structure of the reference compound approaches that of the compound of interest. This method assumes that the compound which is being measured has the same response characteristics as the reference compound. In some cases, it may be appropriate to correct for predictable differences in MS response characteristics (22, 23). This approach does not compensate for possible differences in chromatographic behavior between the target constituent and the reference compound. It should be noted that direct quantification using an authentic standard of the POHC of concern is always preferable to indirect quantification.

F. ANALYSIS METHOD SUMMARIES

The analysis methods (designated with an A) appropriate to each hazardous constituent from Appendix VIII (40 C.F.R. Part 261) are summarized in tabular form on the following pages. Also included are summaries of the methods for the test procedures used in determining the characteristics of the waste (designated with a C).

Method Number:	C001
Method Name:	Ignitability
Basic Method:	Flash Point Determination
Matrices:	Aqueous Liquids Organic Liquids Sludges Solids
Apparatus:	Pensky-Martens Closed Cup Tester Procedure: ASTM D-93-79 (1979) Setaflash Closed Cup Tester Procedure: ASTM D-3278-78 (1978)

Analysis Method Parameters:

The flash point of a liquid will be determined according to either of the ASTM procedures referenced above, or

- the waste will be identified as a compressed gas, as defined in 49 C.F.R. 173.300, or
- the waste will be identified as an oxidizer, as defined in 49 C.F.R. 173.151.

Reference: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980), Section 4.

Method Number:	C002
Method Name:	Corrosivity
Basic Method:	pH Determination Corrosivity Toward Steel
Matrices:	Aqueous Liquids Organic Liquids Sludges Solids
Apparatus:	pH Meter - pH Determination SAE Type 1020 Steel - Corrosivity Toward Steel

Analysis Method Parameters:

pH Determination - The pH of the sample will be determined electronically using either a glass electrode in combination with a reference potential or a combination electrode, as specified in SW-846.

Corrosivity toward steel - The weight loss of a circular coupon of SAE type 1020 steel will be determined after a designated time period (200-2000 hours). The waste must be agitated and maintained at 55°C throughout the duration of exposure. The coupon must be carefully cleansed prior to each weighing.

Reference: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980), Section 5.

Method Number: C003

Method Name: Reactivity

Basic Method: Professional Judgment

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Analysis Method Parameters:

A solid waste will be considered to exhibit the characteristic of reactivity if it shows any of the following properties:

- it readily undergoes violent chemical changes;
- it reacts violently or forms potentially explosive mixtures with water;
- it generates toxic fumes when mixed with water or, in the case of cyanide or sulfide bearing wastes, when exposed to mildly acidic or basic conditions;
- it explodes when subjected to a strong initiating force;
- it explodes at normal temperatures and pressures;
- it fits within the Department of Transportation's forbidden explosives, Class A explosives, or Class B explosives classification.

Reactivity will be determined by applying best professional judgment to the available data. There are no explicit experimental test procedures for the determination of this characteristic.

Reference: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980), Section 6.

Method Number: C004

Method Name: Extraction Procedure Toxicity

Basic Method: Extraction of a sample followed by analysis of the extract by GC/ECD, ICAP, and AAS

Matrices:
Sludges
Solids

Apparatus:
Filtration Apparatus
Structural Integrity Tester
Extraction Apparatus - Stirrer or Tumbler
GC/ECD
ICAP Spectrophotometer
AAS Spectrophotometer

Analysis Method Parameters:

The solid waste sample will be extracted for 24h with aqueous acetic acid at pH = 5.

The extract will then be analyzed for pesticides and herbicides in the leachate by GC/ECD on Supelcoport 100/200 Mesh, coated with 3% OV-1, 180 cm x 4 mm I.D. glass column with 5% methane/95% argon carrier gas at 60 mL/min. The column temperature will be maintained at 200°C.

Analysis of metals in leachate by either AAS or ICAP as specified in the following method numbers:

Metal	Method	Method Number
Arsenic	AAS	A222
Barium	ICAP or AAS	A223
Cadmium	ICAP or AAS	A225
Chromium	ICAP or AAS	A226
Lead	AAS	A227
Mercury	AAS	A228
Selenium	AAS	A231
Silver	ICAP or AAS	A232

Reference: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980), Section 7.

Method Number:	A001a,b
Method Name:	Moisture, Solid and Ash Content - Macroscale Technique
Basic Method:	Sample Drying and Ignition
Matrices:	Aqueous Liquids Organic Liquids Sludges Solids
Apparatus:	Balance Hot Plate Muffle Furnace

Analysis Method Parameters:

An aliquot of the waste sample will be transferred to a prepared evaporating dish and weighed. Any liquid will be removed by drying the liquid at 103°C without boiling. Then, the sample will be cooled, weighed with repeated drying and weighing of the sample to constant weight (difference of less than 4% in weight).

An aliquot of the dried sample will then be ignited for 30 min at 600°C, and the ash weighed to constant weight.

Detection Limit: 1-10 ppm

References:

American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book of ASTM Standards," Method D-1888-78, Part 31 (1979).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A002

Method Name: Moisture, Solid and Ash Content - Microscale Technique

Basic Method: Thermogravimetric Analysis (TGA)

Matrices: Organic Liquids
Sludges
Solids

Apparatus: TGA

Analysis Method Parameters:

An aliquot of the sample ($\leq$50 mg) will be placed in the sample boat of the TGA and heated in air atmosphere by either of two methods:

- at a programmed rate of 10°C/min to 500°C, or
- two isothermal measurements at 125°C and 500°C, allowing two min equilibration at each isothermal temperature.

Data can be reported by:

- a plot of weight (mg) vs. temperature, °C, or
- a plot of percent lost vs. temperature, °C.

Detection Limit: 1-10 ppm

Reference: American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book of ASTM Standards," Method D-1888-78, Part 31 (1979).

Method Number: A003

Method Name: Elemental Composition - Organic

Basic Method: Elemental Analysis

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Apparatus: Varied

Analysis Method Parameters:

	Reference	Measurement
Carbon	ASTM D-3178-73 (1979)	CO_2 & H_2O on combustion
Nitrogen	ASTM D-3179-73 (1979), E-258-67 (1977)	N_2 by Kjeldahl
Oxygen	ASTM D-3176-74 (1979)	Difference method
Phosphorus	ASTM D-2795 (1965)	Spectroscopic method
Sulfur	ASTM D-3177 (1975), D-129-64 (1978)	Sulfate titration
Chlorine	ASTM D-2361-66 (1978), D-808-63 (1976)	Halide titration

Detection Limit: 100 ppm

Reference: American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book of ASTM Standards," Methods for each element, as specified above.

Method Number: A004

Method Name: Total Organic Carbon (TOC)
Total Organic Halogen (TOX)

Basic Method: Combustion

Matrix: Aqueous Liquids

Apparatus: TOC Analyzer
TOX Analyzer

Analysis Method Parameters:

Carbon: An aliquot of the sample will be analyzed using a TOC analyzer by measuring the CO_2 and CH_4 which is evolved.

Halogen: The sample will be combusted and the hydrogen halides collected. The collected halides will be titrated and their concentration compared to the total halogen concentration as determined by potentiometric titration.

Detection Limit: 100 ppm

Reference: Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS.No. PB297686/AS.

Method Number: A005

Method Name: Viscosity

Basic Method: Flow Measurement

Matrices: Aqueous Liquids
Organic Liquids

Apparatus: Kinematic Viscometer
Thermometer

Analysis Method Parameters:

The time will be measured for the flow of a fixed volume of sample through the viscometer.

Detection Limit: 0.002 to 3,000 Stokes (A series of viscometers is needed to cover this range.)

Reference: American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book of ASTM Methods," Method D-445 (1979).

Method Number:	A006
Method Name:	Heating Value of Waste
Basic Method:	Combustion/Calorimetry
Matrices:	Aqueous Liquids Organic Liquids Sludges Solids
Apparatus:	Calibrated isothermal jacket bomb calorimeter under controlled conditions (ASTM D-2015), or adiabatic bomb calorimeter under controlled conditions (ASTM D-3286)

Analysis Method Parameters:

Calorific value will be computed from temperature observations made before, during, and after combustion of a weighed sample. Proper allowance must be made for heat contributed by other processes.

Reference: American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book of ASTM Standards," Method D-2015-77 (1978) and Method D-3286-77 (1977).

Method Number: A101

Method Name: Volatiles

Basic Method: GC/MS - Purge and Trap

Matrices:
Aqueous Liquids
Organic Liquids (neat or diluted)
Sludges
Solids

Constituents from Appendix VIII to which method may be applied:

Acetonitrile
Acrolein
Acrylamide
Acrylonitrile
Benzene
Bromoacetone
Bromomethane
Carbon disulfide
Carbon oxyfluoride
Chlorinated benzenes, N.O.S.
Chlorinated ethane, N.O.S.
Chlorinated fluorocarbons, N.O.S.
Chloroalkyl ethers, N.O.S.
Chlorobenzene
1-Chloro-2,3-epoxypropane
2-Chloroethyl vinyl ether
Chloroform
Chloromethane
Chloromethyl methyl ether
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
Dibromomethane
Dichlorobenzene (meta, ortho, and para isomers)
Dichlorobenzene, N.O.S.
1,4-Dichloro-2-butene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
trans-1,2-Dichloroethene
Dichloroethylene, N.O.S.
1,2-Dichloroethylene
Dichloromethane
Dichloropropane, N.O.S.
1,2-Dichloropropane
Dichloropropene, N.O.S.
1,3-Dichloropropene

1,4-Dioxane
Formic acid
Halomethane, N.O.S.
Hexachloroethane
Hexachloropropene
Hydrazine
Iodomethane
Isocyanic acid, methyl ester
Methanethiol
Methyl ethyl ketone (MEK)
Methyl hydrazine
Tetrachloroethane, N.O.S.
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Tetrachloromethane
Tetranitromethane
Toluene
Tribromomethane
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichloromonofluoromethane
Trichloropropane, N.O.S.
1,2,3-Trichloropropane
Vinyl chloride

Apparatus: Finnigan 4000 GC/MS/DS or equivalent
Purge and Trap Device (Tekmar LSC-1 or equivalent)

Analysis Method Parameters:

Purge and Trap: A 25 cm trap will be prepared which contains 1/3 activated charcoal, 1/3 silica gel, and 1/3 Tenax. A 5 mL sample will be purged onto the trap (Methods A101a, A101b, or A101c) at 40 mL/min with helium or nitrogen for 12 min, and desorbed with backflushing at 180°C with 40 mL inert gas into GC for 4 min.

GC: Column - 6 ft 0.2% Carbowax 1500 on Carbopack C 60/80 mesh

Carrier Gas - He at 50 mL/min

Injector - 160°C

Temperature Program - 30°C for 7 min isothermal (beginning at start of purge); then, 30-160°C at 8°C/min; and 160°C for 15 min isothermal.

MS:	Mass Range - 20-260 amu
	Scan Rate - 2 s/scan
	Ionization - EI, 70 eV
Detection Limit:	10-100 µg/L of each compound on-column.

References: U.S. Environmental Protection Agency, Federal Register, 44, 69464-69575 (December 3, 1979).

U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Method Number: A101a

Method Name: Volatiles

Basic Method: Purge and Trap

Matrix: Aqueous Liquids

Purging Method Parameters:

An aliquot (5 mL) of the aqueous sample will be transferred into the purging device; and purged with helium for 12 min at 40 mL/min.

Reference: U.S. Environmental Protection Agency, Federal Register, 44, 69464-69575 (December 3, 1979).

Method Number: A101b

Method Name: Volatiles

Basic Method: Purge and Trap

Matrix: Sludges (including gels and slurries)

Purging Method Parameters:

An aliquot of a sludge sample will be diluted to 0.5% solids with reagent grade water. A 5-mL portion of this diluted mixture will then be transferred to the purging device and purged for 12 min with helium at 40 mL/min. If the sludge sample is not readily dispersible, polyethylene glycol (MW 400) will be used to dilute the sample.

Reference: Miller, H.C., R.H. James and W.R. Dickson, "Evaluated Methodology for the Analysis of Residual Wastes," Report prepared for U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, D.C., by Southern Research Institute, Birmingham, Alabama under Contract No. 68-02-2685 (December 1980).

Method Number: A101c

Method Name: Volatiles

Basic Method: Purge and Trap

Matrix: Solids

Purging Method Parameters:

An aliquot of the solid sample will be diluted to 2% solids with reagent grade water. A 5-mL portion of this diluted mixture will be transferred to the purging device and purged for 12 min with helium at 40 mL/minute. If the solid sample is not readily dispersible in water, polyethylene glycol (MW 400) will be used to dilute the sample.

Reference: Miller, H.C., R.H. James and W.R. Dickson, "Evaluated Methodology for the Analysis of Residual Wastes," Report prepared for U.S. Environmental Protection Agency/Effluent Guidelines Division, Washington, D.C., by Southern Research Institute, Birmingham, Alabama under Contract No. 68-02-2685 (December 1980).

Method Number: A121

Method Name: Extractables

Basic Method: GC/MS

Matrices: Sample Extracts
Organic Liquids (neat or diluted)

Constituents from Appendix VIII to which method may be applied:

*Acetophenone
2-Acetylaminofluorene
Aldrin
*4-Aminobiphenyl
*5-(Aminomethyl)-3-isoxazolol
*Amitrole
*Aniline
*Aramite
*Auramine
*Benz(c)acridine
Benz(a)anthracene
*Benzene, dichloromethyl-
*Benzenethiol
Benzidine
Benzo(b)fluoranthene
Benzo(j)fluoranthene
Benzo(a)pyrene
*p-Benzoquinone
Benzotrichloride
Benzyl chloride
Bis(2-chloroethoxy)methane
Bis(2-chloroethyl)ether
*N,N-Bis(2-chloroethyl)-2-naphthylamine
Bis(2-chloroisopropyl)ether
*Bis(chloromethyl)ether
Bis(2-ethylhexyl)phthalate
4-Bromophenyl phenyl ether
*2-Butanone peroxide
Butyl benzyl phthalate
*2-sec-Butyl-4,6-dinitrophenol (DNBP)
Chlordane (alpha and gamma isomers)
Chlorinated benzene, N.O.S.
Chlorinated naphthalene, N.O.S.
Chlorinated phenol, N.O.S.
p-Chloroaniline
*Chlorobenzilate
†*p-Chloro-m-cresol
2-Chloronaphthalene
†*2-Chlorophenol
*3-Chloropropionitrile

Chrysene
*Coal Tars
Creosote
†*Cresols
*2-Cyclohexyl-4,6-dinitrophenol
DDD
DDE
DDT
*Diallate
*Dibenz(a,h)acridine
Dibenz(a,j)acridine
Dibenz(a,h)anthracene
*7H-Dibenzo(c,g)carbazole
*Dibenzo(a,e)pyrene
*Dibenzo(a,h)pyrene
*Dibenzo(a,i)pyrene
Di-n-butyl phthalate
Dichlorobenzene (meta, ortho, and para isomers)
Dichlorobenzene, N.O.S.
3,3'-Dichlorobenzidine
*2,4-Dichlorophenol
2,6-Dichlorophenol
Dichloropropanol, N.O.S.
Dieldrin
*1,2:3,4-Diepoxybutane
*N,N-Diethylhydrazine
*O,O-Diethyl S-methyl ester of phosphorodithioic acid
*O,O-Diethylphosphoric acid, O-p-nitrophenyl ester
Diethyl phthalate
*O,O-Diethyl O-2-pyrazinyl phosphorothioate
*Dihydrosafrole
*Diisopropylfluorophosphate
*Dimethoate
*3,3'-Dimethoxybenzidine
*p-Dimethylaminoazobenzene
7,12-Dimethylbenz(a)anthracene
3,3'-Dimethylbenzidine
*●1,1-Dimethylhydrazine
●1,2-Dimethylhydrazine
*alpha,alpha-Dimethylphenethylamine
*2,4-Dimethylphenol
Dimethyl phthalate
Dimethyl sulfate
Dinitrobenzene, N.O.S.
*4,6-Dinitro-o-cresol and salts
*2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Di-n-octyl phthalate
Diphenylamine

1,2-Diphenylhydrazine
*Di-n-propylnitrosamine
*Disulfoton
*2,4-Dithiobiuret
†Endosulfan
Endrin and metabolites
*Ethyl carbamate
*Ethyleneimine
*Ethyl methacrylate
†Ethyl methanesulfonate
Fluoranthene
*Fluoroacetic acid, sodium salt
Formic Acid
Heptachlor
Heptachlor epoxide (alpha, beta, and gamma isomers)
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclohexane (all isomers)
Hexachlorocyclopentadiene
Hexachloroethane
*1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-endo,endo-dimethanonaphthalene
*Hexachlorophene
*Hexaethyl tetraphosphate
●*Hydrazine
Indeno(1,2,3-cd)pyrene
*Isosafrole
*Kepone
Maleic anhydride
*Maleic hydrazide
Malononitrile
*Methacrylonitrile
*Methapyrilene
*Methoxychlor
*2-Methylaziridine
3-Methylcholanthrene
*4,4'-Methylenebis(2-chloroaniline)
*Methyl ethyl ketone
●Methyl hydrazine
*2-Methyllactonitrile
*Methyl methacrylate
*N-Methyl-N'-nitro-N-nitrosoguanidine
*Methyl parathion
*Methylthiouracil
Naphthalene
1,4-Naphthoquinone
†1-Naphthylamine
*2-Naphthylamine
†Nicotine and salts

p-Nitroaniline
Nitrobenzene
*Nitroglycerine
†4-Nitrophenol
*Nitrosamine, N.O.S.
N-Nitrosodi-n-butylamine
*N-Nitrosodiethanolamine
N-Nitrosodiethylamine
N-Nitrosodimethylamine
*N-Nitroso-N-ethylurea
N-Nitrosomethylethylamine
†*N-Nitroso-N-methylurea
N-Nitroso-N-methylurethane
*N-Nitrosomethylvinylamine
*N-Nitrosomorpholine
*N-Nitrosonornicotine
*N-Nitrosopiperidine
N-Nitrosopyrrolidine
*N-Nitrososarcosine
*Octamethylpyrophosphoramide
Parathion
Pentachlorobenzene
Pentachloroethane
*Pentachloronitrobenzene (PCNB)
*Pentachlorophenol
*Phenol
*Phenylenediamine
*Phosphorodithioic acid, O,O-diethyl S-((ethylthio)methyl)ester [Phorate]
*Phosphorothioic acid, O,O-dimethyl O-(p-((dimethylamino)sulfonyl) phenyl)ester [Famphur]
*Phthalic acid esters, N.O.S.
Phthalic anhydride
†2-Picoline
Polychlorinated biphenyl, N.O.S.
*Pronamide
*1,3-Propane sulfone
*n-Propylamine
*Propylthiouracil
*Pyridine
*Saccharin and salts
†Safrole
1,2,4,5-Tetrachlorobenzene
**2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)
†*2,3,4,6-Tetrachlorophenol
*Tetraethyldithiopyrophosphate
*Tetraethylpyrophosphate
Toluenediamine
Tolylene diisocyanate
Toxaphene

†1,2,4-Trichlorobenzene
*Trichloromethanethiol
†2,4,5-Trichlorophenol
*†2,4,6-Trichlorophenol
*O,O,O-Triethyl phosphorothioate
*sym-Trinitrobenzene
*Tris(2,3-dibromopropyl) phosphate

Apparatus: Finnigan 4000 GC/MS/DS or equivalent

Analysis Method Parameters:

GC:
Column - Fused-silica capillary, 25m, 0.31 mm, wall-coated with SE-54

Carrier Gas - He ≈ 2 mL/min

Temperature Program - 40° to 280°C at 10°C min; 280°C, 15 min isothermal

Injector Temperature - 250°C

Injector Type - Splitless

MS:
Mass Range - 41 to 450 amu

Scan Rate - ≤ 1 s/scan

Ionization - EI, 70 eV

Detection Limit:
5 -20 ng of each compound injected on-column (50 ng for mixtures like PCBs)
1 - 4 $\mu m/m^3$ in a 5 m^3 stack gas sample
0.25- 1 µg/g in 20g sludge/solid sample
5 -20 µg/L in a 1L aqueous sample

References:
U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

U.S. Environmental Protection Agency, Federal Register, 44, 69464-69575 (December 3, 1979).

*The compounds marked (*) are not referenced in EPA Method 625 (19), but are additional compounds from Appendix VIII to which this method is expected to apply.

†The compounds marked (†) may also be analyzed by the HPLC techniques outlined in Methods A122 and A123.

•The compounds marked (•) are volatile enough to be partially swept from the splitless injector of the GC/MS system along with the solvent. It is likely that these compounds can be determined, with some loss of sensitivity, by GC/MS with split injection techniques.

**Special sample preparation and selected ion monitoring (rather than full mass range scanning) would be necessary for adequate detection of TCDD.

Method Number: A122

Method Name: HPLC/UV Generalized Procedure (three options)

Basic Method: HPLC/UV

Matrix: Sample Extracts
(aqueous or acetonitrile)

Apparatus: HPLC/UV

Constituents from Appendix VIII to which method (Option 1A) may be applied:

3-(alpha-Acetonylbenzyl)-4-hydroxycoumarin and salts [Warfarin]
6-Amino-1,1a,2,8,8a,8b-hexahydro-8-(hydroxymethyl)-8a-methoxy-5-methylcarbamate azirino[2',3':3,4] pyrrolo[1,2-a]indole-4,7-dione(ester) (Mitomycin C)
Chlorambucil
†p-Chloro-m-cresol
†2-Chlorophenol
†2,4-Dichlorophenol
†*2,6-Dichlorophenol
†*2,4-Dinitrophenol
Melphalan
*Methomyl
†4-Nitrophenol
5-Nitro-o-toluidine
Phenol
Reserpine
Streptozotocin
†2,3,4,6-Tetrachlorophenol
Thiuram
†*2,4,5-Trichlorophenol
†2,4,6-Trichlorophenol

Analysis Method Parameters (Option 1A):

HPLC:

Column - Perkin-Elmer HC-ODS-Sil-X-1 or equivalent reversed-phase column, 10-µm particle size, 25 cm x 2.6 mm I.D.

Column Temperature - 30°C

Solvent A - Distilled, deionized water

Solvent B - Acetonitrile

Solvent Program - 10% B, 5 min isocratic; 10 to 100% B in 35 min; 100% B, 10 min isocratic

Solvent Flow Rate - 1 mL/min

UV: At 254 nm (greater sensitivity can be achieved if compound-specific maximum wavelengths are used - see Table 20)

Constituents from Appendix VIII to which method (Option 1B) may be applied:

Daunomycin
2,4-Dichlorophenoxyacetic acid
2,4,5-Trichlorophenoxyacetic acid
2,4,5-Trichlorophenoxypropionic acid

Analysis Method Parameters (Option 1B):

HPLC: Column - Perkin Elmer HC-ODS-Sil-X-1 or equivalent reversed-phase column, 10-µm particle size, 25 cm x 2.6 mm I.D.

Column Temperature - 30°C

Solvent A - 1% (v/v) acetic acid in distilled, deionized water

Solvent B - Acetonitrile

Solvent Program - 20% B, 10 min isocratic; 20 to 50% B in 10 min; 50% B, 5 min isocratic

Solvent Flow Rate - 2 mL/min

UV: At 254 nm (greater sensitivity can be achieved if compound-specific maximum wavelengths are used - see Table 20)

Constituent from Appendix VIII to which method (Option 1C) may be applied:

4,6-Dinitro-o-cresol (and salts)

Analysis Method Parameters (Option 1C):

HPLC: Column - Perkin Elmer HC-ODS-Sil-X-1 or equivalent reversed-phase column, 10-µm particle size, 25 cm x 2.6 mm I.D.

Column Temperature - 30°C

Solvent A - 1% (v/v) acetic acid in distilled, deionized water

Solvent B - Acetonitrile

Solvent Program - 10% B, 2 min isocratic; 10 to 100% B in 18 min

Solvent Flow Rate - 2 mL/min

UV: At 254 nm (greater sensitivity can be achieved if compound-specific maximum wavelengths are used - see Table 20)

Reference: Dillon, H.K., R.H. James, H.C. Miller and A.K. Wensky (Battelle Columbus Laboratories, Columbus, Ohio), "POHC Sampling and Analysis Methods," Report prepared for U.S. Environmental Protection Agency/Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina by Southern Research Institute, Birmingham, Alabama under Contract No. 68-02-2685 (December 1981).

*The compounds marked (*) are additional constituents from Appendix VIII to which this method is expected to apply.

†The compounds marked (†) can also be determined by the GC/MS techniques in Method A121.

Method Number:	A123
Method Name:	HPLC/UV Generalized Procedure (three options)
Basic Method:	HPLC/UV
Matrix:	Sample Extracts (aqueous or acetonitrile)
Apparatus:	HPLC/UV

Constituents from Appendix VIII to which method (Option 2A) may be applied:

*Azaserine
N-Nitroso-N-methylurea

Analysis Method Parameters (Option 2A):

HPLC:	Column - Waters Associates μBondpack-C_{18} or equivalent reversed-phase column, 10-μm particle size, 30 cm x 3.9 mm I.D.
	Column Temperature - 30°C
	Solvent A - Distilled, deionized water
	Solvent B - Acetonitrile
	Solvent Program - 2% B, isocratic
	Solvent Flow Rate - 1 mL/min
UV:	At 254 nm (greater sensitivity can be achieved if compound-specific maximum wavelengths are used - see Table 20)

Constituent from Appendix VIII to which method (Option 2B) may be applied:

Saccharin (and salts)

Analysis Method Parameters (Option 2B):

HPLC:	Column - Waters Associates μBondpack-C_{18} or equivalent reversed-phase column, 10-μm particle size, 30 cm x 3.9 mm I.D.
	Column Temperature - 30°C
	Solvent A - Distilled, deionized water

Solvent B - Acetonitrile

Solvent Program - 10% B, isocratic

Solvent Flow Rate - 1 mL/min

UV: At 254 nm (greater sensitivity can be achieved if compound-specific maximum wavelengths are used - see Table 20)

Constituents from Appendix VIII to which method (Option 2C) may be applied:

*1-Acetyl-2-thiourea
*1-(o-Chlorophenyl)thiourea
Crotonaldehyde
Diethylstilbestrol (D.E.S.)
3,4-Dihydroxy-alpha-(methylamine)methyl benzyl alcohol (Epinephrine)
Ethylenethiourea
*1-Naphthyl-2-thiourea
*N-Phenylthiourea
Thioacetamide
Thiosemicarbazide
Thiourea
Trypan blue

Analysis Method Parameters (Option 2C):

HPLC: Column - Waters Associates μBondpack-C_{18} or equivalent reversed-phase column 10-μm particle size, 30 cm x 3.9 mm I.D.

Solvent A - Distilled, deionized water

Solvent B - Acetonitrile

Solvent Program - 20 to 100% B in 20 min; 100% B, 10 min isocratic

Solvent Flow Rate - 1 mL/min

Injection Size - 10 μL

UV: At 254 nm (greater sensitivity can be achieved if compound-specific maximum wavelengths are used - see Table 20)

Reference: Dillon, H.K., R.H. James, H.C. Miller and A.K. Wensky (Battelle Columbus Laboratories, Columbus, Ohio), "POHC Sampling and Analysis Methods," Report prepared for U.S. Environmental Protection Agency/Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina by Southern Research Institute, Birmingham, Alabama under Contract No. 68-02-2685 (December 1981).

*Compounds marked (*) are additional compounds from Appendix VIII to which this method is expected to apply.

Method Number:	A131
Method Name:	Aldehydes - Derivatization Procedure
Basic Method:	Derivatization (DNPH), extraction, and analysis by either the GC/MS procedures described in Method A121 or by the HPLC procedures described in Method A132
Matrices:	Aqueous Liquids (including DNPH Impinger Reagents) Sample Extracts

Constituents from Appendix VIII to which method may be applied:

Chloral
Chloroacetaldehyde
Crotonaldehyde
Formaldehyde
Glycidylaldehyde
Paraldehyde

Extraction and Derivatization Method Parameters:

A sample aliquot (20-200 mL) will be taken for derivatization/extraction. If the matrix is a DNPH impinger reagent which has been used for collection of aldehydes, it will immediately be extracted with methylene chloride (100 mL) and n-pentane (100 mL). If the sample is an aqueous liquid such as a scrubber water or an extract prepared from a waste stream or comprehensive stack sampling train, it will be treated by mixing with DNPH reagent (2,4-Dinitrophenylhydrazine in 2N HCl) for 10 min prior to extraction.

After extraction, the combined methylene chloride/pentane layers will be washed with 2N HCl and then distilled water. The extracts will then be evaporated to dryness and the residue dissolved in 2 mL acetonitrile.

These solutions will be analyzed as the DNPH derivatives of the aldehydes by the GC/MS procedures described in Method A121, or by the HPLC procedures described in Method A132.

Reference: Kuwata, K., M. Uebori and Y. Yamasaki, "Determination of Aliphatic and Aromatic Aldehydes in Polluted Airs as their 2,4-Dinitrophenylhydrazones by High Performance Liquid Chromatography," J. Chromatogr. Sci., 17, 264-268 (1979).

Method Number: A132

Method Name: Aldehydes - HPLC Analysis

Basic Method: HPLC/UV

Matrix: Sample Extracts (after derivatization)

Constituents from Appendix VIII to which method may be applied:

Chloral
Chloroacetaldehyde
Crotonaldehyde
Formaldehyde
Glycidylaldehyde
Paraldehyde

Apparatus: HPLC/UV

Analysis Method Parameters:

HPLC: Column - Zorbax-ODS (250 x 4.6 mm I.D.)

Solvent - 75% CH_3OH/25% H_2O

Detector - At 254 nm or 370 nm

Detection Limit:

5 -20 ng of each compound injected on-column
1 - 4 µg/m^3 in a 5 m^3 stack gas sample
5 -20 µg/L in a 1L aqueous sample
0.25- 1 µg/g in a 20g sludge/solid sample

Reference: Kuwata, K., M Uebori and Y. Yamasaki, "Determination of Aliphatic and Aromatic Aldehydes in Polluted Airs as their 2,4-Dinitrophenylhydrazones by High Performance Liquid Chromatography," J. Chromatogr. Sci., 17, 264-268 (1979).

Method Number:	A133
Method Name:	Carboxylic Acids
Basic Method:	Derivatization (followed by GC/MS analysis using Method A121)
Matrices:	Sample Extracts Organic Liquids (neat or diluted)

Constituents from Appendix VIII to which method may be applied:

2,4-Dichlorophenoxyacetic acid (2,4-D)
Formic acid
7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP) (Silvex)

Derivatization Techniques:

Hydrolysis

Distilled water (15 mL) and 75% (w/v) aqueous potassium hydroxide (2 mL) will be added to a Kuderna-Danish (K-D) flask containing the waste sample extract. The extract will be heated on a hot water bath for a total of 60 min. The concentrate will be transferred to a 60-mL separatory funnel, acidified with cold (4°C) 25% H_2SO_4 (2 mL), and extracted once with diethyl ether (10 mL).

The extract will then be transferred to a 125-mL erlenmeyer flask containing sodium sulfate and be allowed to stand for approximately two hours.

Esterification

The ether extract will be transferred through a funnel plugged with glass wool into a (K-D) flask equipped with a 10-mL graduated receiver, with liberal washings of ether. Any caked sodium sulfate will be crushed with a glass rod. The acids in the extract will be esterified using either diazomethane or boron trifluoride.

Diazomethane: The extract will be evaporated to 4 mL. An aliquot (2 mL) of diazomethane will be added to the extract. The mixture will stand for 10 min with occasional swirling and subsequently rinsed with diethyl ether.

Boron Trifluoride: An aliquot (0.5 mL) of benzene will be added to the ether extract. The extract and benzene will be evaporated to 0.5 mL. The ampule will be removed and further concentrated to 0.4 mL using a two-ball microSnyder column. After cooling, boron trifluoride methanol reagent (0.5 mL) will be added to the benzene solution. This mixture will be held at 50°C for 30 min on the steam bath. After cooling, neutral, 5% sodium sulfate (4.5 mL) will be added, and the flask stoppered, shaken, and allowed to stand for three min for phase separation. The solvent layer will be transferred to a small column packed with 2.0 cm sodium sulfate over 1.5 cm florisil adsorbent and eluted with benzene. The final eluent volume will be adjusted to 5 mL with benzene.

The extracts will be analyzed as the methyl esters of the carboxylic acids using the GC/MS procedures described in Method A121.

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Smith, A.E., "Use of Acetonitrile for the Extractions of Herbicide Residues from Soils," J. of Chrom., 129, 309-314 (1976).

Method Number:	A134
Method Name:	Alcohols
Basic Method:	GC/FID, GC/MS
Matrices:	Aqueous Liquids Organic Liquids (neat or diluted)

Constituents from Appendix VIII to which method may be applied:

Allyl alcohol
Isobutyl alcohol
2-Propyn-1-ol
Resorcinol

Apparatus:	GC/MS/DS (Finnigan 4000 or equivalent)
GC:	Column - Carbopack C + 0.8% THEED (tetrahydroxyethylenediamine) packed in 55 cm x 0.2 cm I.D. glass column
	Carrier Gas - He
	Temperature Program - 115°C isothermal
	-or-
	Column - Fused silica capillary, 30 m x 0.25 mm, wall coated with Carbowax 20M or SE-54
	Carrier Gas - He
MS:	Mass Range - 42-450 amu
	Scan Rate - 1-1.5 s/scan
	Ionization - EI, 70 eV
Detection Limit:	5 -20 ng of each compound, injected on-column
	1 - 4 $\mu g/m^3$ of each compound (in a 5 m^3 stack gas sample)
	5 -20 µg/L of each compound (in a 1L aqueous sample)
	0.25- 1 µg/g of each compound (in a 20g sludge/ solid sample)

Reference: DiCorcia, A. and R. Samperi, "Gas Chromatographic Determination of Glycols at the Parts-Per-Million Level in Water by Graphitized Carbon Black," Anal. Chem., 51 776-778 (1979).

Method Number: A136

Method Name: Phosphine

Basic Method: GC/FPD

Matrix: Gas

Constituent from Appendix VIII to which method may be applied:

Phosphine

Apparatus: GC/FPD

Analysis Method Parameters:

Column - 3% Carbowax 20M, 100/120 Gas Chrom Q

Flame Photometric Detector

Detection Limit: 1 µg/mL

Reference: Berck, B., W.E. Westlake and F.A. Gunter, "Microdetermination of Phosphine by Gas-Liquid Chromatography with Microcoulometric, Thermionic and Flame Photometric Detection," J. Agric. Food Chem., 18, 143-147 (1970).

Method Number: A137

Method Name: Fluorine

Matrix: Gas

It has not been possible to obtain an analysis method for the specific determination of free fluorine (F_2) that can be recommended with confidence. Total fluorides may be determined by the procedures outlined in EPA Method 13 (40 C.F.R. Part 60, Appendix A).

A proposed method (Engineering Report No. G115B, Matheson Gas Products) for the sampling and analysis of fluorine involves pre-scrubbing the air stream to remove HF, and then collecting fluorine in dilute base contained in a bubbler. Hydrolysis of the fluorine in the scrubber would result in a solution containing fluoride (as F^-) which could be measured by the ion chromatographic technique, outlined in Method A251.

Method Number: A138

Method Name: Gases - Cyanogens and Phosgene

Basic Method: GC/TCD, GC/ECD (for Cl),
GC/AFID (for N)

Matrix: Gas

Constituents from Appendix VIII to which method may be applied:

Cyanogen
Cyanogen Bromide
Cyanogen Chloride
Phosgene

Apparatus: GC/TCD, GC/ECD, GC/FPD equipped with a gas sampling loop for sample introduction

Analysis Method Parameters:

Column - Kel-F 40, Nickel Tubing
(10 ft x 1/4 in)

Detection Limit: 10 µg/L

Reference: Heftman, E. (ed.), Chromatography - A Laboratory Handbook of Chromatographic and Electrophoretic Methods, 3rd ed., Van Nostrand Reinhold Company, New York (1975).

Method Number:	A139
Method Name:	Gases - Mustards
Basic Method:	GC/FPD
Matrix:	Gas

Constituents from Appendix VIII to which method may be applied:

Mustard Gas
Nitrogen Mustard (and hydrochloride salt)
Nitrogen Mustard N-Oxide (and hydrochloride salt)

Apparatus:	GC/Flame Photometric Detector in Sulfur Mode Bubblers to collect air samples

Analysis Method Parameters:

GC:	Column - 10% QF-1 on 80/100 Chromosorb W-HP
Detection Limit:	0.2 µg/mL

Reference: Hudson, R., "U.S. Army Toxic and Hazardous Materials Agency Report," Aberdeen Proving Ground, Maryland, Report No. 7509. (December 1975).

Method Number: A141

Method Name: Gases

Basic Method: GC/TCD, GC/AFID(N)
GC/FPD(S)

Matrix: Gas

Constituents from Appendix VIII to which method may be applied:

Carbon disulfide
Hydrazine
Hydrocyanic acid
Hydrogen sulfide
Nitric oxide
Nitrogen dioxide

Apparatus: GC/TCD, GC/AFID(N), GC/FPD(S)

Analysis Method Parameters:

GC: Column - Porapak Q

Detection Limit: 10 µg/L

Reference: Waters Associates, Framingham, Massachusetts, "Porapak Resin."

Method Number: A144

Method Name: Acid Chlorides

Matrix: Gas

Constituents from Appendix VIII to which method may be applied:

Acetyl chloride
Dimethylcarbamoyl chloride

It has not been possible to obtain an analysis method that can be recommended with confidence for acid chlorides. A reference to a colorimetric analysis method is provided. However, further research would be needed to validate this method within the context of the matrices which are involved.

It seems unlikely that acetyl chloride, or dimethylcarbamoyl chloride would survive within stack gas effluent streams because of the high concentration of water in these streams.

Reference: Kostyukovskii, Y.L., "Rapid Method for Determining Vapors of Organic Acid Halides in Air," Zh. Anal. Khim, 25 2228-2230 (1970).

Method Number: A145

Method Name: Aflatoxins

Basic Method: HPLC/Fluorescence

Matrices: Sample Extracts
Organic Liquids (neat or diluted)

Constituents from Appendix VIII to which method may be applied:

Aflatoxins

Apparatus: HPLC

Analysis Method Parameters:

LC: Column - Sperisorb ODS

Solvent - H_2O or acetonitrile/methanol (3:2)

Fluorimeter: $\lambda_{excitation}$ - 365 nm

$\lambda_{emmision}$ - 400 nm

Detection Limit: <0.5 ppb (detected in dairy products)

References: Beebe, R.M. and D.M. Takahashi, "Determination of Aflatoxin M_1 by High-Pressure Liquid Chromatography Using Fluorescence Detection," J. Agric. Food Chem., 28, 481-482 (1980).

Gregory, J.F. III and D. Manley, "High Performance Liquid Chromatographic Determination of Aflatoxins in Animal Tissues and Products," J. Assoc. Off. Anal. Chem., 64 144-151 (1981).

Method Number:	A148
Method Name:	Brucine
Basic Method:	GC/FID
Matrices:	Sample Extracts Organic Liquids (neat or diluted)

Constituent from Appendix VIII to which method may be applied:

Brucine

Apparatus:	GC/FID

Analysis Method Parameters:

GC:	Column - Fused-silica capillary, 30 m x 0.25 mm I.D., wall-coated with SE-52
	Carrier Gas - He at 2 mL/min
	Temperature Program - 102° to 300°C at 8°C/min; 300°C, 32 min isothermal
	Injector Temperature - 300°C
FID:	Detector Temperature - 300°C
Detection Limit:	5-20 ng

Reference: Wensky, A.K., Battelle Columbus Laboratories, Columbus, Ohio, personal communication (January 21, 1982).

Method Number:	A149
Method Name:	Citrus Red No. 2
Basic Method:	HPLC
Matrices:	Sample Extracts Organic Liquids (neat or diluted)

Constituent from Appendix VIII to which method may be applied:

Citrus Red No. 2

Apparatus: HPLC/UV

Analysis Method Parameters:

HPLC:	Column - OXS-1025 ODS-2
	Solvent - Methanol/Water gradient (Tetrabutylammonium phosphate as a counter ion)
UV:	At 254 nm
	(It is possible that Citrus Red No. 2 could be analyzed by one of the options described in Method A122 or Method A123.)

Reference: Gloor, R. and E.L. Johnson, "Practical Aspects of Reverse-Phase Ion Pair Chromatography," J. Chromatog. Sci., 15 413-432 (1977).

Method Number: A150

Method Name: Cycasin

Matrices: Sample Extracts
Organic Liquids (neat or diluted)

It has not been possible to obtain an analysis method that can be recommended with confidence for Cycasin within the sample matrices involved. A reference is provided below, however further research would be needed to either validate this method or develop a new method.

(It is possible that Cycasin could be determined by one of the options for HPLC in either Method A122 or Method A123.)

Reference: "Simultaneous Detection of Cycasin, Methylazoxymethanol and Formaldehyde by HPLC," Agric. Biol. Chem., 44, 1423-1425 (1980).

Method Number: A156

Method Name: Ethylene Oxide

Basic Method: GC/FID

Matrix: Gas

Constituent from Appendix VIII to which method may be applied:

Ethylene oxide

Apparatus: GC/FID

Analysis Method Parameters:

GC: Column - 5% Carbowax 20M

Detection Limit: 0.1 mg

References: Greve, P.A. and E.A. Hogendoorn, "Determination of Fumigant Residues in Grain," Meded. Fac. Landbouwwet., Rijksuniv. Gent, 44, 877-884 (1979).

Bicchi, C. and S. Mina, "An Improved Method for the Determination of Low Amounts of Ethylene Oxide in Surgical Plastics," Farmaco, Ed. Prat., 35, 632-641 (1980).

Method Number:	A157
Method Name:	2-Fluoroacetamide
Basic Method:	GC/FID
Matrices:	Sample Extracts Organic Liquids (neat or diluted)

Constituent from Appendix VIII to which method may be applied:

2-Fluoroacetamide

Apparatus: GC/FID

Analysis Method Parameters:

GC: Column - Chromosorb 101 (100/120 mesh) 1.8 m x 2 mm I.D.

Carrier Gas - He at 30 mL/min

Temperature Program - 155°C, isothermal

Detection Limit: ∿ 20 ng

Reference: Warner, J.S. and M.C. Landes, Internal Communication, Battelle Columbus Laboratories, Columbus, Ohio, (November 10, 1981).

Method Number: A160

Method Name: Lasiocarpine

Matrices: Sample Extracts
Organic Liquids (neat or diluted)

It has not been possible to obtain an analysis method that can be recommended with confidence. References to a colorimetric analysis method are provided. However, further research would be needed to validate the method within the context of the sample matrices involved or to develop a new method.

References: Mattocks, A.R., "Spectrophotometric Determination of Pyrrolizidine Alkaloids - Some Improvements," Anal. Chem., 40, 1749-1750 (1968).

Mattocks, A.R., "Spectrophotometric Determination of Unsaturated Pyrrolizidine Alkaloids," Anal. Chem., 39 443-447 (1967).

Method Number: A174

Method Name: Phenacetin

Basic Method: HPLC/UV

Matrices: Sample Extracts
Organic Liquids (neat or diluted)

Constituent from Appendix VIII to which method may be applied:

Phenacetin

Apparatus: HPLC/UV

Analysis Method Parameters:

HPLC: Column - LiChrosorb RP-18

Solvent - Acetonitrile/0.1N acetate buffer

Detection Limit: 0.1 µg

Reference: Ohamoto, M., F. Yanada, M. Ishiguro and A. Umemura, "Liquid Chromatographic Method for Determination of Phenacetin in Serum by HPLC," Gifu-Kien Eisei Keukyusho Ho, 25, 38-40 (1980).

Method Number: A180

Method Name: Strychnine

Basic Method: HPLC

Matrices: Sample Extracts
Organic Liquids (neat or diluted)

Constituent from Appendix VIII to which method may be applied:

Strychnine (and salts)

Apparatus: HPLC/UV

Analysis Method Parameters:

HPLC: Column - n-Propyl sulfonic acid modified silica

Solvent - Methanol/2M NH_4NO_3 (27:2)

References: Wheals, B.B., "Isocratic Multi-Column High-Performance Liquid Chromatography as a Technique for Qualitative Analysis and its Application to the Characteristics of Basic Drugs Using an Aqueous Methanol Solvent," J. Chromatogr., 187, 65-85 (1980).

Lurie, I.S. and S.M. Demchuk, "Optimization of a Reverse Phase Ion-Pair Chromatographic Separation for Drugs of Forensic Interest. Part I. Variables Effecting Capacity Factors," J. Liq. Chromatogr., 4, 337-355 (1981).

Method Number: A183

Method Name: Oximes

Basic Method: GC/FPD

Matrices: Sample Extracts
Organic Liquids (neat or diluted)

Constituents from Appendix VIII to which method may be applied:

3,3-Dimethyl-1(methylthio)-2-butanone-O-(methylamino carbonyl)oxime [Thiofanox]
2-Methyl-2-(methylthio)propionaldehyde-O-(methylcarbonyl)oxime

Apparatus: GC/FPD

Analysis Method Parameters:

The sample will be derivatized with Trimethylphenylammonium hydroxide prior to analysis.

GC: Column - 1.5% OV-17/1.95% OV-210 or 6% DC-200

Carrier Gas - 80 mL/min

Temperature Program - 185°C isothermal

-or-

Column - 0.5% Carbowax 20M/5% SE-30

Carrier Gas - 60 mL/min

Temperature Program - 210°C isothermal

References: DeMey, W., W.J. Pauwels and D.E. Stallard, "Determination of Thiofanox Residues in Sugar Beet Roots and Tops Over a Three-Year Period in Eight European Countries," Meded. Fac. Landbouwwet Rijksuniv. Gent, 42, 1763-1778 (1977).

Chin, W.T., W.C. Duane, M.B. Szalkowski and D.E. Stallard, "Gas Chromatographic Determination of Thiofanox Residues in Soil, Plants, and Water," J. Agric. Food Chem., 23, 963-966 (1975).

Bromilow, R.H. and K.A. Lord, "Analysis of Sulfur-Containing Carbamates by Formation of Derivatives in the Gas-Liquid Chromatograph Using Trimethylphenylammonium Hydroxide," J. Chromatogr., 125, 495-502 (1976).

Method Number: A190

Method Name: Tris(1-aziridinyl)phosphine sulfide

Basic Method: GC/FPD

Matrix: Gas

Constituent from Appendix VIII to which method may be applied:

Tris(1-aziridinyl)phosphine sulfide

Analysis Method Parameters:

GC: Column - 3% Dexsil 410

Carrier Gas - He at 20 mL/min

Temperature Program - 140°C isothermal

FPD: At 526 nm, phosphorus mode

Reference: Carlson, D.A. and D.L. Bailey, "Determination of Mosquito Chemosterilant Recovered from Air During Real and Simulated Use," J. Agric. Food Chem., 29, 78-82 (1981).

Method Number: A221

Method Name: Antimony

Basic Method: ICAP Spectroscopy
Atomic Absorption Spectroscopy

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituent from Appendix VIII to which method may be applied:

Antimony and compounds, N.O.S.

Apparatus: ICAP Spectrophotometer
AA Spectrophotometer
Hydride generator
Graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelengths - 206.8 and 187.1 nm

AA: Analytical Wavelength - 217.6 nm
206.8 nm (or
231.1 nm if Pb is
present at high
concentration)

Furnace Parameters - Dry @ 125°C for 30s
Ash @ 800°C for 30s
Atomize @ 2700°C for 10s
Argon purge
Background correction

Flame Conditions - Air/acetylene
Fuel lean

Detection Limit (Typical Working Range):

ICAP: 0.1 mg/L (0.5-300 mg/L and less if hydride generator is used)

Furnace AA: 3 µg/L (20-300 µg/L)

Flame AA: 0.2 mg/L (1-40 mg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A222

Method Name: Arsenic

Basic Method: Atomic Absorption Spectroscopy

Matrices:
Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituents from Appendix VIII to which method may be applied:

Arsenic and compounds, N.O.S.
Arsenic acid
Arsenic pentoxide
Arsenic trioxide
Benzenearsonic acid
Dichlorophenylarsine
Diethylarsine
Hydroxydimethylarsine oxide

Apparatus:
AA spectrophotometer
Hydride generator
Graphite furnace

Analysis Method Parameters:

Hydride Generation: In the generator $SnCl_2$ will be added to form trivalent arsenic, and then zinc added to form the hydride. ($NaBH_4$ can also be used to generate the hydride.)

AA: Analytical Wavelength - 193.7 nm

Furnace Parameters - Dry @ 125°C for 30s
Ash @ 1100°C for 30s (if nickel has been added to prevent atomization of arsenic)
Atomize @ 2700°C for 10s
Argon purge
Background correction

Flame Conditions - Argon/hydrogen

Detection Limit (Typical Working Range):

Hydride AA: >1 µg/L (2- 20 µg/L)

Furnace AA: 1 µg/L (5-100 µg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A223

Method Name: Barium

Basic Method: ICAP Spectroscopy
Atomic Absorption Spectroscopy

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituents from Appendix VIII to which method may be applied:

Barium and compounds, N.O.S.
Barium cyanide

Apparatus: ICAP spectrophotometer
AA spectrophotometer
Graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelengths - 455.4 and 233.5 nm

AA: Analytical Wavelength - 553.6 nm

Furnace Parameters - Dry @ 125°C for 30s
Ash @ 1200°C for 30s
Atomize @ 2800°C for 10s
Argon purge
Background correction
(Tungsten Iodide lamp)

Flame Conditions - Nitrous oxide/acetylene
Fuel rich

Detection Limit (Typical Working Range):

ICAP: 2 µg/L (0.01-10 mg/L)

Furnace AA: 2 µg/L (10-200 µg/L)

Flame AA: 0.1 mg/L (1-20 mg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A224

Method Name: Beryllium

Basic Method: ICAP Spectroscopy
Atomic Absorption Spectroscopy

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituents from Appendix VIII to which method may be applied:

Beryllium and compounds, N.O.S.

Apparatus: ICAP spectrophotometer
AA spectrophotometer
Graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelengths - 313.0 and 234.9 nm

AA: Analytical Wavelength - 234.9 nm

Furnace Parameters - Dry @ 125°C for 30s
Ash @ 1000°C for 30s
Atomize @ 2800°C for 10s
Argon purge
Background correction

Flame Conditions - Nitrous oxide/acetylene
Fuel rich

Detection Limit (Typical Working Range):

ICAP: 0.5 µg/L (0.005- 5 mg/L)

Furnace AA: 0.2 µg/L (1 - 30 µg/L)

Flame AA: 5 µg/L (0.05 - 2 mg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A225

Method Name: Cadmium

Basic Method: ICAP Spectroscopy
Atomic Absorption Spectroscopy

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituents from Appendix VIII to which method may be applied:

Cadmium and compounds, N.O.S.

Apparatus: ICAP spectrophotometer
AA spectrophotometer
Graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelengths - 226.5 and 214.4 nm

AA: Analytical Wavelength - 228.8 nm

Furnace Parameters - Dry @ 125°C for 30s
Ash @ 500°C for 30s
Atomize @ 1900°C for 10s
Argon purge

Flame Conditions - Air/acetylene
Fuel rich

Detection Limit (Typical Working Range):

ICAP: 0.05 mg/L (0.2- 50 mg/L)

Furnace AA: 1 µg/L (5 -100 µg/L)

Flame AA: 0.05 mg/L (0.5- 10 mg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A226

Method Name: Chromium

Basic Method: ICAP Spectroscopy
Atomic Absorption Spectroscopy

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituents from Appendix VIII to which method may be applied:

Chromium and compounds, N.O.S.
Calcium chromate

Apparatus: ICAP spectrophotometer
AA spectrophotometer
Graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelengths - 267.7 and 294.9 nm

AA: Analytical Wavelength - 357.9 nm

Furnace Parameters - Dry @ 125°C for 30s
Ash @ 1000°C for 30s
Atomize @ 2700°C for 10s
Argon purge

Flame Conditions - Nitrous oxide/acetylene
Fuel rich

Detection Limit (Typical Working Range):

ICAP: 0.05 mg/L (0.2- 50 mg/L)

Furnace AA: 1 µg/L (5 -100 µg/L)

Flame AA: 0.5 mg/L (0.5- 10 mg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A227

Method Name: Lead

Basic Method: Atomic Absorption Spectroscopy
ICAP Spectroscopy

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituents from Appendix VIII to which method may be applied:

Lead and compounds, N.O.S.
Lead acetate
Lead phosphate
Lead subacetate
Tetraethyl lead

Apparatus: ICAP spectrophotometer
AA spectrophotometer
Graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelengths - 220.3 and 217.0 nm

AA: Analytical Wavelength - 217.0 nm

Furnace Parameters - Dry @ 125°C for 30s
Ash @ 500°C for 30s
Atomize @ 2700°C for 10s
Argon purge
Background correction

Flame Conditions - Acetylene/air
Oxidizing

Detection Limit (Typical Working Range):

ICAP: 0.1 mg/L (1-100 mg/L)

Furnace AA: 1 µg/L (5-100 µg/L)

Flame AA: 0.1 mg/L (1- 20 mg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A228

Method Name: Mercury

Basic Method: Cold Vapor/Atomic Absorption Spectroscopy

Matrices:
Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituents from Appendix VIII to which method may be applied:

Mercury fulminate
Mercury and compounds, N.O.S.
Phenylmercury acetate

Apparatus:
AA spectrophotometer
Cold vapor apparatus (Figure 9)

Analysis Method Parameters:

AA: Analytical Wavelength - 253 nm

In a closed system, the sample will be pretreated at 95°C in a water bath with H_2SO_4, HNO_3-potassium permanganate solution and potassium persulfate to digest the sample. Excess permanganate will be removed with sodium chloride-hydroxylamine sulfate. $SnCl_2$ will be added to the cooled solution and mercury signal measured while air is recirculating at 1 L/min.

Detection Limit (Typical Working Range):

Cold Vapor/AA: 0.2 µg/L (0.2-40 µg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

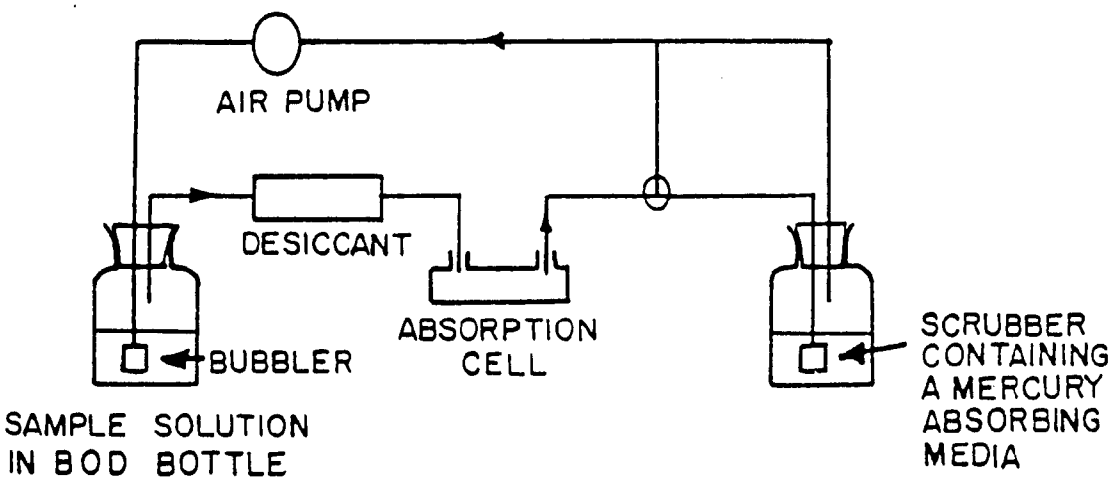


FIGURE 9 APPARATUS FOR FLAMELESS MERCURY DETERMINATION

Method Number: A229

Method Name: Nickel

Basic Method: ICAP Spectroscopy
Atomic Absorption Spectroscopy

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituents from Appendix VIII to which method may be applied:

Nickel and compounds, N.O.S.
Nickel carbonyl
Nickel cyanide

Apparatus: ICAP spectrophotometer
AA spectrophotometer with burner
Graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelengths - 231.6 and 227.0 nm

AA: Analytical Wavelength - 232.0 nm

Furnace Parameters - Dry @ 125°C for 30s
Ash @ 900°C for 30s
Atomize @ 2700°C for 10s
Argon purge
Background correction

Flame Conditions - Air/acetylene
Oxidizing

Detection Limit (Typical Working Range):

ICAP: 0.04 mg/L (0.1- 50 mg/L)

Furnace AA: 1 µg/L (5 -100 µg/L)

Flame AA: 0.04 mg/L (0.3- 5 mg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A230

Method Name: Osmium

Basic Method: ICAP Spectroscopy
Atomic Absorption Spectroscopy

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituent from Appendix VIII to which method may be applied:

Osmium tetroxide

Apparatus: ICAP spectrophotometer
AA spectrophotometer
Graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of sample solution
Analytical Wavelengths - 225.6 and 189.8 nm

AA: Analytical Wavelength - 290.9 nm

Furnace Parameters - Dry @ 105°C for 30s
Ash @ <140°C* for 30s
Atomize @ 2700°C for 10s
Argon purge

Flame Conditions - Nitrous oxide/acetylene
Fuel rich

Detection Limit (Typical Working Range):

ICAP:	5 µg/L	(0.010- 10 mg/L)
Furnace AA:	20 µg/L	(50 -500 µg/L)
Flame AA:	0.3 mg/L	(2 -100 mg/L)

*OsO_4 vaporizes at ca. 150°C.

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A231

Method Name: Selenium

Basic Method: Atomic Absorption Spectroscopy

Matrices:
Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituents from Appendix VIII to which method may be applied:

Selenious acid
Selenium and compounds, N.O.S.
Selenium sulfide
Selenourea

Apparatus:
AA spectrophotometer
Hydride generator
Graphite furnace

Analysis Method Parameters:

Hydride Generation: In generator $SnCl_2$ will be added to form trivalent arsenic, and then zinc added to form the hydride. ($NaBH_4$ can also be used to generate the hydride.)

AA: Analytical Wavelength - 196.0 nm

Furnace Parameters - Dry @ 125°C for 30s
Ash @ 1200°C for 30s
Atomize @ 2700°C for 10s
Argon purge
Background correction

Flame Conditions - Argon/hydrogen

Detection Limit (Typical Working Range):

Hydride AA: >1 µg/L (2- 20 µg/L)

Furnace AA: 2 µg/L (5-100 µg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A232

Method Name: Silver

Basic Method: ICAP Spectroscopy
Atomic Absorption Spectroscopy

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituents from Appendix VIII to which method may be applied

Potassium silver cyanide
Silver and compounds, N.O.S.
Silver cyanide

Apparatus: ICAP spectrophotometer
AA spectrophotometer
Graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelengths - 328.1 and 224.6 nm

AA: Analytical Wavelength - 328.1 nm

Furnace Parameters - Dry @ 125°C for 30s
Ash @ 400°C for 30s
Atomize @ 2700°C for 10s
Argon purge
Background correction

Flame Conditions - Acetylene/air
Oxidizing

Detection Limit (Typical Working Range):

ICAP: 0.01 mg/L (0.1 -50 mg/L)

Furnace AA: 0.2 µg/L (1 -25 µg/L)

Flame AA: 0.01 mg/L (0.14- 4 mg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A233

Method Name: Strontium

Basic Method: ICAP Spectroscopy
Atomic Absorption Spectroscopy

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituent from Appendix VIII to which method may be applied:

Strontium sulfide

Apparatus: ICAP spectrophotometer
AA spectrophotometer
Graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelengths - 407.8 and 346.4 nm

AA: Analytical Wavelength - 460.7 nm

Furnace Parameters - Dry @ 125°C for 30s
Ash @ 1000°C for 30s
Atomize @ 2500°C for 10s
Argon purge
Background correction

Flame Conditions - Nitrous oxide/acetylene
Fuel lean

Detection Limit (Typical Working Range):

ICAP: 2 µg/L (0.05-10 mg/L)

Furnace AA: 0.2 µg/L (0.4 -20 µg/L)

Flame AA: 0.08 mg/L (0.2 - 5 mg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A234

Method Name: Thallium

Basic Method: ICAP Spectroscopy
Atomic Absorption Spectroscopy

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituents from Appendix VIII to which method may be applied:

Thallium and compounds, N.O.S.
Thallic oxide
Thallium(I)acetate
Thallium(I)carbonate
Thallium(I)chloride
Thallium(I)nitrate
Thallium selenite
Thallium(I)sulfate

Apparatus: ICAP spectrophotometer
AA spectrophotometer
Graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelengths - 190.9 and 351.9 nm

AA: Analytical Wavelength - 276.8 nm

Furnace Parameters - Dry @ 125°C for 30s
Ash @ 400°C for 30s
Atomize @ 2400°C for 10s
Argon purge
Background correction

Flame Conditions - Air/acetylene
Oxidizing

Detection Limit (Typical Working Range):

ICAP: 0.1 mg/L (1-100 mg/L)

Furnace AA: 1 µg/L (5-100 µg/L)

Flame AA: 0.1 mg/L (1- 20 mg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A235

Method Name: Vanadium

Basic Method: ICAP Spectroscopy
Atomic Absorption Spectroscopy

Matrices: Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituents from Appendix VIII to which method may be applied:

Vanadic acid, ammonium salt
Vanadium pentoxide

Apparatus: ICAP spectrophotometer
AA spectrophotometer
Graphite furnace

Analysis Method Parameters:

ICAP: Sample input via direct aspiration of solution
Analytical Wavelengths - 309.3 and 214.0 nm

AA: Analytical Wavelength - 318.4 nm

Furnace Parameters - Dry @ 125°C for 30s
Ash @ 1400°C for 30s
Atomize @ 2800°C for 15s
Argon purge
Background correction

Flame Conditions - Nitrous oxide/acetylene
Fuel rich

Detection Limit (Typical Working Range):

ICAP: 0.01 mg/L (0.1-150 mg/L)

Furnace AA: 4 µg/L (10 -200 µg/L)

Flame AA: 0.2 mg/L (2 -100 mg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A251

Method Name: Anions

Basic Method: Ion Chromatography

Matrices: Aqueous Liquids
Sludges
Sample Extracts

Constituents from Appendix VIII to which method may be applied:

Hydrocyanic acid
Hydrofluoric acid

Apparatus: Ion chromatograph
Electrochemical detector

Analysis Method Parameters:

There are many methods which involve ion chromatography for the analysis of anions available in the literature.

One method involves eluting anions from a 500 mm anion separator column and an anion suppressor with a 0.003M $NaHCO_3$/0.0024M Na_2CO_3 solution. This suppressor column must be regenerated every 20 hours of operation with a 1N aqueous H_2SO_4 solution.

Reference: Small, H., T.S. Stevens and W.C. Baumar, "Novel Ion Exchange Chromatographic Method Using Conductimetric Detection," Anal. Chem., 47, 1801-1809 (1975).

Method Number: A252

Method Name: Total Cyanides

Basic Method:
Titration
Colorimetry

Matrices:
Aqueous Liquids
Organic Liquids
Sludges
Solids

Constituents from Appendix VIII to which method may be applied:

Barium cyanide
Calcium cyanide
Copper cyanide
Cyanides, N.O.S.
Ethyl cyanide
Nickel cyanide
Potassium cyanide
Potassium silver cyanide
Silver cyanide
Sodium cyanide
Zinc cyanide

Apparatus:
Spectrophotometer
Microburet
Cyanide distillation apparatus

Analysis Method Parameters:

Sample Preparation: Oxidizing agents (indicated by KI-starch test paper) will be removed with ascorbic acid.

Sulfides (indicated by lead acetate test paper) will be removed with cadmium carbonate.

Fatty acids will be removed in a single extraction with hexane at pH 6 to 7. Following the extraction, the pH of the solution will be raised above 12.

HCN Collection: A vacuum will be adjusted to draw ca. 1 bubble/s through flask, gas will be collected continuously from prior to adding acid to 15 min after removal of heat.

The total cyanide concentration may be determined by either of the following methods:

Titration

The solution will be titrated with standard silver nitrate in the presence of benzalrhodamine indicator to first color change from yellow to brownish pink.

Colorimetry

To solution, Chloramine T will be added and the solution mixed thoroughly. After 1-2 min, pyridine-barbituric acid solution will be added, the adsorbance read at 578 nm after start of color development (8-15 min).

Or after 1-2 min, pyridine-pyrazolone solution can be added and the absorbance read at 620 nm after 40 min.

Detection Limit (Typical Working Range):

Titration: 0.3 mg/L (>1 mg/L)

Colorimetry: 0.01 mg/L(0.02-1 mg/L)

References: U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980).

Kopp, J.F. and G.D. McKee, "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 (March 1979). NTIS No. PB297686/AS.

Method Number: A253

Method Name: Phosphides

Basic Method: GC/FPD

Matrix: Solids

Constituents from Appendix VIII to which method may be applied:

Aluminum phosphide
Zinc phosphate

Apparatus: Gas Chromatograph/Flame Photometric Detector
One-liter calibrated gas flasks

Analysis Method Parameters:

Sample Preparation: A sample will be placed into a calibrated gas flask, flushed with 99.99% N_2 and dilute acid (0.01N HNO_3) added. A measured amount of N_2 from a second calibrated gas flask will then be replaced with equilibrated phosphine-containing gas.

GC: Column - 3% Carbowax 20M on Gas Chrom Q.

Detection Limit: 10 µg/L

Reference: Berck, B., W.E. Westlake and F.A. Gunter, "Microdetermination of Phosphine by Gas-Liquid Chromatography with Microcoulometric, Thermionic, and Flame Photometric Detection," J. Agric. Food Chem., 18, 143-147 (1970).

It has been impossible to find an analysis method which can be recommended with confidence for the following constituents from Appendix VIII:

Cyclophosphamide
Ethylenebisdithiocarbamic acid (salts and esters)
Iron dextran
Methyl chlorocarbonate
4-Nitroquinoline-1-oxide
o-Toluidine hydrochloride
Uracil mustard

VII. QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

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 (1) document the quality (i.e., accuracy and precision) of the generated data; (2) maintain the quality of the data within predetermined tolerance limits for specific sampling and analysis procedures; and (3) provide guidelines for corrective actions if the QC data indicate that a particular procedure is out of control. It should be noted that, at this stage in the development of the hazardous waste incineration program, predetermined tolerance limits for the overall precision and accuracy of the recommended sampling and analysis procedures have not been established. Tolerance limits may be established as experience with trial burns accumulates and a data base is generated.

In this section, specific QA/QC procedures are described. For any individual sampling and analysis program, these procedures and 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 definitions, which represent interdependent activities, serve to differentiate between the complementary activities of QA and QC.

- Quality Assurance (QA) activities address delegation of program responsibilities to individuals, documentation, data review, and audits. The objective of QA procedures is to permit an assessment of the reliability of the data.

- Quality Control (QC) 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 predetermined limits. QC data are immediately evaluated by the analysts and if the QC data fall outside of their predetermined (tolerance) limits, corrective actions specified in the work plan are taken.

The following discussion of QA/QC procedures is based upon a guidelines document (24) issued by the Office of Monitoring Systems and Quality Assurance of the EPA Office of Research and Development. That document, QAMS-005/80, entitled "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans," and the references cited

therein provide an extensive resource for the permit applicant and the permit writer in selecting the appropriate QA/QC procedures for the sampling and analysis effort in a particular trial burn and/or operating burn.

This section of the report presents a brief description of the essential elements of a QA project plan. The guidelines presented here are intended to be sufficient to allow the permit writer to select the features that must be treated in detail for any particular trial burn. It should be noted that these guidelines are necessarily general and would not, in themselves, suffice as a QA plan for a specific project. In each case, it would be necessary to develop a specific plan that addresses the specific POHCs, necessary detection limits for the 99.99 percent DRE, waste feed sampling frequency, and the like.

The QAMS-005/80 document has identified sixteen essential elements of a QA project plan. These are listed in Table 24. Although every trial burn plan need not have a QA project plan organized in strict accordance with this list, each of these elements should be explicitly addressed somewhere in the trial burn plan. Each element is therefore discussed briefly in this section.

B. TITLE PAGE AND TABLE OF CONTENTS

These elements are self-explanatory. It may be noted, however, that the title page should indicate the cognizant individuals with QA responsibility for the project both at the applicant (and/or sampling and analysis contractor) institution and at the EPA. If the organization of the QA plan as outlined in the table of contents, does not follow the list of 16 QAMS-005/80 QA elements, a supplementary table which cross-references the plan to the QAMS-005/80 list should be provided.

C. PROJECT DESCRIPTION

The project description is typically presented in some detail elsewhere in a hazardous waste incineration permit application. In the QA project plan, it is sufficient to present a brief summary of the project, including a list of the wastes to be treated, the POHCs for which DREs are to be determined, and the target stack gas detection limits that correspond to 99.99 percent DRE.

D. PROJECT ORGANIZATION AND RESPONSIBILITY

Individuals should be designated who will have responsibility for the following functions in specifying the QA/QC program, as part of the program work plan, and in carrying out all elements of the QA/QC plan:

The trial burn project manager has overall responsibility for management of the project. The project manager must ensure that proper materials, instruments, and qualified personnel are available, and he must designate individuals to assist in discharging the QA/QC responsibilities.

TABLE 24

ESSENTIAL ELEMENTS OF A QA PROJECT PLAN

1. Title Page
2. Table of Contents
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 Assess Data Precision, Accuracy, and Completeness
15. Corrective Action
16. Quality Assurance Reports to Management

Source: Reference 24.

The quality assurance coordinator is responsible for reviewing and advising on all aspects of QA/QC. His responsibilities include:

- assisting the project manager in specifying the QA/QC procedures to be used during the program,
- making on-site evaluations and submitting audit samples to assist in reviewing QA/QC procedures, and
- if problems are detected, making recommendations to the project manager and upper corporate/institutional management to ensure that appropriate corrective actions are taken.

The quality assurance coordinator must be autonomous, i.e., not reporting to the project manager. The QA coordinator is responsible to upper management independently of project management. An example of a management structure that meets this requirement for independence is shown in Figure 10.

The analysis coordinator is responsible for laboratory activities. These include:

- training and qualifying personnel in specified laboratory QC and analytical procedures, prior to receiving samples,
- receiving samples from the field and verifying that incoming samples correspond to the packing list or chain-of-custody sheet, and
- verifying that laboratory QC and analytical procedures are being followed as specified in the work plan and reviewing sample and QC data during the course of analyses. If questionable data exist, the analysis coordinator determines which repeat samples or analyses are needed.

The sampling coordinator is responsible for field activities. These include:

- determining (with the analysis coordinator) appropriate sampling equipment and sample containers to minimize contamination,
- ensuring that samples are collected, preserved and transported, as specified in the work plan, and
- checking that all sample documentation (labels, field notebooks, chain-of-custody records, packing lists) are correct and transmitting that information, along with the samples, to the analytical laboratory.

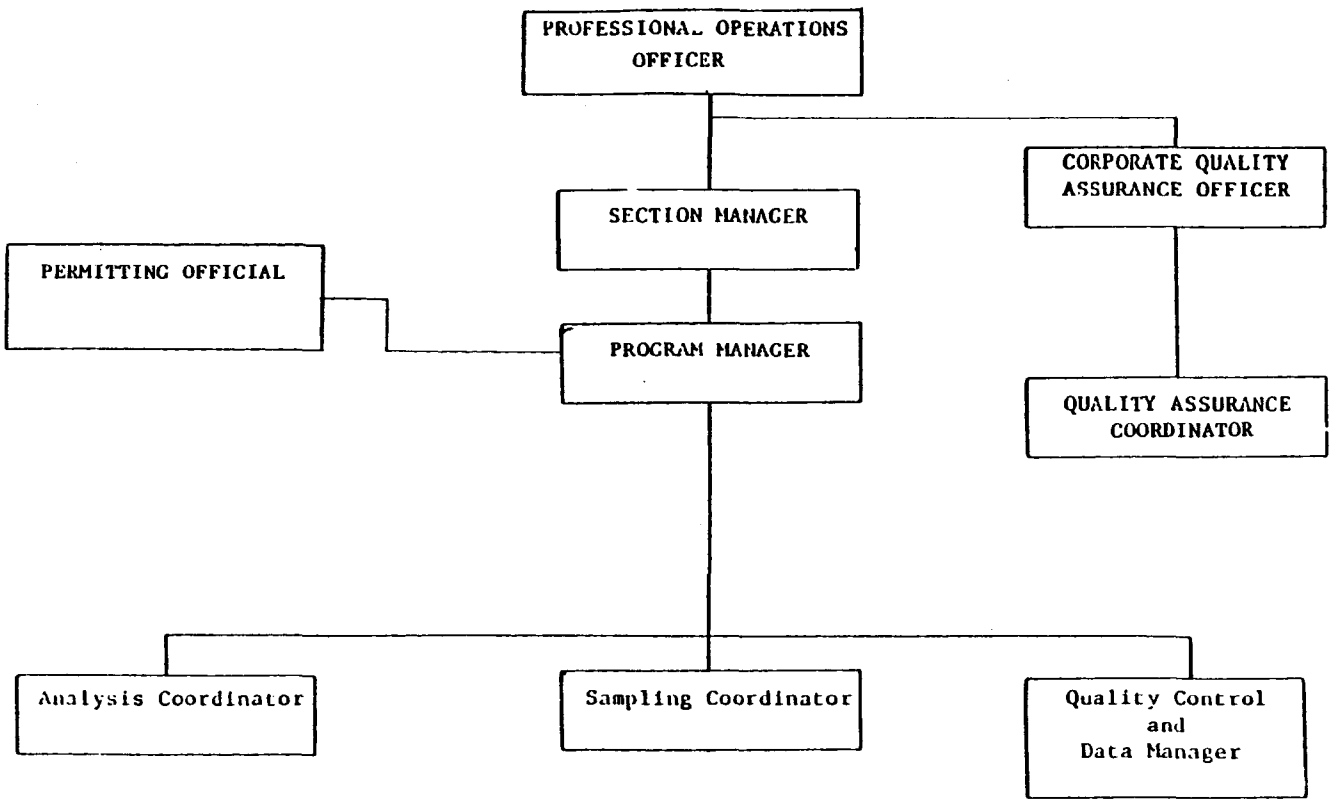


FIGURE 10 EXAMPLE OF PROJECT ORGANIZATION AND RESPONSIBILITY

The quality control and data manager is responsible for QC activities and data management. These include:

- maintaining records of all incoming samples, tracking those samples through subsequent processing and analysis and ultimately appropriately disposing of those samples at the conclusion of the program,
- preparing quality control samples for analysis prior to and during the program,
- preparing QC and sample data for review by the analysis coordinator and the program manager, and
- preparing QC and sample data for transmission and entry into a computer data base, if appropriate.

E. QUALITY ASSURANCE OBJECTIVES

The overall measurement objective is to determine, for each of the waste feed materials selected for testing, the effectiveness of the incineration facility in achieving thermal destruction of the principal organic hazardous constituents (POHCs) of the waste, according to criteria established in 40 C.F.R. Part 264. At the present time, the EPA has not established quantitative guidelines as to the precision, accuracy, completeness, representativeness and/or comparability criteria that must be met by data generated in a trial burn. However, numerical QA objectives for accuracy and precision of the sampling system calibration, sample preparation, and analysis procedures have been developed. These guidelines are based on previous experience in applying comparable procedures to a variety of complex sample matrices. In the event that the QA objectives given in this section are not achievable (due to the fact that sample matrices are highly variable as well as complex), revised objectives must be formulated in consultation with the trial burn permitting official(s).

1. Accuracy

Accuracy is defined in QAMS-005/80 as the degree of agreement of a measurement, or average of measurements, with an accepted reference or true value. In general, appropriate accuracy goals would include using reference materials of highest, known purity for calibrations and spiking so that (a) the determinate errors due to instrument response and incomplete preparation recoveries can be corrected, and (b) the primary uncertainties in the analytical data due to random errors do not exceed those specified in Table 25. The QA objectives for accuracy may be expressed in terms of the following parameters:

TABLE 25

PRECISION GOALS FOR ANALYSIS

Analysis Procedure	Matrix	Precision RSD* (%)
Proximate		
Moisture, Solid, and Ash Content	Waste Feed	<10
Elemental Analysis	Waste Feed	<10
Viscosity	Waste Feed	<10
Survey		
GRAV	Waste Feed Stack Gas Samples	<10
TCO		<30
IR		Factor of 3
LRMS		Factor of 3
Directed		
GC/MS	Waste Feed Stack Gas Samples Scrubber Water Bottom Ash	<30
HPLC		<30
GC		<30
ICAP/AAS		<30
IC		<30

*RSD = Relative Standard Deviation

- Reference materials: All reference materials used as calibration standards or surrogate compounds should be of the highest purity commercially available, usually >98%. Mass spectra of surrogates, POHCs and other organic Appendix VIII compounds used as reference materials must be obtained on each new lot of material to confirm qualitative identification;

- Instrument performance: Each instrument used in a project must be checked each day samples are analyzed to demonstrate performance. One of the QA objectives should be that the absolute instrument response (e.g., area counts/ng injected for the internal standard(s) or surrogates in a GC/MS analysis) be within a stated percentage of comparable measurements made subsequent to the most recent calibration of the instrument;

- Recovery of surrogates: The recovery of a surrogate compound(S) added to a sample is defined as follows:

$$\text{Recovery (\%)} = \frac{\mu g \text{ S found in sample}}{\mu g \text{ S added to sample}} \times 100$$

This equation assumes that the surrogate is not present in the sample. The mean and standard deviation of the recovery data should be compiled on a cumulative basis for each surrogate compound in each type of sample matrix. The objectives for recovery of surrogates are:

	Mean	Standard Deviation
Aqueous liquids	$\leq$70%	$\leq$30%
Organic liquids Stack gas samples	$\leq$50%	$\leq$40%

- Recovery of POHCs or other Appendix VIII Compounds: The recovery of a POHC, or other Appendix VIII compound (P), can be defined as follows:

$$\text{Recovery (\%)} = \frac{\mu g \text{ P found in spiked sample} - \mu g \text{ P in native sample}}{\mu g \text{ P added to sample}} \times 100$$

It may not be appropriate to specify numerical targets for recovery of POHCs or Appendix VIII compounds from the waste sample. It is expected that recoveries of the target compounds will approximate the recoveries given for surrogates. This type of recovery data is generated only in those cases for which the sample shows detectable levels of the POHC or Appendix VIII compound, and the spiked level is high enough to be measurable above the native level in the sample. If recovery data are generated, they should be reported with the sample data.

2. Precision

Precision is defined in QAMS-005/80 as a measure of mutual agreement among individual measurements of the sample property. The QA objectives for precision might be expressed in terms of the following parameters:

- Analysis of standards: One of the QA objectives should be that the correlation coefficient for each calibration curve, including all data points for standards analyzed subsequent to the most recent recalibration of the instrument, be greater than some specified value (e.g., 0.9, 0.99);

- Analysis of surrogates: Another QA objective for a trial burn project should be that the relative standard deviation for analysis of surrogate compounds in replicate samples from a given waste stream be within the limits specified in Table 25;

- Analysis of replicate samples: A final QA objective should be that results of directed analysis of laboratory replicate samples (i.e., replicate samples drawn from the same field composite sample) be within the limits specified in Table 25, when at least three replicate samples are analyzed. At least 10 percent of all analyses performed should be triplicate QC checks.

3. Completeness

The QA objective for completeness during a trial burn project is to obtain analytical results for at least 95 percent (or other specified percentage) of the samples collected during that project.

4. Representativeness

The following factors, which must be addressed to ensure, as much as possible, a representative sample, are discussed in Section IV and V of this report: sampling sites, process cycles, catch flow rates (sampling frequency), sample preservation, sampling procedures, sampling equipment, and sample preparation procedures.

5. Comparability

All data are reported in mg, µg, or ng of analyte per kilogram, liter, or cubic meter of orginal sample. When precise recovery values for a given component are known, the recovery information and the corrected concentration data should also be provided.

F. SAMPLING PROCEDURES

The sampling procedures to be used for hazardous waste incineration are described in Section IV of this report. This element of the trial burn QA plan specifies which of the Methods S001-S012 should be applied to each of the streams to be sampled. Any method modifications that are anticipated must be described in detail. The plan should indicate the frequency with which waste, stack gas, and other effluent samples should be taken to ensure that feed and emission measurement for DRE calculations correspond to comparable test periods. Figure 11 illustrates a possible approach to this aspect of the sampling methodology.

The number of replicate tests to be run (triplicate determinations are specified as a minimum in Section IV of this report), and the provisions for generation of sufficiently large samples to allow a specified number of split and spiked QC samples to be prepared must be explicitly addressed.

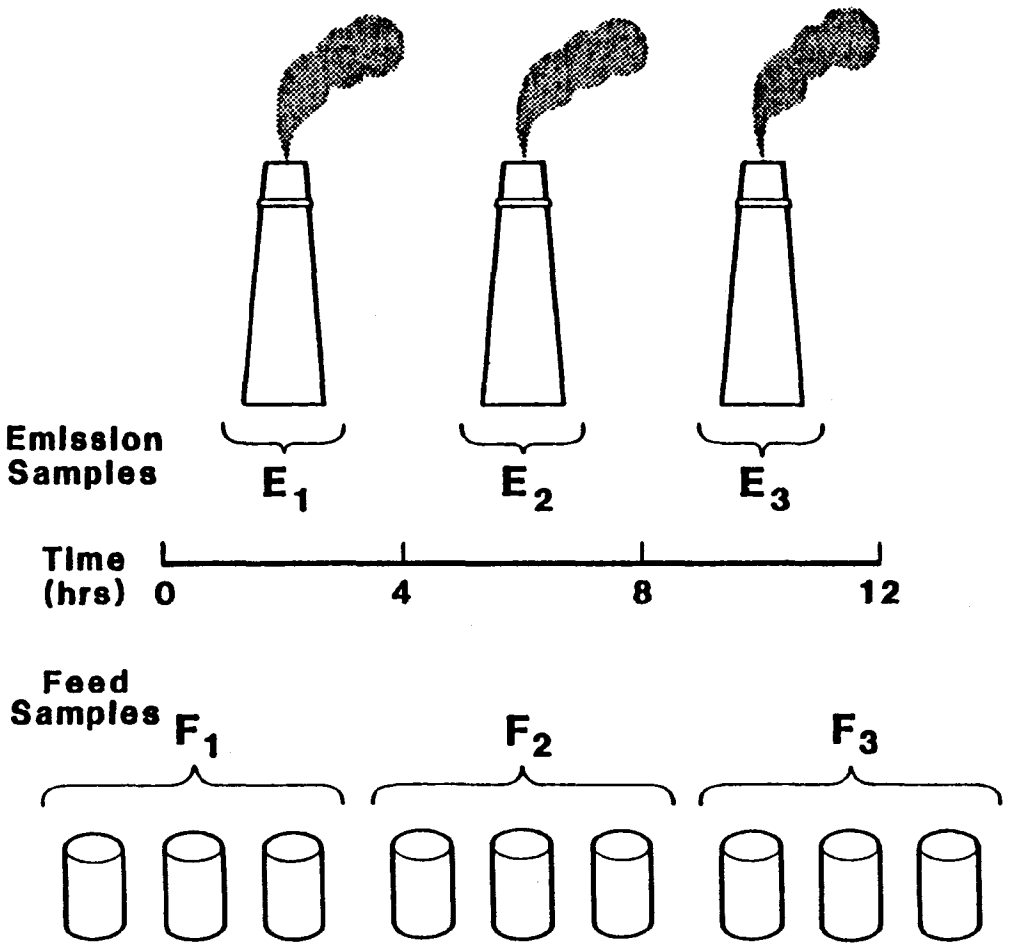
G. SAMPLE CUSTODY

Since trial burn data are part of the regulatory permitting process, it is essential that adequate chain-of-custody procedures be established for each project. This section provides a brief description of the appropriate procedures. A complete and detailed chain-of-custody protocol that will satisfy EPA enforcement requirements for litigation is provided in reference 25.

H. DATA MAINTENANCE AND CHAIN-OF-CUSTODY

Guidelines for the maintenance of records for the engineering data and the routine operating parameters of the incinerator are described in detail in the engineering guidelines manual (3) and are not repeated here. For any sampling and analysis test of an incinerator facility, the collected data must be documented and maintained for as long as there may be questions concerning the results of the test. Typically, this may mean storage of the collected data for a minimum of one to two years following the sampling and analysis effort. The data may be kept in any one of several forms, such as laboratory notebooks, reports, raw data on magnetic tape and/or disk media. For routine data and calibration information, laboratory notebooks are appropriate. To answer identification questions and to confirm the identities of additional POHCs at a later date, storage of the raw data as computer data files is a more practical method of archiving the data. Specific guidelines for data maintenance should be incorporated into the QA/QC plan for each test; representative information is found in documents, such as SW-846 (4).

Chain-of-custody procedures cover both field sampling and laboratory analysis. For field work, the protocols described in Chapter II of SW-846 (4) should be observed. These procedures include detailed labeling of each sample, permanent recording of information pertinent to the sample collection, and any field observations made at the same time the sample was collected. A copy of all such materials must accompany



Source: J.E. Picker and B.N. Colby, S-Cubed (26).

FIGURE 11 SAMPLES OF WASTE FEED AND STACK EMISSIONS ARE TAKEN AS COMPOSITES OVER FOUR-HOUR LONG PERIODS. THREE DESTRUCTION AND REMOVAL EFFICIENCIES (DRE) ARE CALCULATED FROM THE RATIOS E_1/F_1, E_2/F_2, E_3/F_3

each sample returning from the field. In the laboratory, similar paperwork tracks the samples completely through the analysis procedure. A typical example of a chain-of-custody record is illustrated by Figures 12 through 14.

I. CALIBRATION PROCEDURES AND FREQUENCY

1. Sampling

Calibration of stack sampling equipment is performed within two weeks prior to the initiation of field sampling activity. The calibration procedures should conform to the specifications of the EPA document, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods" (27). Dry gas meters, nozzles, orifices and pitot tubes are included in the calibration. Tables 26 and 27 summarize the methods to be used for calibration.

The other types of sampling equipment described in Section IV (Coliwasa, dipper, scoop, etc.) require no calibration.

2. Analysis

Instrument calibration procedures have been described in Section VI. The QA plan for each project specifies the materials and concentration ranges of standards for calibration of each instrument to be used in the project.

J. ANALYTICAL PROCEDURES

The analytical procedures used in trial burns are detailed in Section VI. The majority of these methods have not yet been validated for application to hazardous wastes or to effluent samples associated with trial burns, although considerable experience has been accumulated from their use in other contexts.

Extensive method validation may be beyond the scope of most trial burn projects. The QC data on analysis of surrogates, duplicates, and spiked samples serve as indicators of the performance of the sample preparation and analytical methods.

K. DATA REDUCTION, VALIDATION, AND REPORTING

1. Data Reduction

The QA project plan includes explicit procedures for data reduction, showing all equations and conversion factors. An example data reduction procedure for GC/MS analysis, which is expected to be the most commonly used technique for trial burn POHC analysis, is given here.

Field Sampling Chain-of-Custody Form

Leader	Name of Survey or Activity	Date of Collection	Sheet

Description of Shipment

Type of Sample

Total Number Sample Containers

Contents of Shipment

Field Sample No.	No. of Containers/Field No.			Analyses Required — Check Where Appropriate						
	Plastic	Glass	VOA	Cyanide	Phenols	Asbestos	Pesticides	Metals	VOA	Semi-

Personnel Custody Record

Relinquished by (Sampler)	Received by	Date	Time	Reason
Sealed ☐ Unsealed ☐	Sealed ☐ Unsealed ☐			
Relinquished by	Received by	Date	Time	Reason

FIGURE 12 FIELD SAMPLING CHAIN-OF-CUSTODY FORM

Collector's Sample No. _____

CHAIN-OF-CUSTODY RECORD

Location of Sampling: _____ Producer _____ Hauler _____ Disposal Site

_____ Other _____
Sample

Shipper's Name: _____

Address: _____
number street city state zip

Collector's Name _____
signature

Date Sampled _____ Time Sampled _____ Hours _____

Type of Process Producing Waste _____

Field Information _____

_____

_____

Sample Receiver:

1. _____
name and address of organization receiving sample

2. _____

3. _____

Chain of Possession:

1.	signature	title	inclusive dates
2.	signature	title	inclusive dates
3.	signature	title	inclusive dates

FIGURE 13 CHAIN-OF-CUSTODY RECORD

TO:

SAMPLE NO.: _____ _____

SAMPLE DESCRIPTION: _____

ANALYSIS PERFORMED: TYPE _____

ON _____ (date)

BY _____ (name)

_____ (organi-

_____ zation)

METHOD USED: _____

_____ (ref)

VARIATIONS IN CONDITIONS/PROCEDURES (if any) _____

_____

_____

_____

_____

SAMPLE SIZE TAKEN FOR ANALYSIS: _____

CALIBRATION METHOD USED: _____ (reference

_____ material used)

_____ (# and name of cal. stds.)

DETECTION LIMIT _____

PRECISION OF DETERMINATION: _____

ANALYSIS LOG NO. (or other reference to raw data) _____

SIGNATURE OF ANALYST _____

FIGURE 14 RECORD OF ANALYSIS REPORT FORM WITH ACCEPTABLE DOCUMENTATION

TABLE 26

ACTIVITY MATRIX FOR CALIBRATION OF EQUIPMENT

Apparatus	Acceptance Limits	Frequency and Method of Measurement	Action if Requirements Are Not Met
Wet test meter	Capacity $\geq$3.4 m^3/h (120 ft^3/h); accuracy within ±1.0%.	Calibrate initially, and then yearly by liquid displacement.	Adjust until specifications are met, or return to manufacturer.
Dry gas meter	$Y_i = Y \pm 0.02Y$.	Calibrate vs. wet test meter initially, and when post-test check exceeds $Y \pm 0.05Y$.	Repair, or replace; recalibrate.
Thermometers	Impinger thermometer ± 1°C (2°F); dry gas meter thermometer ± 3°C (5.4°F) over range; stack temperature sensor ± 1.5% of absolute temperature.	Calibrate each initially as a separate component against a mercury-in-glass thermometer; then before each field trip compare each as part of the train with the mercury-in-glass thermometer.	Adjust; determine a constant correction factor, or reject.
Probe heating system	Capable of maintaining 120° ± 14°C (248° ± 25°F) at a flow rate of 21 L/min (0.71 ft^3/min).	Calibrate component initially by APTD-0576 (12), if constructed by APTD-0581 (11), or use published calibration curves.	Repair, or replace; reverify the calibration.
Barometer	± 2.5 mm (0.1 in) Hg of mercury-in-glass barometer.	Calibrate initially vs. mercury-in-glass barometer; check before and after each field test.	Adjust to agree with a certified barometer.
Probe nozzle	Average of three I.D. measurements of nozzle; difference between high and low $\leq$0.1 mm (0.004 in).	Use a micrometer to measure to nearest 0.025 mm (0.001 in).	Recalibrate, reshape, and sharpen when nozzle becomes nicked, dented, or corroded.
Analytical balance	± 1 mg of Class-S weights.	Check with Class-S weights upon receipt.	Adjust or repair.

Source: EPA-600/4-77-027b (27).

TABLE 27

ACTIVITY MATRIX FOR CALIBRATION OF APPARATUS

Apparatus	Acceptance Limits	Frequency and Method of Measurement	Action if Requirements Are Not Met
Type S pitot tube and/or probe assembly	All dimension specifications met.	Calibrate initially and visually inspect after each field test.	Do not use pitot tubes that do not meet face opening specifications; repair or replace as required.
Stack gas temperature measurement system	Capable of measuring within 1.5% of minimum stack temperature (absolute)	Calibrate initially and after each field test.	Adjust to agree with Hg bulb thermometer, or construct a calibration curve to correct the readings.
Barometer	Agrees within 2.5 mm (0.1 in) Hg of mercury-in-glass barometer.	Initially and after every field use, compare to a liquid-in-glass barometer.	Adjust, repair, or discard.
Differential pressure gauge (does not include inclined manometer)	Agree within ± 5% of inclined manometers.	Calibrate initially and after each field use.	Reject test results, or consult administrator if post-test calibration is out of specification.

Source: EPA-600/4-77-027b (27).

Raw data for the quantitative GC/MS analysis procedure consist of peak areas for the surrogate species and analytes of concern. Raw data are converted to concentrations by use of a calibration curve that relates peak area to the quantity of analyte introduced into the instrument. A calibration curve for each analyte and analytical method can be constructed by fitting a linear regression equation to the results of the analyses of calibration standard solutions which contain the analyte at five different concentration levels.

The raw data are converted to concentration of analyte in a sample by automated data processing routines or by the analyst. Peak areas for the series of known calibration standards are first entered and a regression line computed. A plot of the calibration curve with the actual calibration data superimposed should be generated for visual examination of deviations from linearity or of outlying data points. Peak areas from the analyses of the unknown samples are then entered, corresponding quantities of analyte are computed from the regression line, and a summary of the raw and converted data printed. The original copy of the data summary should be included in the analyst's notebook and copies forwarded to the analysis coordinator and the project manager.

An internal standard (such as d_{10}-anthracene) is added to each standard solution or concentrated sample extract immediately prior to analysis. The quantity added is sufficient to give the same concentration (ng/μL) of internal standard in all solutions/extracts analyzed.

A calibration curve and regression equation are then created, using the relative area, A', where:

$$A' = \frac{\text{Raw area for peak corresponding to analyte (POHC)}}{\text{Raw area for peak corresponding to internal standard}} .$$

Blank corrections are made by subtracting A' for the method blank from A' for the standard. The calibration curve consists of a plot of A' vs. ng of analyte (POHC) injected.

The concentration of analyte or surrogate in an unknown sample, C, is calculated as follows:

Quantity injected, Q (ng)

Q is calculated from the regression equation of the calibration curve:

$$A' = m \times Q + b$$

where:

A' = the relative area corrected by subtracting A' for the blank from A' for the sample,

Q = the quantity of analyte injected (ng),

m = the slope of the regression line, and

b = the intercept of the regression line (which will not be force-fit to zero).

Thus:

$$Q\ (ng) = \frac{A' - b}{m}\ .$$

Concentration in Extract, C^* (ng/μL)

C^* is calculated from Q and the injection volume, V_i (μL). Thus:

$$C^*\ (ng/\mu L) = \frac{Q}{V_i}$$

Concentration in Sample, C (mg/L, mg/kg, or mg/dscm)

C is calculated from C^*, the volume of the concentrated sample extract, V_x, and the initial quantity of sample extracted, V_s.

For aqueous liquids, organic liquids and slurries:

$$C\ (mg/L) = \frac{C^* \times V_x}{V_s} \div 1000$$

where:

C^* = concentration in extract (ng/μL ≡ μg/mL),

V_x = volume of concentrated extract (mL), and

V_s = volume of sample taken for extraction (L).

For solids and sludges:

$$C\ (mg/kg) = \frac{C^* \times V_x}{W_s} \div 1000$$

where:

C^* = concentration in extract (ng/μL ≡ μg/mL),

V_x = volume of concentrated extract (mL), and

W_s = weight of sample taken for extraction (kg).

For stack gas samples:

$$C\ (mg/dscm) = \frac{C^* \times V_x}{V_g} \div 1000$$

where:

C^* = concentration in extract (ng/μL ≡ μg/mL),

V_x = volume of concentrated extract (mL), and

V_g = volume of stack gas sampled (dscm).

2. Data Validation

The principal criteria that are used to validate the data integrity during collection and reporting of data include:

- frequent verification by the QC and data manager that all raw data generated in the preceding week have been stored on magnetic tape and/or in hard copy, and that storage locations have been documented in the laboratory chain-of-custody records;
- examination of at least 5 percent of the raw data (e.g., chromatograms, AAS recorder outputs) on a frequent basis by the analysis coordinator to verify adequacy of documentation, confirm peak shape and resolution, assure that the automatic integrator was sensing peaks appropriately, and so forth;
- confirmation that raw areas for internal standards and calibration standards and raw and relative areas for surrogate compounds are within 50 percent of the expected value;
- reporting of all associated blank, standard, and QC data along with results for analyses of each batch of samples; and
- reporting of all analytical data for samples with no values rejected as outliers, because of the small number of replicate samples for analysis.

3. Data Reporting

Results of directed, survey, and proximate analyses are reported in the formats, or equivalent, presented in Section VI.

L. 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.

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.

1. 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:

- Field Blanks--These blank samples are exposed to field and sampling conditions and analyzed to assess possible contamination from the field (one for each type of sample preparation).

- Method Blanks--These blank samples are prepared in the laboratory and are analyzed to assess possible laboratory contamination (one for each lot of samples analyzed).

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

2. Analytical Replicates

Replicate analysis of specific samples may be undertaken by the analyst to check on the validity of certain anomalous samples. For example, if the internal standard response for a specific sample changes drastically from its prior value, a problem could be present in the instrument or in the sample workup. Repeat analyses of the sample in question and a previous "normal" sample serve to indicate which of the possible problems is, in fact, present.

3. Spiked Samples

All samples are spiked with one or more selected surrogate compounds prior to extraction and analysis. The data on surrogate concentration are used to calculate the recovery of the surrogate compounds as one measure of the accuracy of the sample preparation and analysis procedures.

For directed analysis of POHCs, one sample from each set of three replicates should be spiked with each analyte at a concentration corresponding to two times the expected POHC concentration for waste feed samples and corresponding to two times the target detection limit (based on 99.99 percent) DRE for stack gas samples. Scrubber water or ash samples should be spiked with analyte at a concentration of 10-100 ppm if no specific target detection level has been established in the trial burn permit.

M. PERFORMANCE AND SYSTEM AUDIT

A system audit by the project manager and quality assurance officer is made prior to the implementation of any new experimental procedures.

Systems audits for trial burn projects include frequent review by the QC and data manager and project manager of all recent data to ensure that all required QC checks are made and evaluation criteria followed.

The quality assurance officer participates in these reviews on a regular basis. Because of the anticipated difficulty in obtaining reference samples with matrices similar to the hazardous waste incinerator samples, performance audits must rely heavily on the replicate analyses of real samples, spiked and unspiked. However, standard reference materials should also be employed as a means of auditing performance. At the discretion of the EPA, the preliminary systems audit may include analysis of a simple performance evaluation standard and/or analysis of spiked resin traps, feed samples, or other materials supplied by the EPA.

N. PREVENTIVE MAINTENANCE

The QA project plan for a trial burn should itemize the procedures for preventive maintenance that are relevant to the analyses required in the project.

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

1. Calculation of Mean Values and Estimates of Precision

The mean, $\overline{C}$, of a series of replicate measurements of concentration, C_i, for a given surrogate compound or analyte is calculated as:

$$\overline{C} = \frac{1}{n} \sum_{i=1}^{n} C_i$$

where:

n = number of replicate measurements, and

C_i = concentration in the sample (mg/L, mg/kg, or mg/dscm).

The estimate of precision of a series of replicate measurements is expressed as the relative standard deviation (RSD):

$$RSD\ (\%) = \frac{SD}{\overline{C}} \times 100$$

where

SD = standard deviation

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (C_i - \overline{C})^2}{(n-1)}}, \text{ and}$$

$\overline{C}$ = mean of the concentration for the sample set.

Alternatively, for data sets with a small number of points (e.g., concentration of POHC in triplicate samples of one waste stream), the estimate of precision may be expressed as a range percent, R:

$$R\ (\%) = \frac{C_1 - C_2}{\overline{C}} \times 100$$

where:

C_1 = highest concentration value measured in data set, and

C_2 = lowest concentration value measured in data set.

The standard deviations calculated should be compared on a frequent basis with the respective goals identified in Table 25.

2. Assessment of Accuracy

Accuracy is evaluated by comparing the mean recovery of surrogate compounds on a weekly basis. The recovery of a surrogate compound is defined as:

$$\text{Recovery}\ (\%) = \frac{C_s \times V_s\ (\text{or } W_s)}{Q_s} \times 100$$

where:

C_s = measured concentration of surrogate compound in sample (mg/L or mg/kg),

$V_s(W_s)$ = total volume (or weight) of sample to which surrogate was added (L or kg), and

Q_s = quantity of surrogate compound added to sample (mg).

3. Assessment of Causes of Variance

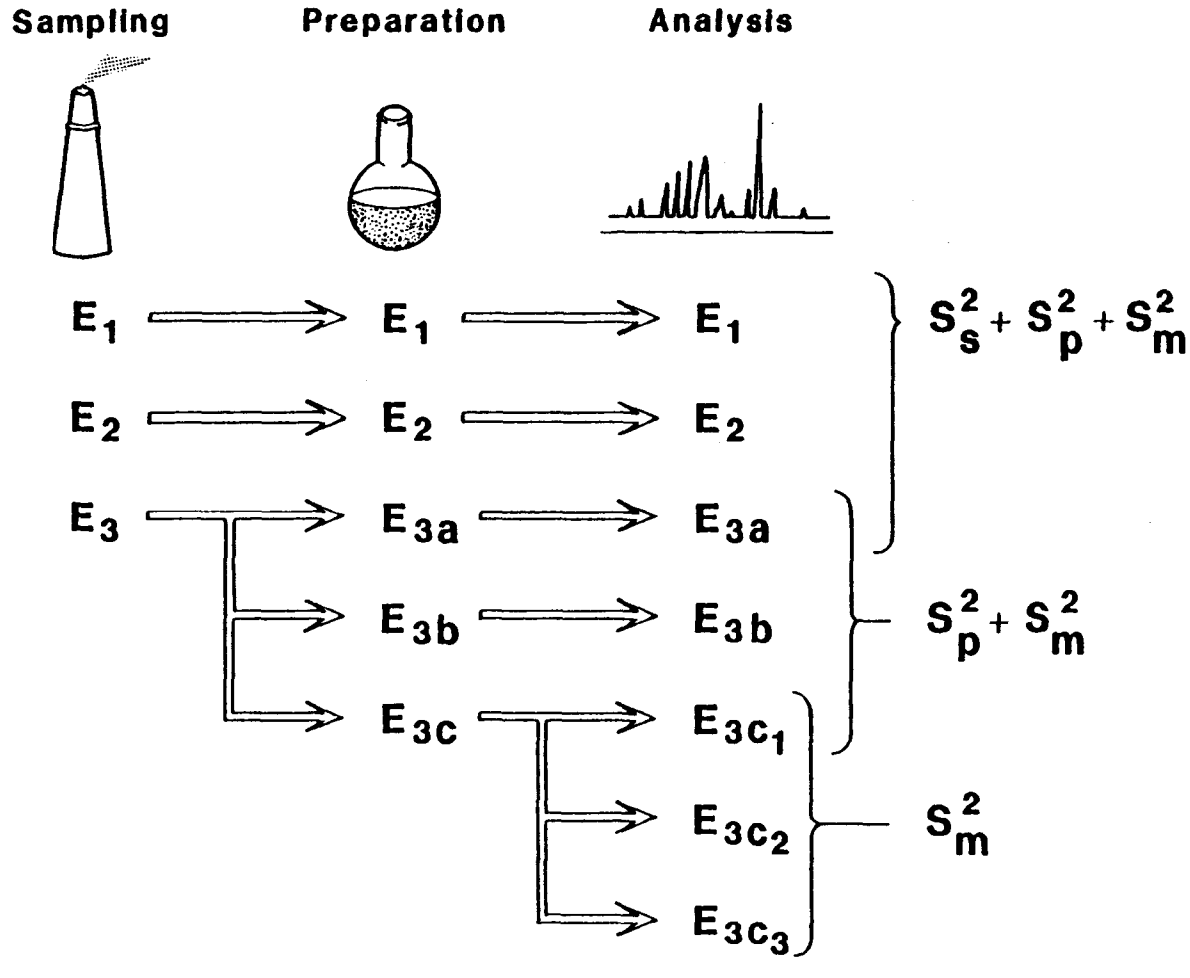
If the calculated destruction and removal efficiencies have very small variance, the three composite four-hour samples are all that would be necessary to provide quality assurance. If variances in the calculated DREs are large, however, it would be useful to identify the cause of the large variance. A sample preparation and analysis protocol similar to the one pictured in Figure 15 is helpful in identifying some of the causes of variances. When the rule of additivity of variance is used, the precision (expressed as total variance for a particular sampling and analysis scheme) is expressed as the sum of the variances for the separate activities of sampling, sample preparation and measurement. This is expressed as follows:

$$S^2_{Total} = S^2_{Sampling} + S^2_{Preparation} + S^2_{Measurement}.$$

It is possible to subdivide the variances into more detailed steps in the sampling scheme, if necessary. To determine sampling variance (S^2_s) the variance obtained from analyzing E_{3a}, E_{3b}, and E_3Cl, is subtracted from that obtained for E_1, E_2, and E_{3a}. Similarly, sample preparation precision (S^2_p) is determined by subtracting the variance obtained from triplicate measurements (S^2_m, variance of E_3Cl, E_{3c^2}, and E_{3c^3}) from the variance of E_{3a}, E_{3b}, and E_{3Cl}. This type of variance analysis would also be applied to the sampling and analysis of waste feed in the same way it is applied to the stack emissions. Ideally, variance analysis is done for each of the POHCs identified for evaluation in a trial burn. These data are extremely useful in identifying the sources of imprecision and subsequently in directing adjustments in sampling and analysis methodology.

P. CORRECTIVE ACTION

For each analytical method employed in a trial burn project, it is appropriate to compute the standard deviation or range of results of replicate analyses. Periodic determinations of recovery of the surrogates and POHCs should also be made. The mean recovery and the standard deviation data for replicate sets are accumulated for each kind of sample



Source: J.E. Picker and B.N. Colby, S-Cubed (26).

FIGURE 15 DIAGRAM OF A SAMPLING AND ANALYSIS PROCEDURE WHICH USES REPLICATE SAMPLES TO PROVIDE INFORMATION ON SOURCES OF VARIANCE

matrix analyzed (e.g., solid, stack gas, aqueous liquid, and ash) and updated from lot to lot as additional analyses are performed and more experience is gained. When either the relative standard deviation of replicate samples or the surrogate recoveries exceed the performance goals established for that trial burn project (Part E of this section), corrective action should be taken to improve performance prior to analysis of the next lot. If weaknesses or problems are uncovered during system or performance audits, corrective action should be initiated immediately.

Corrective action includes, but is not necessarily limited to: recalibration of instruments using freshly prepared calibration standards; replacement of lots of solvent or other reagents that give unacceptable blank values; additional training of laboratory personnel in correct implementation of sample preparation and analysis methods; and reassignment of personnel, if necessary, to improve the overlap between operator skills and method requirements.

Whenever a long-term corrective action (28) is necessary to eliminate the cause of nonconformance, the following closed-loop corrective action system should 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.

Q. QUALITY ASSURANCE REPORTS

On a regular basis, the quality assurance officer meets with the project manager and key staff responsible for sampling, analysis, QC and data management to review QC data summaries, documentation, and other aspects of the project quality assurance performance. The QC officer's assessment of the adequacy of project quality control/quality assurance performance is summarized in a memorandum which would be distributed to upper corporate/ institutional management, as well as to the project manager and his/her

immediate superior in the line management. The memorandum must identify any areas that appear to require remedial action and present the remedies that have been proposed. The results of any earlier remedial action must be described as well. The permit writer would receive documented copies of all QA reports along with the trial burn sampling and analysis results.

VIII. REFERENCES

1. Resource Conservation and Recovery Act, Subtitle C §§3001-3013, 42 U.S.C. §§6921-6934 (1976) and Supplement IV (1980).

2. U.S. Environmental Protection Agency/Office of Solid Waste (U.S. EPA/OSW), Washington, D.C. "Guidance Manual for Hazardous Waste Incinerator Permits," Report prepared by U.S. EPA/OSW, Washington, D.C. and the MITRE Corporation, McLean, Virginia (September 1982). This draft is a revision of a draft report entitled, "Guidance Manual for Evaluating Permit Applications for the Operation of Hazardous Waste Incinerator Units," (April 1981).

3. U.S. Environmental Protection Agency/Industrial Environmental Research Laboratory, Office of Environmental Engineering and Technology, Cincinnati, Ohio, "Engineering Handbook for Hazardous Waste Incineration," SW-889 (September 1981).

4. U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846 (1980), SW-846 Revision A (August 8, 1980), and SW-846 Revision B (July 1981).

5. deVera, E.R., B.P. Simmons, R.D. Stephens and D.L. Strom, "Samplers and Sampling Procedures for Hazardous Waste Streams," EPA-600/2-80-018 (January 1980). NTIS No. PB80-135-353.

6. Title 40, Code of Federal Regulations, Part 60, Appendix A (1980).

7. Lentzen, D.E., D.E. Wagoner, E.D. Estes and W.F. Gutknecht, "EPA/IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," EPA-600/7-78-201 (October 1978). NTIS No. PB293795/AS.

8. American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book of ASTM Standards," Method D-270 (1975).

9. American Society for Testing and Materials, Philadelphia, Pennsylvania, "Annual Book of ASTM Standards," Method E-300 (1973).

10. Stern, A.C. (ed.), Air Pollution: Third Edition, Academic Press, New York, Vol. III (1976).

11. Martin, R.M., "Construction Details for Isokinetic Source Sampling Equipment," EPA-APTD-0581 (1972). NTIS No. PB-209060.

12. Rom, J.J., "Maintenance, Calibration and Operation of Isokinetic Source Sampling Equipment," EPA-APTD-0576 (1972). NTIS No. PB-209022.

13. Adams, J.W., N.J. Cunningham, E.H. Dohnert, J.C. Harris, P.L. Levins, J.L. Stauffer, K.E. Thrun, L.R. Woodland, D.G. Akerman, J.F. Clausen, A. Grant, R.J. Johnson, C.C. Shih, R.F. Tobias and C.A. Zee, "Destroying Chemical Wastes in Commercial Scale Incinerators," (May 1978). NTIS No. PB278-816/3WP.

14. Adams, J.W., K.T. Menzies and P.L. Levins, "Selection and Evaluation of Sorbent Resins for Collection of Organic Compounds," EPA-600/7-77-044 (April 1977). NTIS No. PB268559.

15. Gallant, R.F., J.W. King, P.L. Levins and J.F. Piecewicz, "Characterization of Sorbent Resins for Use in Environmental Sampling," EPA-600/7-78-054 (March 1978). NTIS No. PB284347.

16. Piecewicz, J.F., J.C. Harris and P.L. Levins, "Further Characterization of Sorbents for Environmental Sampling," EPA-600/7-79-216 (September 1979). NTIS No. PB80-118763.

17. Harris, J.C., M.J. Hayes, P.L. Levins and D.B. Lindsay, "EPA/IERL-RTP Procedures for Level 2 Sampling and Analysis of Organic Materials," EPA-600/7-79-033 (February 1979). NTIS No. PB293800.

18. Stauffer, J.L., "Interpretation of Low Resolution Mass Spectra for Level 1 Analysis of Environmental Mixtures," EPA-600/7-82-033 (May 1982).

19. U.S. Environmental Protection Agency, Federal Register, 44, 69464-69575 (December 3, 1979).

20. Dillon, H.K., R.H. James, H.C. Miller and A.K. Wensky (Battelle Columbus Laboratories, Columbus, Ohio), "POHC Sampling and Analysis Methods," Report prepared for U.S. Environmental Protection Agency/ Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina by Southern Research Institute, Birmingham, Alabama under Contract No. 68-02-2685 (December 1981).

21. Small, H., T.S. Stevens and W.C. Baumer, "Novel Ion Exchange Chromatographic Method Using Conductimetric Detection," Anal. Chem., 47, 1801-1809 (1975).

22. Otvos, J.W. and D.P. Stevenson, "Cross-Sections of Molecules for Ionization by Electrons," J. Am. Chem. Soc., 78, 546-551 (1956).

23. Hood, A., "Standardization of Mass Spectra by Means of Total Ion Intensity," Anal. Chem., 30, 1218-1220 (1958).

24. 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).

25. U.S. Environmental Protection Agency/Office of Enforcement, "NEIC Policies and Procedures Manual," Report prepared by U.S. Environmental Protection Agency/National Enforcement Investigations Center, Denver, Colorado, EPA-300/9-78-001-R (October 1979).

26. Picker, J.E. and B.N. Colby, "Quality Assurance Review of 'Sampling and Analysis Methods for Hazardous Waste Incineration,'" (August 1981).

27. U.S. Environmental Protection Agency/Environmental Monitoring and Support Laboratory, Research Triangle Park, North Carolina, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods," EPA-600/4-77-027b (January 1980).

28. vonLehmden, D.J. and C. Nelson, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I, Principles," EPA-600/9-76-005 (January 1976). NTIS No. PB254658.

Note: References with assigned NTIS Numbers are available from the National Technical Information Service, Springfield, Virginia 22161.

APPENDIX A

Hazardous Constituents - Physical/Chemical Data

Appendix A catalogs the Hazardous Constituents listed in 40 C.F.R. Part 261, Appendix VIII (May 20, 1981) with the following chemical and physical data for each compound (when available):

CAS Registry Number

Formula

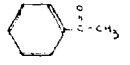
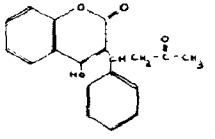
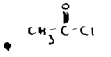
Boiling Point (°C)

Melting Point (°C)

ΔH Combustion (kcal/mol) (kcal/gram)

Molecular Weight

Structure

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Acetonitrile	75-05-8	C_2H_3N	81.6	-45	302 (7.37)	41.06	CH_3-CN
Acetophenone	98-86-2	C_8H_8O	202.6	20.5	992 (8.26)	120.15	
3-(alpha-Acetonyl benzyl)-4-hydroxy coumarin and salts [Warfarin]	81-81-2	$C_{19}H_{16}O_4$		161	2160* (7.004)	308.33	
2-Acetylaminofluorene	53-96-3	$C_{15}H_{13}NO$		194	1770* (7.928)	223.29	
Acetyl chloride	75-36-5	C_2H_3ClO	50.9	-112	217* (2.77*)	78.50	

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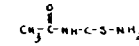
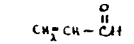
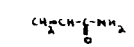
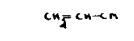
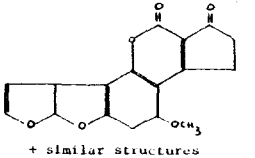
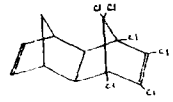
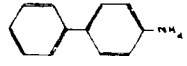
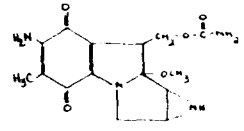
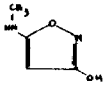
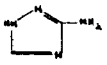
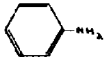
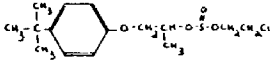
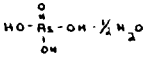
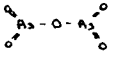
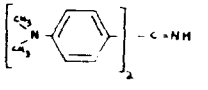
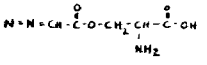
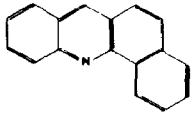
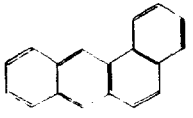
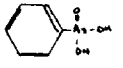
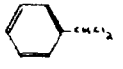
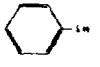
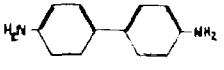
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
1-Acetyl-2-thiourea	591-08-2	$C_3H_6N_2OS$		165	538 (4.55*)	118.17	
Acrolein	107-02-8	C_3H_4O	52.5-53.5	-86.9	390 (6.95)	56.07	
Acrylamide	79-06-1	C_3H_5NO	125(at 25mm)	84.5	409 (5.57*)	71.08	
Acrylonitrile	107-13-1	C_3H_3N	77.5-77.9	-83.55	421 (7.93)	53.07	
Aflatoxins	1402-68-2	$C_{17}H_{12-14}O_{6-7}$		ca. 237-299d	(5.73*)		 + similar structures

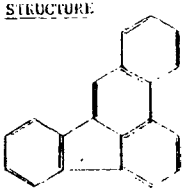
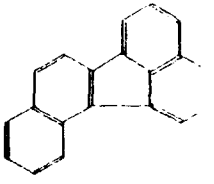
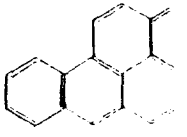
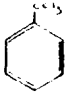
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Aldrin	309-00-2	$C_{12}H_8Cl_6$		104-104.5	1370* (3.75*)	364.90	
Allyl alcohol	107-18-6	C_3H_6O	97.0	-129.0	450 (7.75)	58.09	$CH_2=CH-CH_2OH$
Aluminum phosphide	20859-73-8	AlP				57.96	
4-Aminobiphenyl	92-67-1	$C_{12}H_{11}N$	302.0	53.0	1520 (9.00)	169.24	
6-Amino-1,1a,2,8,8a,8b-hexahydro-8-(hydroxymethyl)-8a-methoxy-5-methyl-carbamate azirino(2',3':3,4)pyrrolo(1,2-a)indole-4,7-dione, (ester) (Mitomycin C)	50-07-7	$C_{15}H_{18}N_4O_5$		>360	1860* (5.41*)	344.37	

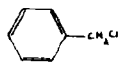
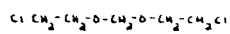
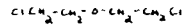
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
5-(Aminomethyl)-3-isoxazolol	2763-96-4	$C_4H_6N_2O_2$		175d	545 (4.78)	114.12	
Amitrole	61-82-5	$C_2H_4N_4$		159	337* (4.01*)	84.10	
Aniline	62-53-3	C_6H_7N	184	-6(solidifies)	813 (8.73)	93.12	
Antimony and compounds, N.O.S. (as Antimony)	7440-36-0	Sb	1750	630.5		121.75	
Aramite	140-57-8	$C_{15}H_{23}ClO_4S$	195(at 2mm)	-37.1		334.86	

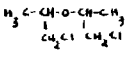
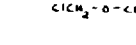
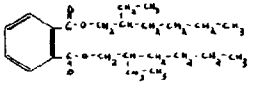
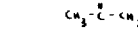
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Arsenic and compounds N.O.S. (as Arsenic)	7440-38-2	As	613 subl.	817(at 3.0×10^{4}mm)		74.92	
Arsenic acid	7778-39-4	$H_3AsO_4 \cdot 1/2\ H_2O$		35.5		150.95	
Arsenic pentoxide	1303-28-2	As_2O_5		315d		229.84	
Arsenic trioxide	1327-53-3	As_2O_3	457.2	193 subl.		197.84	
Auramine	492-80-8	$C_{17}H_{21}N_3$		136	2060* (7.69*)	267.41	

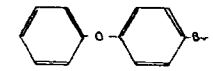
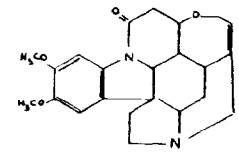
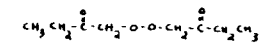
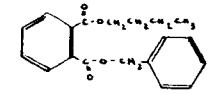
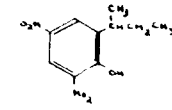
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Azaserine	115-02-6	$C_5H_7N_3O_4$	146-162d		556* (3.21*)	173.13	
Barium and compounds, N.O.S. (as Barium)	*1304-28-5*	*Ba*	*1640*	*725*		137.34	
Barium cyanide	542-62-1	C_2BaN_2		dec in air		189.38	
Benz(c)acridine	225-51-4	$C_{17}H_{11}N$	108		2040* (8.92*)	229.29	
Benz(a)anthracene	56-55-3	$C_{18}H_{12}$	435 subl.	162	2140 (9.39)	228.30	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Benzene	71-43-2	C_6H_6	80.1	5.5	783 (10.03)	78.11	
Benzenearsonic acid	98-05-5	$C_6H_7AsO_3$		158-162d	687* (3.40*)	202.05	
Benzene, dichloromethyl-	98-87-3	$C_7H_6Cl_2$	205.2	-16.4	820* (5.09*)	161.03	
Benzenethiol	108-98-5	C_6H_6S	168.7	-14.8	929 (8.43)	110.18	
Benzidine	92-87-5	$C_{12}H_{12}N_2$	400(at 740mm)	128	1691 (9.18)	184.24	

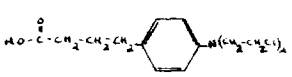
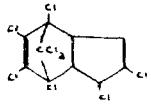
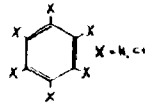
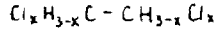
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Benzo(b)fluoranthene	205-99-2	$C_{20}H_{12}$		168	2330 (9.25)	252.32	
Benzo(j)fluoranthene	205-82-3	$C_{20}H_{12}$		166	2330 (9.25)	252.32	
Benzo(a)pyrene	50-32-8	$C_{20}H_{12}$	310-312(at 10mm)	176-177	2330 (9.25)	252.32	
p-Benzoquinone	106-51-4	$C_6H_4O_2$	subl.	115.7	656 (6.07)	108.09	
Benzotrichloride	98-07-7	$C_7H_5Cl_3$	220.8	-5.0	762 (3.90*)	195.47	

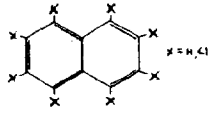
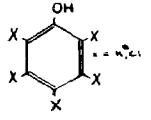
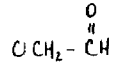
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Benzyl chloride	100-44-7	C_7H_7Cl	179.3	-39.0	782 (6.18)	126.59	
Beryllium and compounds, N.O.S. (as Beryllium)	7440-41-7	Be	2970(at 5mm)	1278±5		9.0122	
Bis(2-chloroethoxy) methane	111-91-1	$C_5H_{10}Cl_2O_2$			796* (4.60*)	173.05	
Bis(2-chloroethyl) ether	111-44-4	$C_4H_8Cl_2O$	178	-24.5	483* (3.38*)	143.02	
N,N-Bis(2-chloro-ethyl)-2-naphthylamine	494-03-1	$C_{14}H_{15}Cl_2N$	210(at 5mm)	54-56	1780* (6.64*)	268.20	

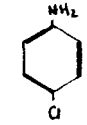
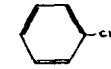
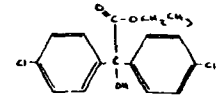
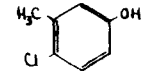
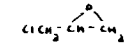
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Bis(2-chloroisopropyl) ether	108-60-1	$C_6H_{12}Cl_2O$	187		843* (4.93*)	171.07	
Bis(chloromethyl) ether	542-88-1	$C_2H_4Cl_2O$	104	-41.5	226* (1.97*)	114.96	
Bis(2-ethylhexyl) phthalate	117-81-7	$C_{24}H_{38}O_4$			3290* (8.42*)	390.54	
Bromoacetone	598-31-2	C_3H_5BrO	136.5(at 725mm)	-36.5	364* (2.66*)	136.98	
Bromomethane	74-83-9	CH_3Br	3.56	-93.6	161* (1.70*)	94.94	

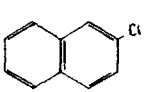
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
4-Bromophenyl phenyl ether	101-55-3	$C_{12}H_9BrO$	310.14	18.72	1450* (5.84*)	249.11	
Brucine	357-57-3	$C_{23}H_{26}N_2O_4$		178	688 (7.42)	394.51	
2-Butanone peroxide	1338-23-4	$C_8H_{16}O_4$			2930* (6.96*)	176.24	
Butyl benzyl phthalate	85-68-7	$C_{19}H_{20}O_4$			2590* (8.29*)	312.39	
2-sec-Butyl-4,6 dinitrophenol (DNBP)	88-85-7	$C_{10}H_{12}N_2O_5$			1310* (5.46*)	240.24	

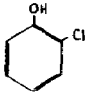
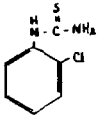
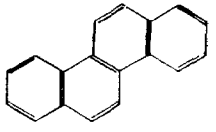
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Cadmium and compounds, N.O.S. (as Cadmium)	7440-43-9	Cd	765	320.9		112.40	
Calcium chromate	8012-75-7	$CaCrO_4 \cdot 2H_2O$				192.09	$CaCrO_4 \cdot 2H_2O$
Calcium cyanide	592-01-8	C_2CaN_2		>350 d		92.12	NC - Ca - CN
Carbon disulfide	75-15-0	CS_2	46.3	-111.5		76.14	S = C = S
Carbon oxyfluoride	353-50-4	CF_2O	-83	-114		66.01	

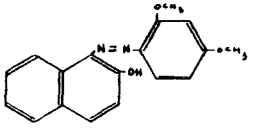
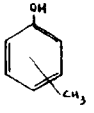
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Chloral (as hydrate)	302-17-0	$C_2HCl_3O \cdot H_2O$	96.3d(at 764mm)	-57	132* (0.80*)	165.40	
Chlorambucil	305-03-3	$C_{14}H_{19}Cl_2NO_2$		64-66	1800* (5.93*)	304.23	
Chlordane (alpha and gamma isomers)	57-74-9	$C_{10}H_6Cl_8$	175	104-106	1110* (2.71*)	409.80	
Chlorinated benzenes, N.O.S.		$C_6H_{6-x}Cl_x$					
Chlorinated ethane, N.O.S.		$C_2H_{6-x}Cl_x$					

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Chlorinated fluorocarbons, N.O.S.							
Chlorinated naphthalene, N.O.S.		$C_{10}H_{8-x}Cl_x$					
Chlorinated phenol, N.O.S.		$C_6H_{6-x}Cl_xO$					
Chloroacetaldehyde	107-20-0	C_2H_3ClO	85-85.5(at 748mm)		229* (2.92*)	78.50	
Chloroalkyl ethers, N.O.S.							

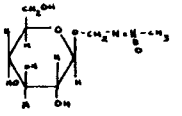
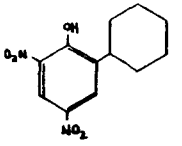
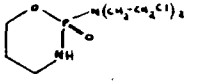
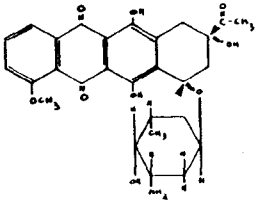
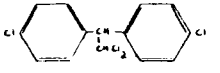
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
p-Chloroaniline	106-47-8	C_6H_6ClN	232	72.5	783* (6.14*)	127.58	
Chlorobenzene	108-90-7	C_6H_5Cl	132	-45.6	743 (6.60)	112.56	
Chlorobenzilate	510-15-6	$C_{16}H_{14}Cl_2O_3$			1790* (5.50*)	325.20	
p-Chloro-m-cresol	59-50-7	C_7H_7ClO	235	66-68	724* (5.08*)	142.59	
1-Chloro-2,3-epoxypropane	106-89-8	C_3H_5ClO	116.5	-48	480* (5.19*)	92.53	

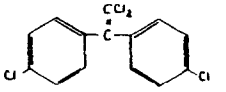
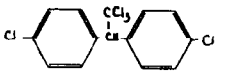
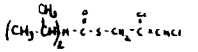
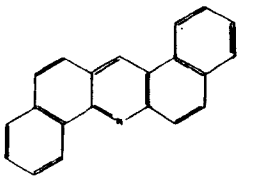
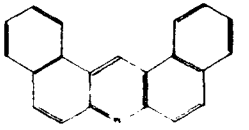
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
2-Chloroethyl vinyl ether	110-75-8	C_4H_7ClO	108		553* (5.19*)	106.55	$H_2C=CH-O-CH_2CH_2Cl$
Chloroform	67-66-3	$CHCl_3$	61.7	-63.5	89.5 (0.75)	119.38	$HCCl_3$
Chloromethane	74-87-3	CH_3Cl	-24.2	-97.73	164 (3.25)	50.49	H_3CCl
Chloromethyl methyl ether	107-30-2	C_2H_5ClO	59.15	-103.5	280* (3.48*)	80.52	$ClCH_2-O-CH_3$
2-Chloronaphthalene	91-58-7	$C_{10}H_7Cl$	256	61	1199 (7.37)	162.62	

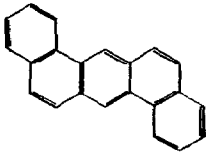
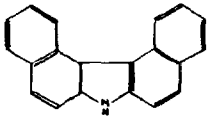
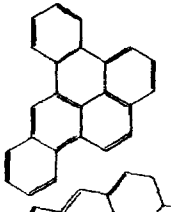
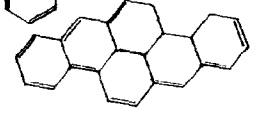
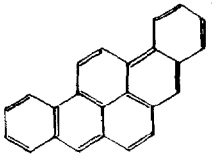
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
2-Chlorophenol	95-57-8	C_6H_5ClO	175	9.3	886 (6.89)	128.56	
1-(o-Chlorophenyl) thiourea		$C_7H_7ClN_2S$		146	989* (5.30*)	186.67	
3-Chloropropio-nitrile	542-76-7	C_3H_4ClN	175-176		403* (4.50*)	89.53	$ClCH_2CH_2CN$
Chromium and compounds, N.O.S. (as Chromium)	7440-47-3	Cr	2672	1857±20		51.996	
Chrysene	218-01-9	$C_{18}H_{12}$	448	255-256	2140 (9.37)	228.30	

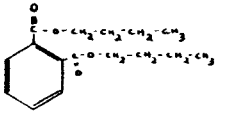
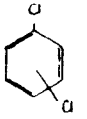
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Citrus Red No. 2	6358-53-8	$C_{18}H_{16}N_2O_3$				308.36	
Coal Tars	8007-45-2						
Copper cyanide	544-92-3	CCuN		473(in N_2)		89.56	Cu - CN
Creosote	8001-58-9		ca. 203	< -20			mixture of phenols
Cresols	1319-77-3	C_7H_8O	191-202.2	11-35	884 (8.18)	108.13	

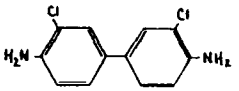
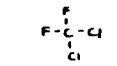
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Croton-aldehyde	123-73-9	C_4H_6O	104.0	-76.5	542 (7.73)	70.09	$CH_3CH=CHCH$ (O)
Cyanides (soluble salts and complexes), N.O.S.							
Cyanogen	460-19-5	C_2N_2	-21.17	-27.9	353 (6.79)	52.04	NC - CN
Cyanogen bromide	506-68-3	CBrN	61-62	52	85.8* (0.81*)	105.93	Br - CN
Cyanogen chloride	506-77-4	CClN	12.66	-6	79.3* (1.29*)	61.47	Cl - CN

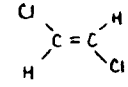
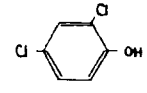
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Cycasin	14901-08-7	$C_8H_{16}N_2O_7$		154d	989* (3.92*)	252.22	
2-Cyclohexyl-4,6-dinitrophenol	131-89-5	$C_{12}H_{14}N_2O_5$		106.5-107.5	1530* (5.74*)	266.25	
Cyclophosphamide	50-18-0	$C_7H_{15}Cl_2N_2O_2P$		41-45	1040* (3.97*)	261.10	
Daunomycin	20830-81-3	$C_{27}H_{29}NO_{10}$			3010* (5.70*)	527.51	
DDD	72-54-8	$C_{14}H_{10}Cl_4$		109-110	1640* (5.14*)	320.05	

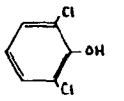
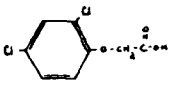
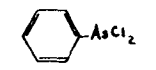
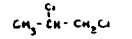
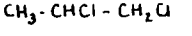
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
DDE	72-55-9	$C_{14}H_8Cl_4$		ca. 88-90	1610* (5.05*)	318.03	
DDT	50-29-3	$C_{14}H_9Cl_5$	260	108.5-109	1600* (4.51*)	354.49	
Diallate	2303-16-4	$C_{10}H_{17}Cl_2NOS$	150		1520* (5.62*)	270.24	
Dibenz(a,h) acridine	226-36-8	$C_{21}H_{13}N$		228	2660* (9.53*)	279.35	
Dibenz(a,j) acridine	224-42-0	$C_{21}H_{13}N$		216	2660* (9.53*)	279.35	

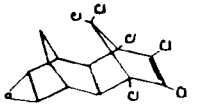
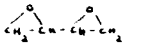
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Dibenz(a,h) anthracene	53-70-3	$C_{22}H_{14}$	subl.	269-270	2620* (9.40*)	278.36	
7H-Dibenzo(c,g) carbazole	194-59-2	$C_{20}H_{13}N$		158	2380* (8.90*)	267.34	
Dibenzo(a,e) pyrene	192-65-4	$C_{24}H_{14}$		233-234	2820* (9.33*)	302.38	
Dibenzo(a,h) pyrene	189-64-0	$C_{24}H_{14}$		281.5-282	2820* (9.33*)	302.38	
Dibenzo(a,i) pyrene	189-55-9	$C_{24}H_{14}$		353-355	2820* (9.33*)	302.38	

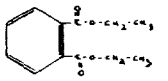
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
1,2-Dibromo-3-chloropropane	96-12-8	$C_3H_5Br_2Cl$	196		350* (1.48*)	236.36	$BrCH_2-CHBr-CH_2Cl$
1,2-Dibromoethane	106-93-4	$C_2H_4Br_2$	131-132	9.0	269* (1.43*)	187.88	$BrCH_2-CH_2Br$
Dibromomethane	74-95-3	CH_2Br_2	97	-52.55	86.9* (0.50*)	173.85	CH_2Br_2
Di-n-butyl phthalate	84-74-2	$C_{16}H_{22}O_4$	340		2040* (7.34*)	278.38	
Dichlorobenzene (meta, ortho and para isomers) Dichlorobenzene, N.O.S.	25321-22-6	$C_6H_4Cl_2$	ca. 174-181	ca. -24 -53	672 (4.57)	147.00	

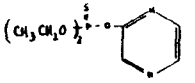
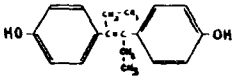
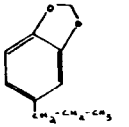
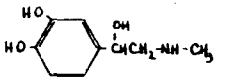
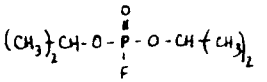
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
3,3'-Dichloro-benzidine	91-94-1	$C_{12}H_{10}Cl_2N_2$		132-133	1450* (5.72*)	253.14	
1,4-Dichloro-2-butene	764-41-0	$C_4H_6Cl_2$	152.5(at 758mm)	-48	534* (4.27*)	125.00	$ClCH_2CH=CHCH_2Cl$
Dichlorodi-fluoromethane	75-71-8	CCl_2F_2	-29.8	-158	26.6* (0.22*)	120.92	
1,1-Dichloroethane	75-34-3	$C_2H_4Cl_2$	57.28	-96.98	297 (3.00)	98.96	CH_3CHCl_2
1,2-Dichloroethane	107-06-2	$C_2H_4Cl_2$	83.5	-35.36	297 (3.00)	98.96	ClH_2C-CH_2Cl

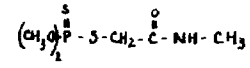
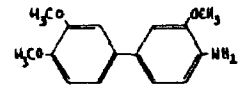
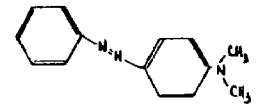
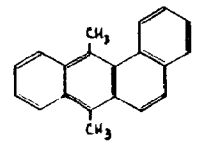
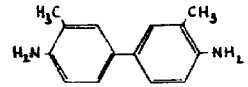
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
trans-1,2-Dichloroethene	156-60-5	$C_2H_2Cl_2$	47.5	-49.4	290 (3.00)	96.94	
Dichloroethylene, N.O.S.	25323-30-2	$C_2H_2Cl_2$	37-61	-50-(-122)	262 (2.70)	96.94	
1,1-Dichloroethylene	75-35-4	$C_2H_2Cl_2$	37	-122.1	262 (2.70)	96.94	$Cl_2C=CH_2$
Dichloromethane	75-09-2	CH_2Cl_2	40	-95.1	144 (1.70)	84.93	CH_2Cl_2
2,4-Dichlorophenol	120-83-2	$C_6H_4Cl_2O$	210	45	621* (3.81*)	163.00	

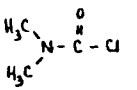
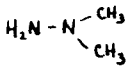
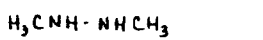
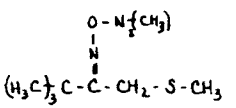
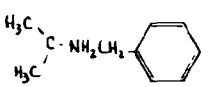
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
2,6-Dichlorophenol	87-65-0	$C_6H_4Cl_2O$	219	68-69	621* (3.81*)	163.00	
2,4-Dichlorophenoxy acetic acid	94-75-7	$C_8H_6Cl_2O_3$	160(at 0.4mm)	138	800* (3.62*)	221.04	
Dichlorophenyl-arsine	696-28-6	$C_6H_5AsCl_2$	254-257		520* (2.31*)	224.93	
Dichloropropane, N.O.S	26638-19-7	$C_3H_6Cl_2$	69-122	ca. -99-(-100)	447 (3.99)	111.97	
1,2-Dichloropropane	78-87-5	$C_3H_6Cl_2$	96.37	-100.44	451 (3.99)	112.99	

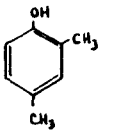
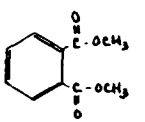
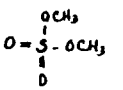
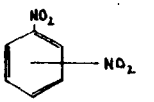
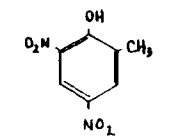
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Dichloropropanol, N.O.S.		$C_3H_6Cl_2O$	ca. 146-176		366 (2.84)	128.99	
Dichloropropene, N.O.S.		$C_3H_4Cl_2$	76-112		382* (3.44*)	110.97	
1,3-Dichloropropene	542-75-6	$C_3H_4Cl_2$	104-112		382* (3.44*)	110.97	$ClCH_2-CH=CHCl$
Dieldrin	60-57-1	$C_{12}H_8Cl_6O$		175-176	2120* (5.56*)	380.90	
1,2:3,4-Diepoxybutane	1464-53-5	$C_4H_6O_2$	144	-16-4	494 (5.74)	86.10	

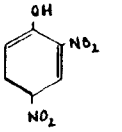
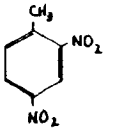
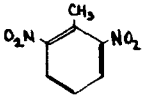
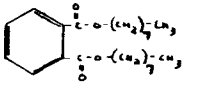
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Diethylarsine	692-42-2	$C_4H_{11}As$	105		704* (5.25*)	134.05	$(CH_3CH_2)_2AsH$
N,N-Diethylhydrazine	1615-80-1	$C_4H_{12}N_2$	85-86		765* (8.68*)	88.18	$CH_3CH_2-NH-NH-CH_2CH_3$
O,O-Diethyl S-methyl ester of phosphorodithioic acid	3288-58-2	$C_5H_{13}O_2PS_2$				200.25	$(CH_3CH_2O)_2P(=S)-S-CH_3$
O,O-Diethylphosphoric acid, O-p-nitrophenyl ester	311-45-5	$C_{10}H_{14}NO_6P$	169-170(at 1mm)			275.22	$(CH_3CH_2O)_2P(=O)-O-C_6H_4-NO_2$
Diethyl phthalate	84-66-2	$C_{12}H_{14}O_4$	298		1420 (6.39)	222.26	

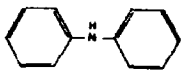
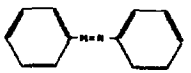
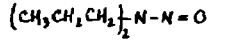
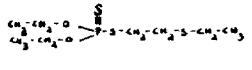
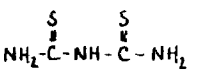
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
O,O-Diethyl O-2-pyrazinyl phosphorothioate	297-97-2	$C_8H_{13}N_2O_3PS$	80	-1.7		248.26	
Diethylstilbestrol	56-53-1	$C_{18}H_{20}O_2$		169-172		268.38	
Dihydrosafrole	94-58-6	$C_{10}H_{12}O_2$			1260* (7.66*)	164.22	
3,4-Dihydroxy-alpha-(methyl-amino)methyl benzyl alcohol	51-43-4	$C_9H_{13}NO_3$		211-212d	1110* (6.05*)	183.23	
Diisopropyl fluorophosphate (DFP)	55-91-4	$C_6H_{14}FO_3P$	183	-82		184.17	

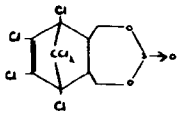
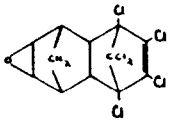
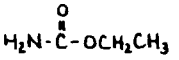
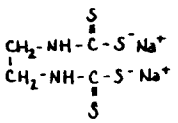
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Dimethoate	60-51-5	$C_5H_{12}NO_3PS_2$		52-52.5	922 (4.02)	229.27	
3,3'-Dimethoxybenzidine	119-90-4	$C_{14}H_{16}N_2O_2$		137-138	1800* (7.36*)	244.32	
p-Dimethylaminoazo-benzene	60-11-7	$C_{14}H_{15}N_3$		114-117	1570* (6.97*)	225.32	
7,12-Dimethylbenz(a) anthracene	57-97-6	$C_{20}H_{16}$		122-123	2460 (9.61)	256.36	
3,3'-Dimethyl-benzidine	119-93-7	$C_{14}H_{16}N_2$		129-131	1870* (8.81*)	212.32	

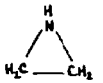
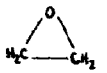
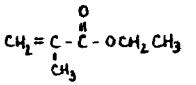
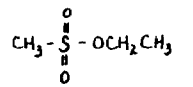
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Dimethylcarbamoyl chloride	79-44-7	C_3H_6ClNO			546* (5.08*)	107.55	
1,1-Dimethyl-hydrazine	57-14-7	$C_2H_8N_2$	63(at 752mm)	-58	473 (7.87)	60.12	
1,2-Dimethyl-hydrazine	540-73-8	$C_2H_8N_2$	81(at 753mm)		473 (7.87)	60.12	
3,3-Dimethyl-1-(methylthio)-2-butanone, O-((methylamino) carbonyl) oxime [Thiofanox]	39196-18-4	$C_9H_{18}N_2O_2S$			1270* (5.82*)	218.35	
alpha, alpha-Dimethylphenethyl-amine	122-09-8	$C_{10}H_{15}N$			1420* (9.54*)	149.26	

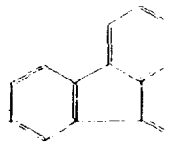
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
2,4-Dimethylphenol	105-67-9	$C_8H_{10}O$	211.5	27-28	1040 (8.51)	122.17	
Dimethyl phthalate	131-11-3	$C_{10}H_{10}O_4$	283.8	0-2	1110 (5.74)	194.19	
Dimethyl sulfate	77-78-1	$C_2H_6O_4S$	ca. 188d	-27	361 (2.86)	126.13	
Dinitrobenzene, N.O.S.	25154-54-5	$C_6H_4N_2O_4$	291-319	89-174	698 (4.15)	168.11	
4,6-Dinitro-o-cresol (and salts)	534-52-1	$C_7H_6N_2O_5$		86.5	804* (4.06*)	198.14	

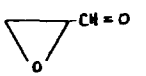
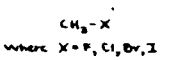
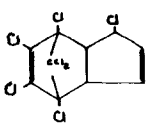
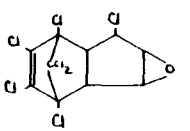
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
2,4-Dinitrophenol	51-28-5	$C_6H_4N_2O_5$	subl.	115-116	648 (3.52)	184.11	
2,4-Dinitrotoluene	121-14-2	$C_7H_6N_2O_4$	300d	70-71	852 (4.68)	182.14	
2,6-Dinitrotoluene	606-20-2	$C_7H_6N_2O_4$		66	852 (4.68)	182.14	
Di-n-octyl phthalate	117-81-7	$C_{24}H_{38}O_4$			2600* (6.67*)	390.54	
1,4-Dioxane	123-91-1	$C_4H_8O_2$	101(at 750mm)	11.8	565 (6.41)	88.10	

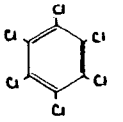
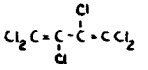
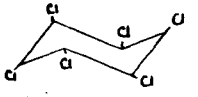
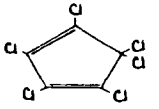
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Diphenylamine	122-39-4	$C_{12}H_{11}N$	302	53-55	1470 (9.09)	162.24	
1,2-Diphenyl hydrazine	122-66-7	$C_{12}H_{12}N_2$		131	1610* (8.73*)	184.26	
Di-n-propyl-nitrosamine	621-64-7	$C_6H_{14}N_2O$	205.9		1020* (7.83*)	130.22	
Disulfoton	298-04-4	$C_8H_{19}O_2PS_3$	132-133(at 1.5mm)		1570* (5.73*)	274.38	
2,4-Dithiobiuret	541-53-7	$C_2H_5N_3S_2$		181d	287* (2.12*)	135.22	

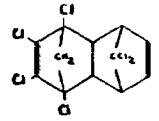
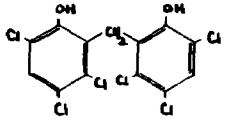
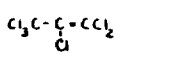
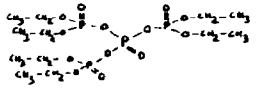
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Endosulfan	115-29-7	$C_9H_6Cl_6O_3S$		106	948* (2.33*)	406.91	
Endrin (and metabolites)	72-20-8	$C_{12}H_8Cl_6O$		245d	1320* (3.46*)	380.90	
Ethyl carbamate	51-79-6	$C_3H_7NO_2$	182-184	48-50	421* (4.73*)	89.11	
Ethyl cyanide	107-12-0	C_3H_5N	79(at 775mm)	< -66	252 (4.57)	55.09	CH_3CH_2CN
Ethylenebis-dithiocarbamic acid (salts and esters)	142-59-6	$C_4H_6N_2Na_2S_4$			1460* (5.70*)	256.34	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Ethyleneimine	151-56-4	C_2H_5N	56-57		339* (7.86*)	43.08	
Ethylene oxide	75-21-8	C_2H_4O	10.7	-111	302 (6.86)	44.06	
Ethylene-thiourea	96-45-7	$C_3H_6N_2S$		203-204	611* (5.98*)	102.17	
Ethyl methacrylate	97-63-2	$C_6H_{10}O_2$	117		830* (7.27*)	114.16	
Ethyl methanesulfonate	62-50-0	$C_3H_8O_3S$	ca. 85-86 (at 10mm)			124.17	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Fluoranthene	206-44-0	$C_{16}H_{10}$	ca. 375	111	1890 (9.35)	202.26	
Fluorine	7782-41-4	F_2	-188.13	-219.61		38.00	F_2
2-Fluoroacetamide	640-19-7	C_2H_4FNO	subl.		250 (3.24)	77.07	$CH_2F-\overset{O}{\overset{\|}{C}}-NH_2$
Fluoroacetic acid, sodium salt	62-74-8	$C_2H_2FNaO_2$				100.03	$Na^+(CH_2F-\overset{O}{\overset{\|}{C}}-O)^-$
Formaldehyde	50-00-0	CH_2O	-19.5	-92	134 (4.47)	30.03	$H_2C=O$

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Formic acid	64-18-6	CH_2O_2	100.5	8.4	60.8 (1.32)	46.03	
Glycidylaldehyde	765-34-4	$C_3H_4O_2$	ca. 112-113	ca. -62	414 (5.74)	72.07	
Halomethane, N.O.S.		CH_3X					
Heptachlor	76-44-8	$C_{10}H_5Cl_7$		95-96	1100* (2.96*)	373.30	
Heptachlor epoxide (alpha, beta and gamma isomers)	1024-57-3	$C_{10}H_5Cl_7O$			1060* (2.71*)	389.30	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Hexachloro-benzene	118-74-1	C_6Cl_6	323-326	231	510 (1.79)	284.76	
Hexachloro-butadiene	87-68-3	C_4Cl_6	215	-21	553* (2.12*)	260.74	
Hexachloro-cyclohexane (all isomers)	608-73-1	$C_6H_6Cl_6$		112-315	326* (1.12*)	290.83	 + isomers
Hexachloro-cyclopentadiene	77-47-4	C_5Cl_6	239(at 753mm)	-9	573* (2.10*)	272.75	
Hexachloroethane	67-72-1	C_2Cl_6	186.8	subl.	109 (0.46)	236.72	CCl_3-CCl_3

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-endo, endo-dimethanonaphthalene	465-73-6	$C_{12}H_8Cl_6$		240-242	1230* (3.38*)	364.90	
Hexachlorophene	70-30-4	$C_{13}H_6Cl_6O_2$		164-165	1550* (3.82*)	406.89	
Hexachloropropene	1888-71-7	C_3Cl_6		ca. 209-210	174* (0.70*)	248.73	
Hexaethyl tetraphosphate	757-58-4	$C_{12}H_{30}O_{13}P_4$	>150d	ca. -40		506.30	
Hydrazine	302-01-2	H_4N_2	113.5	2.0	142* (4.44*)	32.06	

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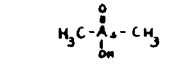
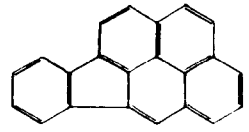
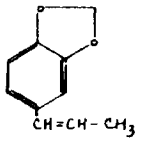
Hydrocyanic acid	74-90-8	CHN	25.7	-13.4		27.03	HC≡N
Hydrofluoric acid	7664-39-3	HF				20.01	HF
Hydrogen sulfide	7783-06-4	H_2S	-60.33	-85.49		34.08	H_2S
Hydroxydimethylarsine oxide	75-60-5	$C_2H_7AsO_2$		195-196		138.01	
Indeno (1,2,3-c,d) pyrene	193-39-5	$C_{22}H_{12}$			2350* (8.52*)	276.34	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Iodomethane	74-88-4	CH_3I	42.4	-66.5	190 (1.34)	141.94	CH_3I
Iron dextran (complex)	9004-66-4					~180,000	
Isocyanic acid, methyl ester	624-83-9	C_2H_3NO	59.6	-45	268* (4.69*)	57.06	$O=C=N-CH_3$
Isobutyl alcohol	78-83-1	$C_4H_{10}O$	108	-108	639 (8.62)	74.14	CH_3CHCH_2OH (CH3 branch)
Isosafrole	120-58-1	$C_{10}H_{10}O_2$	253	8.2	1230 (7.62)	162.20	

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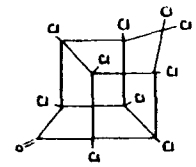
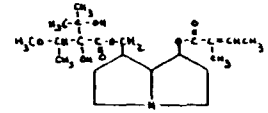
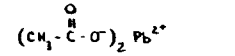
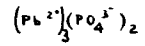
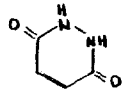
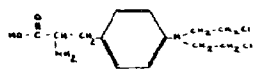
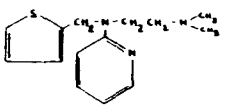
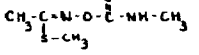
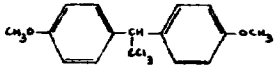
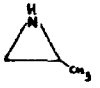
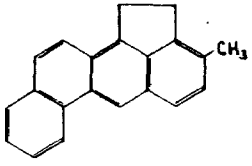
Kepone	143-50-0	$C_{10}Cl_{10}O$			1050* (2.15*)	490.60	
Lasiocarpine	303-34-4	$C_{21}H_{33}NO_7$				411.55	
Lead and compounds, N.O.S. (as Lead)	7439-92-1	Pb	1740	327.4		207.19	
Lead acetate	301-04-2	$C_4H_6O_4Pb$	200d	75		325.29	
Lead phosphate	7446-27-7	$O_8P_2Pb_3$		1014		811.59	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Lead subacetate	1335-32-6	$C_4H_{10}O_8Pb_3$				807.71	$Pb^{2+}(CH_3\overset{O}{\overset{\|}{C}}\text{-}O^-)_2 \cdot 2\,[Pb^{2+}(OH^-)_2]$
Maleic anhydride	108-31-6	$C_4H_2O_3$	202.0	52.8	333 (3.40)	98.06	
Maleic hydrazide	123-33-1	$C_4H_4N_2O_2$	260d	>300	460* (4.10*)	112.10	
Malononitrile	109-77-3	$C_3H_2N_2$	218-219	32	395 (5.98)	66.07	
Melphalan	148-82-3	$C_{13}H_{18}Cl_2N_2O_2$		182-183d	1590* (5.21*)	305.23	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Mercury fulminate	628-86-4	$C_8H_{10}HgO_3S$		explodes		284.63	$Hg(CNO)_2$
Mercury and compounds N.O.S. (as Mercury)	7439-97-6	Hg	356.72	-38.87		200.59	
Methacrylonitrile	126-98-7	C_4H_5N	90.3	-35.8	574* (8.55*)	67.10	$CH_2=C(CH_3)-CN$
Methanethiol	74-93-1	CH_4S	5.95	-123	284* (5.91*)	48.11	CH_3SH
Methapyrilene	91-80-5	$C_{14}H_{19}N_3S$	173-175(at 3mm)		2070* (7.93*)	261.42	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Metholmyl	16752-77-5	$C_5H_{10}N_2O_2S$		78-79	844* (5.20*)	162.23	
Methoxychlor	72-43-5	$C_{16}H_{15}Cl_3O_2$		78-78.2 86-88	1930* (5.59*)	345.66	
2-Methylaziridine	75-55-8	C_3H_7N			519* (9.09*)	57.11	
3-Methylcholanthrene	56-49-5	$C_{21}H_{16}$	280 (at 80mm)	179-180	2570* (9.57*)	268.37	
Methylchlorocarbonate	79-22-1	$C_2H_3ClO_2$	71			94.50	

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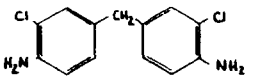
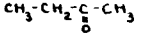
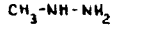
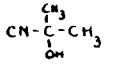
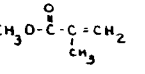
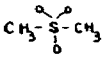
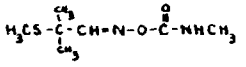
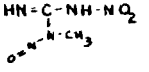
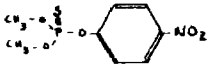
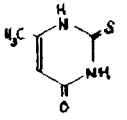
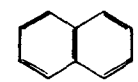
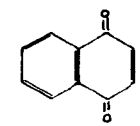
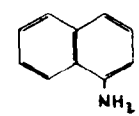
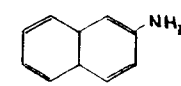
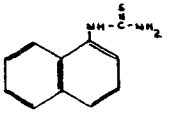
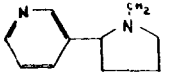
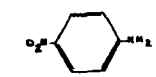
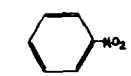
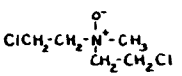
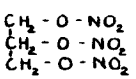
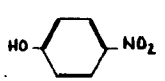
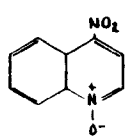
4,4'-Methylene-bis(2-chloro-aniline)	101-14-4	$C_{13}H_{12}Cl_2N_2$			1290* (4.84*)	267.17	
Methyl ethyl ketone (MEK)	78-93-3	C_4H_8O	79.6	-86	582 (8.07)	72.12	
Methyl hydrazine	60-34-4	CH_6N_2	87.5	-52.4	312* (6.78*)	46.09	
2-Methyllacto-nitrile	75-86-5	C_4H_7NO	95	-19	547 (6.43)	85.12	
Methyl methacrylate	80-62-6	$C_5H_8O_2$	100-101	-48	653* (6.52*)	100.13	

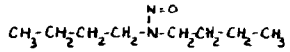
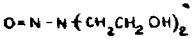
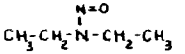
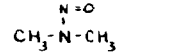
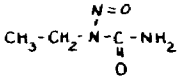
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Methyl methanesulfonate	66-27-3	$C_2H_6O_3S$	203 (at 753mm)		412 (3.74)	110.14	
2-Methyl-2-(methylthio) propionaldehyde -O-(methylcarbonyl) oxime	116-06-3	$C_7H_{14}N_2O_2S$		99-100	1020* (5.34*)	190.29	
N-Methyl-N'-nitro-N-nitrosoguanidine	70-25-7	$C_2H_5N_5O_3$			597* (4.06*)	147.12	
Methyl parathion	298-00-0	$C_8H_{10}NO_5PS$		37-38	1050* (4.00*)	263.22	
Methyl chiouracil	56-04-2	$C_5H_6N_2OS$		326-331d	681* (4.79*)	142.19	

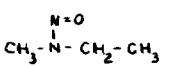
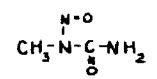
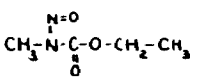
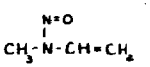
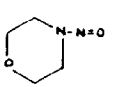
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Mustard gas	505-60-2	$C_4H_8Cl_2S$	215-217	13-14	646* (4.06*)	159.08	$CH_2Cl-CH_2-S-CH_2-CH_2Cl$
Naphthalene	91-20-3	$C_{10}H_8$	217.9	80.2	1230 (9.62)	128.18	
1,4-Naphthoquinone	130-15-4	$C_{10}H_6O_2$	subl.	126	1100 (6.97)	158.16	
1-Naphthylamine	134-32-7	$C_{10}H_9N$	301	50	1220 (8.54)	143.20	
2-Naphthylamine	91-59-8	$C_{10}H_9N$	306	111-113	1220 (8.54)	143.20	

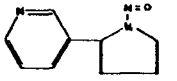
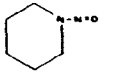
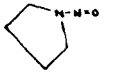
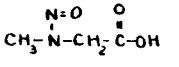
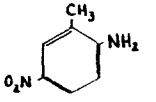
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
1-Naphthyl -2-thiourea	86-88-4	$C_{11}H_{10}N_2S$		198	1520* (7.50*)	202.29	
Nickel and compounds, N.O.S. (as Nickel)	7440-02-0	Ni	2837	1555		58.71	
Nickel carbonyl	13463-39-3	C_4NiO_4	43	-19.3		170.75	$Ni^{4+}(CO^-)_4$
Nickel cyanide	557-19-7	C_2N_2Ni				110.7	$Ni^{2+}(CN^-)_2$
Nicotine (and salts)	54-11-5	$C_{10}H_{14}N_2$	247 (at 745mm)		1450* (8.92*)	162.26	

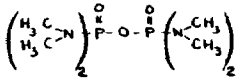
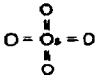
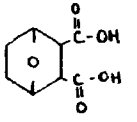
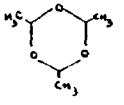
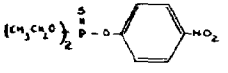
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Nitric oxide	10102-43-9	NO	-151.7	-163.6		30.01	N = O
p-Nitroaniline	100-01-6	$C_6H_6N_2O_2$	332	146	760 (5.50)	138.14	
Nitrobenzene	98-95-3	$C_6H_5NO_2$	210-211	6	677 (5.50)	123.12	
Nitrogen dioxide	10102-44-0	NO_2	21.15	-9.3		46.01	O=N=O
Nitrogen Mustard (and hydrochloride salt)	51-75-2	$C_5H_{11}Cl_2N$	87	-60	668* (4.28*)	156.07	$CH_3-N<^{CH_2-CH_2Cl}_{CH_2-CH_2Cl}$

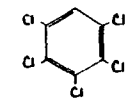
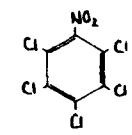
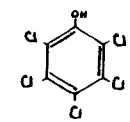
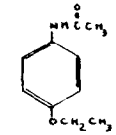
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Nitrogen mustard N-Oxide (and hydrochloride salt)	126-85-2 302-70-5-Cl(·HCl)	$C_5H_{11}Cl_2NO$(·HCl)			613 (3.56)	172.07 208.53 (·HCl)	
Nitroglycerine	55-63-0	$C_3H_5N_3O_9$	50-60d	2.8	861 (3.79)	227.11	
4-Nitrophenol	100-02-7	$C_6H_5NO_3$	279d	113-114	689 (4.95)	139.12	
4-Nitroquinoline -1-oxide	56-57-5	$C_9H_6N_2O_3$		154	1060 (5.59)	190.17	
Nitrosamine, N.O.S.							

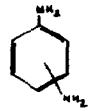
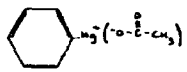
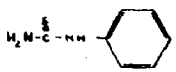
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
N-Nitrosodi-n-butylamine	924-16-3	$C_8H_{18}N_2O$			1340* (8.46*)	158.28	
N-Nitrosodi-ethanolamine	1116-54-7	$C_4H_{10}N_2O_3$			942* (7.02*)	134.16	
N-Nitrosodi-ethylamine	55-18-5	$C_4H_{10}N_2O$	175-177		701* (6.86*)	102.16	
N-Nitrosodi-methylamine	62-75-9	$C_2H_6N_2O$	151-153		381* (5.14*)	74.10	
N-Nitroso-N-ethylurea	759-73-9	$C_3H_7N_3O_2$			459* (3.92*)	117.13	

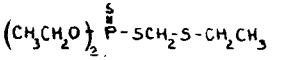
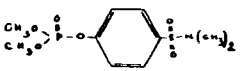
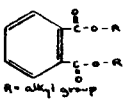
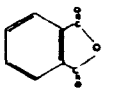
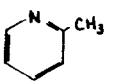
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
N-Nitrosomethyl-ethylamine	10595-95-6	$C_3H_8N_2O$			540* (6.13*)	88.13	
N-Nitroso-N-methylurea	684-93-5	$C_2H_5N_3O_2$		123-124d	298* (2.89*)	103.10	
N-Nitroso-N-methylurethane	615-53-2	$C_4H_8N_2O_3$	65(at 13mm)	< -20	552* (4.18*)	132.14	
N-Nitroso-methylvinylamine	4549-40-0	$C_3H_6N_2O$			681* (7.91*)	86.11	
N-Nitroso-morpholine	59-89-2	$C_4H_8N_2O_2$			606* (5.22*)	116.14	

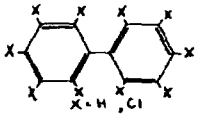
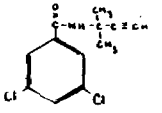
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
N-Nitroso-nornicotine	16543-55-8	$C_9H_{11}N_3O$			1250* (7.07*)	177.23	
N-Nitroso-piperidine	100-75-4	$C_5H_{10}N_2O$	217(at 721mm)		804* (7.04*)	114.15	
N-Nitroso-pyrrolidine	930-55-2	$C_4H_8N_2O$	ca. 214		644* (6.43*)	100.14	
N-Nitroso-sarcosine	13256-22-9	$C_3H_6N_2O_3$			377* (3.19*)	118.11	
5-Nitro-o-toluidine	99-55-8	$C_7H_8N_2O_2$		107-108	910 (5.98)	152.17	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Octamethylpyrophosphoramide	152-16-9	$C_8H_{24}N_4O_3P_2$	154 (at 2.0mm)			286.30	
Osmium tetroxide	20816-12-0	O_4Os	130	40.6		254.20	
7-Oxabicyclo[2.2.1] heptane-2,3-dicarboxylic acid	145-73-3	$C_8H_{10}O_5$				186.18	
Paraldehyde	123-63-7	$C_6H_{12}O_3$	ca. 124	12	833[a] (6.30[a])	132.18	
Parathion	56-38-2	$C_{10}H_{14}NO_5PS$	375	6	1050* (3.61*)	291.28	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Pentachlorobenzene	608-93-5	C_6HCl_5	277	86	513* (2.05*)	250.32	
Pentachloroethane	76-01-7	C_2HCl_5	161-162	-29	107* (0.53*)	202.28	$Cl_2CH\,CCl_3$
Pentachloronitrobenzene (PCNB)	82-68-8	$C_6Cl_5NO_2$	328d	144	478* (1.62*)	295.32	
Pentachlorophenol	87-86-5	C_6HCl_5O	309-310d	190-191	557 (2.09)	266.32	
Phenacetin	62-44-2	$C_{10}H_{13}NO_2$		134-135	1290 (7.17)	179.24	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Phenol	108-95-2	C_6H_6O	181.75	43	732 (7.78)	94.12	
Phenylenediamine	m 108-45-2 o 95-54-5 p 106-50-3	$C_6H_8N_2$	m 284-287 o 256-258 p 267	m 62-63 o 103-104 p 145-147	845 (7.81)	108.16	
Phenylmercury acetate	62-38-4	$C_8H_8HgO_2$		149	913* (2.71*)	336.75	
N-Phenylthiourea	103-85-5	$C_7H_8N_2S$		154	1050* (6.93*)	152.23	
Phosgene	75-44-5	$COCl_2$	8.2	-118		98.91	$Cl_2C=O$

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Phosphine	7803-51-2	H_3P	-87.7	-133		34.00	PH_3
Phosphorodithioic acid, O,O-diethyl S-((ethylthio)methyl) ester[Phorate]	298-02-2	$C_7H_{17}O_2PS_3$	125-127(at 2.0mm)			260.39	
Phosphorothioic acid, O,O-dimethyl O-(p-((dimethylamino)sulfonyl) phenyl)ester[Famphur]	52-85-7	$C_{10}H_{16}NO_5PS_2$		52.5-53.5		325.36	
Phthalic acid esters, N.O.S.							
Phthalic anhydride	85-44-9	$C_8H_4O_3$	295	130.8	784 (5.29)	148.12	
2-Picoline	109-06-8	C_6H_7N	128-129	-70	812 (8.72)	93.14	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Polychlorinated biphenyl, N.O.S.	1336-36-3	$C_{12}H_{10-x}Cl_x$					
Potassium cyanide	151-50-8	CKN		634		65.12	$K^+(CN^-)$
Potassium silver cyanide	506-61-6	C_2AgKN_2				199.01	$K^+Ag^+(CN^-)_2$
Pronamide	23950-58-5	$C_{12}H_{11}Cl_2NO$			1470* (5.72#)	256.14	
1,3-Propane sultone	1120-71-4	$C_3H_6O_3S$	ca. 180 (at 30mm)	ca. 30-33	448* (3.67#)	122.15	

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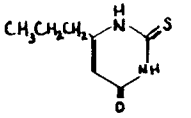
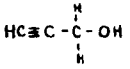
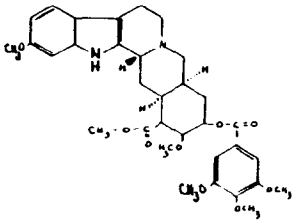
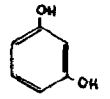
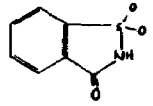
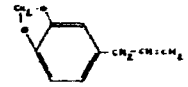
n-Propylamine	107-10-8	C_3H_9N	48-49	-83	566 (9.58)	59.13	$CH_3CH_2CH_2NH_2$
Propylthiouracil	51-52-5	$C_7H_{10}N_2OS$		219-221	1070* (6.28*)	170.25	
2-Propyn-1-ol	107-19-7	C_3H_4O	114-115	-48-(-52)	417* (7.43*)	56.07	
Pyridine	110-86-1	C_5H_5N	115-116	-42	619 (7.83)	79.11	
Reserpine	50-55-5	$C_{33}H_{40}N_2O_9$	264-265d		4080* (6.70*)	608.75	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Resorcinol	108-46-3	$C_6H_6O_2$	280	109-111	682 (6.19)	110.12	
Saccharin (and salts)	81-07-2	$C_7H_5NO_3S$		288.6-289.7	823* (4.49*)	183.19	
Safrole	94-59-7	$C_{10}H_{10}O_2$	232-234	11	1250 (7.68)	162.20	
Selenious acid	7783-00-8	H_2O_3Se				128.98	
Selenium and compounds, N.O.S. (as Selenium)	7782-49-2	Se	685			78.96	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Selenium sulfide	7446-34-6	SSe		113-121.5		111.02	S=Se
Selenourea	630-10-4	CH_4N_2Se		200d		123.03	$H_2N-\overset{\overset{Se}{\|}}{C}-NH_2$
Silver and compounds, N.O.S. (as Silver)	7440-22-4	Ag	ca. 2000	960.5		107.87	
Silver cyanide	506-64-9	CAgN	320d			133.89	$Ag^+(CN^-)$
Sodium cyanide	143-33-9	CNNa		563		49.01	$Na^+(CN^-)$

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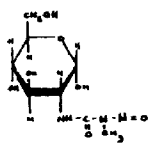
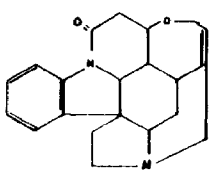
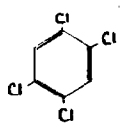
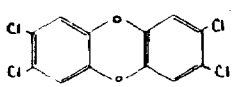
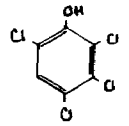
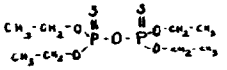
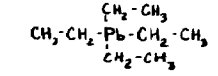
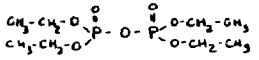
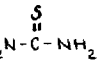
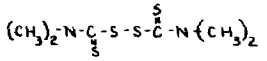
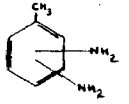
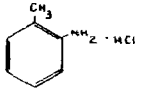
Streptozotocin	18883-66-4	$C_8H_{15}N_3O_7$		115d		265.26	
Strontium sulfide	1314-96-1	SSr				119.68	S = Sr
Strychnine (and salts)	57-24-9	$C_{21}H_{22}N_2O_2$	270(at 5mm)	268-290	2690 (8.03)	334.45	
1,2,4,5-Tetrachloro-benzene	95-94-3	$C_6H_2Cl_4$	243-246	139.5-140.5	563* (2.61*)	215.88	
2,3,7,8-Tetrachlorodi-benzo-p-dioxin (TCDD)	1746-01-6	$C_{12}H_4Cl_4O_2$	> 700d	305	1100* (3.43*)	321.96	

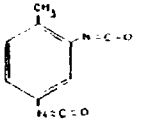
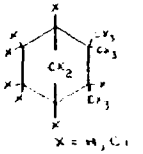
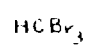
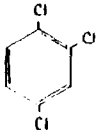
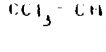
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Tetrachloroethane, N.O.S.	25322-20-7	$C_2H_2Cl_4$			233 (1.39)	167.84	
1,1,1,2-Tetrachloroethane	630-20-6	$C_2H_2Cl_4$	130.5	-70.2	233 (1.39)	167.84	Cl_3C-CH_2Cl
1,1,2,2-Tetrachloroethane	79-34-5	$C_2H_2Cl_4$	146.5	-44	233 (1.39)	167.84	$Cl_2HC-CHCl_2$
Tetrachloroethene	127-18-4	C_2Cl_4	121	-22	197 (1.19)	165.82	$Cl_2C=CCl_2$
Tetrachloromethane	56-23-5	CCl_4	76.7	-23	36.9 (0.24)	153.81	

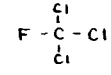
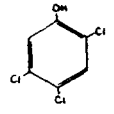
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
2,3,4,6-Tetrachlorophenol	58-90-2	$C_6H_2Cl_4O$	150 (at 15mm)	70	517* (2.23*)	231.88	
Tetraethyldithiopyrophosphate	3689-24-5	$C_8H_{20}O_5P_2S_2$	136-139 (at 2mm)			322.34	
Tetraethyl lead	78-00-2	$C_8H_{20}Pb$	200d	-136.80	1310* (4.04*)	323.47	
Tetraethylpyrophosphate	107-49-3	$C_8H_{20}O_7P_2$	155(at 5mm)	170-213d		290.22	
Tetranitromethane	509-14-8	CN_4O_8	126	13.8	80.4* (0.41*)	196.05	

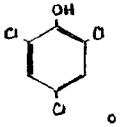
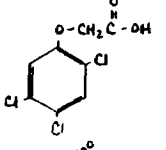
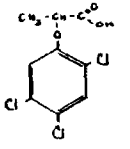
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Thallium and compounds N.O.S. (as Thallium)	7440-28-0	Tl	1457	303.5		204.37	
Thallic oxide	1314-32-5	O_3Tl_2		717		456.74	O = Tl - O - Tl = O
Thallium(I)acetate	563-68-8	$C_2H_3O_2Tl$				263.42	$\left[CH_3-C\begin{matrix}O\\ \\ O\end{matrix}\right]^-(Tl^+)$
Thallium(I)carbonate	6533-73-9	CO_3Tl_2		272		468.75	$(CO_3^{2-})(Tl^+)_2$
Thallium(I)chloride	7791-12-0	ClTl		430		239.82	$Cl^- \; Tl^+$

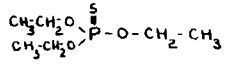
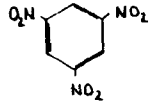
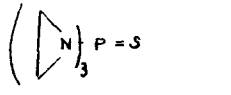
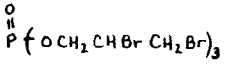
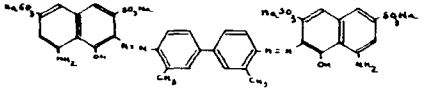
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Thallium(I)nitrate	10102-45-1	NO_3Tl	450d	206		266.38	$(NO_3^-)(Tl^+)$
Thallium selenite	12039-52-0	$SeTl$				283.33	$(Se^{2-})(Tl^{2+})$
Thallium(I)sulfate	7446-18-6	O_4STl_2		632		504.80	$(SO_4^{2-})(Tl^+)_2$
Thioacetamide	62-55-5	C_2H_5NS		113-114	447* (5.95*)	75.14	$CH_3-\overset{S}{\overset{\|}{C}}-NH_2$
Thiosemicarbazide	79-19-6	CH_5N_3S		182-184	415 (4.55)	91.15	$H_2N-\overset{S}{\overset{\|}{C}}-NH-NH_2$

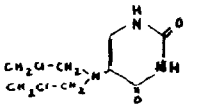
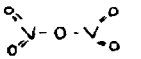
NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Thiourea	62-56-6	CH_2N_2S		176-178	346 (4.55)	76.13	
Thiuram	137-26-8	$C_6H_{12}N_2S_4$		155-156	1410* (5.85*)	240.44	
Toluene	108-88-3	C_7H_8	110.6	-95	934 (10.14)	92.15	
Toluenediamine	25376-45-8	$C_7H_{10}N_2$	255-292	< 0-106	1010* (8.24*)	122.19	
o-Toluidine hydrochloride	636-21-5	$C_7H_{10}ClN$	242.2	215	952* (6.63*)	143.63	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Tolylene diisocyanate	584-84-9	$C_9H_6N_2O_2$	251	19.5-21.5	1030* (5.92*)	174.15	
Toxaphene	8001-35-2	$C_{10}H_{10}Cl_8$ (or mixture)		65-90	1030* (2.50*)	413.80	
Tribromomethane	75-25-2	$CHBr_3$	149-150	7.5	32.9 (0.13)	252.75	
1,2,4-Trichloro-benzene	120-82-1	$C_6H_3Cl_3$	213	17	617* (3.40*)	181.44	
1,1,1-Trichloroethane	71-55-6	$C_2H_3Cl_3$	74.1	-32.5	265 (1.99)	133.40	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
1,1,2-Trichloroethane	79-00-5	$C_2H_3Cl_3$	113-114	-35	265 (1.99)	133.40	CCl_2H-CH_2Cl
Trichloroethene	79-01-6	C_2HCl_3	86.7	-84.8	229 (1.74)	131.38	$CCl_2=CClH$
Trichloromethanethiol	75-70-7	$CHCl_3S$			127* (0.84*)	151.43	CCl_3-SH
Trichloromonofluoromethane	75-69-4	CCl_3F	23.7	-111	15.1* (0.11*)	137.36	
2,4,5-Trichlorophenol	95-95-4	$C_6H_3Cl_3O$	253	67	569* (2.88*)	197.44	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
2,4,6-Trichlorophenol	88-06-2	$C_6H_3Cl_3O$	246	69	569* (2.88*)	197.44	
2,4,5-Trichlorophenoxy-acetic acid (2,4,5-T)	93-76-5	$C_8H_5Cl_3O_3$		153	733* (2.87*)	255.48	
2,4,5-Trichlorophenoxy-propionic acid (2,4,5-TP) (Silvex)	93-72-1	$C_9H_7Cl_3O_3$		181.6	1500* (5.58*)	269.51	
Trichloropropane, N.O.S.		$C_3H_5Cl_3$			414 (2.81)	147.43	
1,2,3-Trichloropropane	96-18-4	$C_3H_5Cl_3$	156.85	-14.7	414 (2.81)	147.43	$CH_2Cl-CHCl-CH_2Cl$

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
0,0,0-Triethyl phosphorothioate	126-68-1	$C_6H_{15}O_3PS$				198.22	
sym-Trinitrobenzene	99-35-4	$C_6H_3N_3O_6$		122.5	656 (3.08)	213.12	
Tris(1-azridinyl) phosphine sulfide	52-24-4	$C_6H_{12}N_3PS$		51.5		189.24	
Tris(2,3-dibromopropyl) phosphate	126-72-7	$C_9H_{15}Br_6O_4P$				697.67	
Trypan blue	72-57-1	$C_{34}H_{24}N_6Na_4O_{14}S_4$			3690* (3.84*)	960.83	

NAME	CAS REGISTRY NO.	FORMULA	BOILING POINT °C	MELTING POINT °C	ΔH COMBUSTION kcal/mol (kcal/gram)	MOLECULAR WEIGHT	STRUCTURE
Uracil mustard	66-75-1	$C_8H_{11}Cl_2N_3O_2$		206d	1010* (4.00*)	252.12	
Vanadic Acid, ammonium salt	7803-55-6	H_4NO_3V				116.99	$(VO_3^-)(NH_4^+)$
Vanadium pentoxide	1314-62-1	O_5V_2		690	278* (4.45*)	181.88	
Vinyl chloride	75-01-4	C_2H_3Cl	-14	-160		62.50	$ClHC=CH_2$
Zinc cyanide	557-21-1	C_2N_2Zn		800d		117.41	$(Zn^{2+})(CN^-)_2$
Zinc phosphide	1314-84-7	P_2Zn_3	1100	420		258.05	$(Zn^{2+})_3(P^{3-})_2$

APPENDIX B

Hazardous Constituents - Stack Gas Sampling Methods

Appendix B catalogs the Hazardous Constituents listed in 40 C.F.R. Part 261, Appendix VIII (May 20, 1981) with a description of their most probable location in the stack gas effluent sampling scheme.

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS

Compound	Description
Acetonitrile	Gas Bulb
Acetophenone	Sorbent
3-(alpha-Acetonylbenzyl)-4-hydroxycoumarin and salts (Warfarin)	Particulate/Sorbent
2-Acetylaminofluorene	Particulate/Sorbent
Acetyl chloride	Gas Bulb
1-Acetyl-2-thiourea	Sorbent
Acrolein	Gas Bulb
Acrylamide	Sorbent
Acrylonitrile	Gas Bulb
Aflatoxins	Particulate/Sorbent
Aldrin	Particulate/Sorbent
Allyl alcohol	Gas Bulb
Aluminum phosphide	Particulate
4-Aminobiphenyl	Particulate/Sorbent
6-Amino-1,1a,2,8,8a,8b-hexahydro-8-(hydroxymethyl)-8a-methoxy-5-methylcarbamate azirino[2',3':3,4]pyrrolo [1,2-a]indole-4,7-dione(ester) (Mitomycin C)	Particulate/Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
5-(Aminomethyl)-3-isoxazolol	Sorbent
Amitrole	Sorbent
Aniline	Sorbent
Antimony and compounds, N.O.S.	Particulate/Impingers
Aramite	Particulate/Sorbent
Arsenic and compounds, N.O.S.	Particulate/Impingers
Arsenic acid	Particulate/Impingers
Arsenic pentoxide	Particulate/Impingers
Arsenic trioxide	Particulate/Impingers
Auramine	Particulate/Sorbent
Azaserine	Sorbent
Barium and compounds, N.O.S.	Particulate
Barium cyanide	Particulate(metal)/Impingers(CN)
Benz(c)acridine	Sorbent
Benz(a)anthracene	Particulate/Sorbent
Benzene	Gas Bulb

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Benzenearsonic acid	Particulate/Impingers
Benzene, dichloromethyl-	Sorbent
Benzenethiol	Sorbent
Benzidine	Particulate/Sorbent
Benzo(b)fluoranthene	Particulate/Sorbent
Benzo(j)fluoranthene	Particulate/Sorbent
Benzo(a)pyrene	Particulate/Sorbent
p-Benzoquinone	Sorbent
Benzotrichloride	Sorbent
Benzyl chloride	Sorbent
Beryllium and compounds, N.O.S.	Particulate
Bis(2-chloroethoxy)methane	Sorbent
Bis(2-chloroethyl) ether	Sorbent
N,N-Bis(2-chloroethyl)-2-naphthylamine	Particulate/Sorbent
Bis(2-chloroisopropyl) ether	Sorbent
Bis(chloromethyl) ether	Gas Bulb/Sorbent
Bis(2-ethylhexyl) phthalate	Particulate/Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Bromoacetone	Sorbent
Bromomethane	Gas Bulb
4-Bromophenyl phenyl ether	Particulate/Sorbent
Brucine	Particulate/Sorbent
2-Butanone peroxide	Sorbent
Butyl benzyl phthalate	Particulate/Sorbent
2-sec-Butyl-4,6-dinitrophenol (DNBP)	Particulate/Sorbent
Cadmium and compounds, N.O.S.	Particulate
Calcium chromate	Particulate
Calcium cyanide	Particulate(metal)/Impingers(CN)
Carbon disulfide	Gas Bulb
Carbon oxyfluoride	Gas Bulb
Chloral	Special Reagent
Chlorambucil	Particulate/Sorbent
Chlordane (alpha and gamma isomers)	Sorbent
Chlorinated benzenes, N.O.S.	Sorbent
Chlorinated ethane, N.O.S.	Gas Bulb/Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Chlorinated fluorocarbons, N.O.S.	Gas Bulb/Sorbent
Chlorinated naphthalene, N.O.S.	Sorbent
Chlorinated phenol, N.O.S.	Sorbent
Chloroacetaldehyde	Special Reagent
Chloroalkyl ethers, N.O.S.	Gas Bulb/Sorbent
p-Chloroaniline	Sorbent
Chlorobenzene	Sorbent
Chlorobenzilate	Particulate/Sorbent
p-Chloro-m-cresol	Sorbent
1-Chloro-2,3-epoxypropane	Sorbent
2-Chloroethyl vinyl ether	Gas Bulb/Sorbent
Chloroform	Gas Bulb
Chloromethane	Gas Bulb
Chloromethyl methyl ether	Gas Bulb
2-Chloronaphthalene	Sorbent
2-Chlorophenol	Sorbent
1-(o-Chlorophenyl)thiourea	Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
3-Chloropropionitrile	Sorbent
Chromium and compounds, N.O.S.	Particulate
Chrysene	Particulate/Sorbent
Citrus red No. 2	Particulate/Sorbent
Coal Tars	Particulate/Sorbent
Copper cyanide	Particulate(metal)/Impingers(CN)
Creosote	Sorbent
Cresols	Sorbent
Crotonaldehyde	Special Reagent
Cyanides (soluble salts and complexes), N.O.S.	Impingers (CN)
Cyanogen	Gas Bulb
Cyanogen bromide	Gas Bulb
Cyanogen chloride	Gas Bulb
Cycasin	Particulate/Sorbent
2-Cyclohexyl-4,6-dinitrophenol	Particulate/Sorbent
Cyclophosphamide	Particulate/Sorbent
Daunomycin	Particulate/Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
DDD	Particulate/Sorbent
DDE	Particulate/Sorbent
DDT	Particulate/Sorbent
Diallate	Sorbent
Dibenz(a,h)acridine	Particulate/Sorbent
Dibenz(a,j)acridine	Particulate/Sorbent
Dibenz(a,h)anthracene	Particulate/Sorbent
7H-Dibenzo(c,g)carbazole	Particulate/Sorbent
Dibenzo(a,e)pyrene	Particulate/Sorbent
Dibenzo(a,h)pyrene	Particulate/Sorbent
Dibenzo(a,i)pyrene	Particulate/Sorbent
1,2-Dibromo-3-chloropropane	Sorbent
1,2-Dibromoethane	Sorbent
Dibromomethane	Gas Bulb/Sorbent
Di-n-butyl phthalate	Particulate/Sorbent
Dichlorobenzene(meta, ortho and para isomers)	Sorbent
Dichlorobenzene, N.O.S.	Sorbent
3,3'-Dichlorobenzidine	Particulate/Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
1,4-Dichloro-2-butene	Sorbent
Dichlorodifluoromethane	Gas Bulb
1,1,-Dichloroethane	Gas Bulb
1,2-Dichloroethane	Gas Bulb
trans-1,2-Dichloroethene	Gas Bulb
Dichloroethylene, N.O.S.	Gas Bulb
1,1-Dichloroethylene	Gas Bulb
Dichloromethane	Gas Bulb
2,4-Dichlorophenol	Sorbent
2,6-Dichlorophenol	Sorbent
2,4-Dichlorophenoxyacetic acid (2,4-D)	Particulate/Sorbent
Dichlorophenylarsine	Particulate/Impingers
Dichloropropane, N.O.S.	Gas Bulb/Sorbent
1,2-Dichloropropane	Gas Bulb/Sorbent
Dichloropropanol, N.O.S.	Sorbent
Dichloropropene, N.O.S.	Gas Bulb/Sorbent
1,3-Dichloropropene	Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Dieldrin	Particulate/Sorbent
1,2:3,4-Diepoxybutane	Sorbent
Diethylarsine	Gas Bulb/Sorbent/Impingers
N,N-Diethylhydrazine	Gas Bulb
O,O-Diethyl S-methyl ester of phosphorodithioic acid	Sorbent
O,O-Diethylphosphoric acid, O-p-nitrophenyl ester	Particulate/Sorbent
Diethyl phthalate	Particulate/Sorbent
O,O-Diethyl O-2-pyrazinyl phosphorothioate	Gas Bulb
Diethylstilbestrol (D.E.S.)	Particulate/Sorbent
Dihydrosafrole	Sorbent
3,4-Dihydroxy-alpha-(methylamino)methyl benzyl alcohol	Sorbent
Diisopropylfluorophosphate (DFP)	Sorbent
Dimethoate	Sorbent
3,3'-Dimethoxybenzidine	Particulate/Sorbent
p-Dimethylaminoazobenzene	Particulate/Sorbent
7,12-Dimethylbenz(a)anthracene	Particulate/Sorbent
3,3'-Dimethylbenzidine	Particulate/Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Dimethylcarbamoyl chloride	Sorbent
1,1-Dimethylhydrazine	Gas Bulb
1,2-Dimethylhydrazine	Gas Bulb
3,3-Dimethyl-1-(methylthio)-2-butanone,O-((methylamino) carbonyl)oxime [Thiofanox]	Particulate/Sorbent
alpha,alpha-Dimethylphenethylamine	Sorbent
2,4-Dimethylphenol	Sorbent
Dimethyl phthalate	Sorbent
Dimethyl sulfate	Sorbent
Dinitrobenzene, N.O.S.	Particulate/Sorbent
4,6-Dinitro-o-cresol (and salts)	Particulate/Sorbent
2,4-Dinitrophenol	Sorbent
2,4-Dinitrotoluene	Sorbent
2,6-Dinitrotoluene	Sorbent
Di-n-octyl phthalate	Particulate/Sorbent
1,4-Dioxane	Sorbent
Diphenylamine	Particulate/Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
1,2-Diphenylhydrazine	Sorbent
Di-n-propylnitrosamine	Sorbent
Disulfoton	Particulate/Sorbent
2,4-Dithiobiuret	Sorbent
Endosulfan	Particulate/Sorbent
Endrin (and metabolites)	Particulate/Sorbent
Ethyl carbamate	Sorbent
Ethyl cyanide	Gas Bulb/Impingers (CN)
Ethylenebisdithiocarbamic acid (salts and esters)	Particulate/Sorbent
Ethyleneimine	Gas Bulb
Ethylene oxide	Gas Bulb
Ethylenethiourea	Sorbent
Ethyl methacrylate	Sorbent
Ethyl methanesulfonate	Gas Bulb
Fluoranthene	Particulate/Sorbent
Fluorine	Special Reagent
2-Fluoroacetamide	Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Fluoroacetic acid, sodium salt	Sorbent
Formaldehyde	Special Reagent
Formic acid	Gas Bulb/Sorbent
Glycidylaldehyde	Special Reagent
Halomethane, N.O.S.	Gas Bulb
Heptachlor	Particulate/Sorbent
Heptachlor epoxide (alpha, beta, and gamma isomers)	Particulate/Sorbent
Hexachlorobenzene	Particulate/Sorbent
Hexachlorobutadiene	Sorbent
Hexachlorocyclohexane (all isomers)	Particulate/Sorbent
Hexachlorocyclopentadiene	Sorbent
Hexachloroethane	Sorbent
1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-endo,endo-dimethanonaphthalene	Particulate/Sorbent
Hexachlorophene	Particulate/Sorbent
Hexachloropropene	Particulate/Sorbent
Hexaethyl tetraphosphate	Particulate/Sorbent
Hydrazine	Gas Bulb/Sorbent
Hydrocyanic acid	Gas Bulb/Impingers (CN)

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Hydrofluoric acid	Gas Bulb/Special Reagent
Hydrogen sulfide	Gas Bulb/Special Reagent
Hydroxydimethylarsine oxide	Particulate/Impingers
Indeno(1,2,3-c,d)pyrene	Particulate/Sorbent
Iodomethane	Gas Bulb
Iron dextran	Particulate
Isocyanic acid, methyl ester	Gas Bulb
Isobutyl alcohol	Sorbent
Isosafrole	Sorbent
Kepone	Particulate/Sorbent
Lasiocarpine	Particulate/Sorbent
Lead and compounds, N.O.S.	Particulate/Impingers
Lead acetate	Particulate/Impingers
Lead phosphate	Particulate/Impingers
Lead subacetate	Particulate/Impingers
Maleic anhydride	Sorbent
Maleic hydrazide	Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Malononitrile	Sorbent
Melphalan	Particulate/Sorbent
Mercury fulminate	Particulate/Impingers
Mercury and compounds, N.O.S.	Particulate/Impingers
Methacrylonitrile	Particulate/Sorbent
Methanethiol	Gas Bulb
Methapyrilene	Sorbent
Metholmyl	Sorbent
Methoxychlor	Particulate/Sorbent
2-Methylaziridine	Gas Bulb
3-Methylcholanthrene	Particulate/Sorbent
Methylchlorocarbonate	Gas Bulb
4,4'-Methylenebis(2-chloroaniline)	Particulate/Sorbent
Methyl ethyl ketone (MEK)	Gas Bulb
Methyl hydrazine	Gas Bulb
2-Methyllactonitrile	Gas Bulb
Methyl methacrylate	**Gas Bulb/Sorbent**

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Methyl methanesulfonate	Sorbent
2-Methyl-2-(methylthio)propionaldehyde-o-(methylcarbonyl) oxime	Sorbent
N-Methyl-N'-nitro-N-nitrosoguanidine	Sorbent
Methyl parathion	Particulate/Sorbent
Methylthiouracil	Sorbent
Mustard gas	Sorbent
Naphthalene	Sorbent
1,4-Naphthoquinone	Sorbent
1-Naphthylamine	Particulate/Sorbent
2-Naphthylamine	Particulate/Sorbent
1-Naphthyl-2-thiourea	Particulate/Sorbent
Nickel and compounds, N.O.S.	Particulate
Nickel carbonyl	Particulate
Nickel cyanide	Particulate(metal)/Impingers(CN)
Nicotine (and salts)	Sorbent
Nitric oxide	Gas Bulb

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
p-Nitroaniline	Particulate/Sorbent
Nitrobenzene	Sorbent
Nitrogen dioxide	Gas Bulb
Nitrogen mustard (and hydrochloride salt)	Gas Bulb
Nitrogen mustard N-Oxide (and hydrochloride salt)	Sorbent
Nitroglycerine	Gas Bulb/Sorbent
4-Nitrophenol	Sorbent
4-Nitroquinoline-1-oxide	Sorbent
Nitrosamine, N.O.S.	Gas Bulb/Sorbent/Particulate
N-Nitrosodi-n-butylamine	Sorbent
N-Nitrosodiethanolamine	Sorbent
N-Nitrosodiethylamine	Sorbent
N-Nitrosodimethylamine	Sorbent
N-Nitroso-N-ethylurea	Sorbent
N-Nitrosomethylethylamine	Sorbent
N-Nitroso-N-methylurea	Sorbent
N-Nitroso-N-methylurethane	Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
N-Nitrosomethylvinylamine	Gas Bulb/Sorbent
N-Nitrosomorpholine	Sorbent
N-Nitrosonornicotine	Sorbent
N-Nitrosopiperidine	Sorbent
N-Nitrosopyrrolidine	Sorbent
N-Nitrososarcosine	Sorbent
5-Nitro-o-toluidine	Sorbent
Octamethylpyrophosphoramide	Particulate/Sorbent
Osmium tetroxide	Particulate
7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid	Sorbent
Paraldehyde	Special Reagent
Parathion	Particulate/Sorbent
Pentachlorobenzene	Sorbent
Pentachloroethane	Sorbent
Pentachloronitrobenzene (PCNB)	Particulate/Sorbent
Pentachlorophenol	Particulate/Sorbent
Phenacetin	Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Phenol	Sorbent
Phenylenediamine	Sorbent
Phenylmercury acetate	Particulate/Impingers
N-Phenylthiourea	Sorbent
Phosgene	Gas Bulb
Phosphine	Gas Bulb
Phosphorodithioic acid, 0,0-diethyl S-((ethylthio)methyl) ester[Phorate]	Particulate/Sorbent
Phosphorothioic acid, 0,0-dimethyl 0-(p-((dimethylamino)sulfonyl) phenyl)ester [Famphur]	Particulate/Sorbent
Phthalic acid esters, N.O.S.	Particulate/Sorbent
Phthalic anhydride	Particulate/Sorbent
2-Picoline	Sorbent
Polychlorinated biphenyl, N.O.S.	Particulate/Sorbent
Potassium cyanide	Particulate(metal)/Impingers(CN)
Potassium silver cyanide	Particulate(metal)/Impingers(CN)
Pronamide	Particulate/Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
1,3-Propane sulfone	Sorbent
n-Propylamine	Gas Bulb
Propylthiouracil	Sorbent
2-Propyn-1-ol	Sorbent
Pyridine	Sorbent
Reserpine	Particulate/Sorbent
Resorcinol	Sorbent
Saccharin (and salts)	Particulate/Sorbent
Safrole	Sorbent
Selenious acid	Particulate/Impingers
Selenium and compounds, N.O.S.	Particulate/Impingers
Selenium sulfide	Particulate/Impingers
Selenourea	Particulate/Impingers
Silver and compounds, N.O.S.	Particulate
Silver cyanide	Particulate(metal)/Impingers(CN)
Sodium cyanide	Particulate(metal)/Impingers(CN)
Streptozotocin	Particulate/Sorbent
Strontium sulfide	Particulate

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Strychnine (and salts)	Particulate/Sorbent
1,2,4,5-Tetrachlorobenzene	Sorbent
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	Particulate/Sorbent
Tetrachloroethane, N.O.S.	Sorbent
1,1,1,2-Tetrachloroethane	Sorbent
1,1,2,2-Tetrachloroethane	Sorbent
Tetrachloroethene	Sorbent
Tetrachloromethane	Sorbent
2,3,4,6-Tetrachlorophenol	Particulate/Sorbent
Tetraethyldithiopyrophosphate	Particulate/Sorbent
Tetraethyl lead	Particulate/Sorbent/Impingers
Tetraethylpyrophosphate	Particulate/Sorbent
Tetranitromethane	Sorbent
Thallium and compounds, N.O.S.	Particulate
Thallic oxide	Particulate
Thallium(I)acetate	Particulate
Thallium(I)carbonate	Particulate

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Thallium(I)chloride	Particulate
Thallium(I)nitrate	Particulate
Thallium selenite	Particulate
Thallium(I)sulfate	Particulate
Thioacetamide	Sorbent
Thiosemicarbazide	Sorbent
Thiourea	Sorbent
Thiuram	Particulate/Sorbent
Toluene	Sorbent
Toluenediamine	Sorbent
o-Toluidine hydrochloride	Sorbent
Tolylene diisocyanate	Sorbent
Toxaphene	Particulate/Sorbent
Tribromomethane	Sorbent
1,2,4-Trichlorobenzene	Sorbent
1,1,1-Trichloroethane	Gas Bulb
1,1,2-Trichloroethane	Sorbent

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Trichloroethene	Gas Bulb
Trichloromethanethiol	Sorbent
Trichloromonofluoromethane	Gas Bulb
2,4,5-Trichlorophenol	Sorbent
2,4,6-Trichlorophenol	Sorbent
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	Particulate/Sorbent
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP)(Silvex)	Particulate/Sorbent
Trichloropropane, N.O.S.	Sorbent
1,2,3-Trichloropropane	Sorbent
0,0,0-Triethyl phosphorothioate	Particulate/Sorbent
sym-Trinitrobenzene	Sorbent
Tris(1-azridinyl) phosphine sulfide	Sorbent
Tris(2,3,-dibromopropyl)phosphate	Particulate/Sorbent
Trypan blue	Particulate/Sorbent
Uracil mustard	Particulate/Sorbent
Vanadic acid, ammonium salt	Particulate
Vanadium pentoxide	Particulate

HAZARDOUS CONSTITUENTS - STACK GAS SAMPLING METHODS (Continued)

Compound	Description
Vinyl chloride	Gas Bulb
Zinc cyanide	Particulate(metal)/Impingers(CN)
Zinc phosphide	Particulate

N.O.S. = Not Otherwise Specified.

APPENDIX C

Hazardous Constituents - Analysis Methods

Appendix C catalogs the Hazardous Constituents listed in 40 C.F.R. Part 261, Appendix VIII (May 20, 1981) with their corresponding Analysis Method Numbers, as recommended in Section VI.

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS

Compound	Method Number	Description
Acetonitrile	A101	Volatiles
Acetophenone	A121	Extractables
3-(alpha-Acetonylbenzyl)-4-hydroxycoumarin and salts (Warfarin)	A122	HPLC
2-Acetylaminofluorene	A121	Extractables
Acetyl chloride	A144	Acid chlorides
1-Acetyl-2-thiourea	A123	HPLC
Acrolein	A101	Volatiles
Acrylamide	A101	Volatiles
Acrylonitrile	A101	Volatiles
Aflatoxins	A145	--
Aldrin	A121	Extractables
Allyl alcohol	A134	Alcohols
Aluminum phosphide	A253	Phosphides
4-Aminobiphenyl	A121	Extractables
6-Amino-1,1a,2,8,8a,8b-hexahydro-8-(hydroxymethyl)-8a-methoxy-5-methylcarbamate azirino[2',3':3,4]pyrrolo [1,2-a]indole-4,7-dione(ester) (Mitomycin C)	A122	HPLC

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
5-(Aminomethyl)-3-isoxazolol	A121	Extractables
Amitrole	A121	Extractables
Aniline	A121	Extractables
Antimony and compounds, N.O.S.	A221	Antimony
Aramite	A121	Extractables
Arsenic and compounds, N.O.S.	A222	Arsenic
Arsenic acid	A222	Arsenic
Arsenic pentoxide	A222	Arsenic
Arsenic trioxide	A222	Arsenic
Auramine	A121	Extractables
Azaserine	A123	HPLC
Barium and compounds, N.O.S.	A223	Barium
Barium cyanide	A223 A252	Barium Cyanides
Benz(c)acridine	A121	Extractables
Benz(a)anthracene	A121	Extractables
Benzene	A101	Volatiles

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Benzenearsonic acid	A222	Arsenic
Benzene, dichloromethyl-	A121	Extractables
Benzenethiol	A121	Extractables
Benzidine	A121	Extractables
Benzo(b)fluoranthene	A121	Extractables
Benzo(j)fluoranthene	A121	Extractables
Benzo(a)pyrene	A121	Extractables
p-Benzoquinone	A121	Extractables
Benzotrichloride	A121	Extractables
Benzyl chloride	A121	Extractables
Beryllium and compounds, N.O.S.	A224	Beryllium
Bis(2-chloroethoxy)methane	A121	Extractables
Bis(2-chloroethyl) ether	A121	Extractables
N,N-Bis(2-chloroethyl)-2-naphthylamine	A121	Extractables
Bis(2-chloroisopropyl) ether	A121	Extractables
Bis(chloromethyl) ether	A121	Extractables
Bis(2-ethylhexyl) phthalate	A121	Extractables

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Bromoacetone	A101	Volatiles
Bromomethane	A101	Volatiles
4-Bromophenyl phenyl ether	A121	Extractables
Brucine	A148	--
2-Butanone peroxide	A121	Extractables
Butyl benzyl phthalate	A121	Extractables
2-sec-Butyl-4,6-dinitrophenol (DNBP)	A121	Extractables
Cadmium and compounds, N.O.S.	A225	Cadmium
Calcium chromate	A226	Chromium
Calcium cyanide	A252	Cyanides
Carbon disulfide	A101 A141	Volatiles Gases
Carbon oxyfluoride	A101	Volatiles
Chloral (as hydrate)	A131	Aldehydes
Chlorambucil	A122	HPLC
Chlordane (alpha and gamma isomers)	A121	Extractables
Chlorinated benzenes, N.O.S.	A101 A121	Volatiles Extractables
Chlorinated ethane, N.O.S.	A101	Volatiles

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Chlorinated fluorocarbons, N.O.S.	A101	Volatiles
Chlorinated naphthalene, N.O.S.	A121	Extractables
Chlorinated phenol, N.O.S.	A121	Extractables
Chloroacetaldehyde	A131	Aldehydes
Chloroalkyl ethers, N.O.S.	A101	Volatiles
p-Chloroaniline	A121	Extractables
Chlorobenzene	A101	Volatiles
Chlorobenzilate	A121	Extractables
p-Chloro-m-cresol	A121 A122	Extractables HPLC
1-Chloro-2,3-epoxypropane	A101	Volatiles
2-Chloroethyl vinyl ether	A101	Volatiles
Chloroform	A101	Volatiles
Chloromethane	A101	Volatiles
Chloromethyl methyl ether	A101	Volatiles
2-Chloronaphthalene	A121	Extractables
2-Chlorophenol	A121 A122	Extractables HPLC

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
1-(o-Chlorophenyl)thiourea	A123	HPLC
3-Chloropropionitrile	A121	Extractables
Chromium and compounds, N.O.S.	A226	Chromium
Chrysene	A121	Extractables
Citrus Red No. 2	A149	--
Coal tars	A121	Extractables
Copper cyanide	A252	Cyanides
Creosote	A121	Extractables
Cresols	A121	Extractables
Crotonaldehyde	A123 A131	HPLC Aldehydes
Cyanides (soluble salts and complexes), N.O.S.	A252	Cyanides
Cyanogen	A138	Gases
Cyanogen bromide	A138	Gases
Cyanogen chloride	A138	Gases
Cycasin	A150	--
2-Cyclohexyl-4,6-dinitrophenol	A121	Extractables

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Cyclophosphamide	--	--
Daunomycin	A122	HPLC
DDD	A121	Extractables
DDE	A121	Extractables
DDT	A121	Extractables
Diallate	A121	Extractables
Dibenz(a,h)acridine	A121	Extractables
Dibenz(a,j)acridine	A121	Extractables
Dibenz(a,h)anthracene	A121	Extractables
7H-Dibenzo(c,g)carbazole	A121	Extractables
Dibenzo(a,e)pyrene	A121	Extractables
Dibenzo(a,h)pyrene	A121	Extractables
Dibenzo(a,i)pyrene	A121	Extractables
1,2-Dibromo-3-chloropropane	A101	Volatiles
1,2-Dibromoethane	A101	Volatiles
Dibromomethane	A101	Volatiles
Di-n-butyl phthalate	A121	Extractables

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Dichlorobenzene(meta, ortho and para isomers)	A101	Volatiles
	A121	Extractables
Dichlorobenzene, N.O.S.	A101	Volatiles
	A121	Extractables
3,3'-Dichlorobenzidine	A121	Extractables
1,4-Dichloro-2-butene	A101	Volatiles
Dichlorodifluoromethane	A101	Volatiles
1,1-Dichloroethane	A101	Volatiles
1,2-Dichloroethane	A101	Volatiles
trans-1,2-Dichloroethene	A101	Volatiles
Dichloroethylene, N.O.S.	A101	Volatiles
1,1-Dichloroethylene	A101	Volatiles
Dichloromethane	A101	Volatiles
2,4-Dichlorophenol	A121	Extractables
	A122	HPLC
2,6-Dichlorophenol	A121	Extractables
	A122	HPLC
2,4-Dichlorophenoxyacetic acid (2,4-D)	A122	HPLC
	A133	Carboxylic acids
Dichlorophenylarsine	A222	Arsenic
Dichloropropane, N.O.S.	A101	Volatiles

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
1,2-Dichloropropane	A101	Volatiles
Dichloropropanol, N.O.S.	A121	Extractables
Dichloropropene, N.O.S.	A101	Volatiles
1,3-Dichloropropene	A101	Volatiles
Dieldrin	A121	Extractables
1,2:3,4-Diepoxybutane	A121	Extractables
Diethylarsine	A222	Arsenic
N,N-Diethylhydrazine	A121	Extractables
O,O-Diethyl S-methyl ester of phosphorodithioic acid	A121	Extractables
O,O-Diethylphosphoric acid, O-p-nitrophenyl ester	A121	Extractables
Diethyl phthalate	A121	Extractables
O,O-Diethyl O-2-pyrazinyl phosphorothioate	A121	Extractables
Diethylstilbestrol	A123	HPLC
Dihydrosafrole	A121	Extractables
3,4-Dihydroxy-alpha-(methylamino)methyl benzyl alcohol (Epinephrine)	A123	HPLC
Diisopropylfluorophosphate (DFP)	A121	Extractables
Dimethoate	A121	Extractables
3,3'-Dimethoxybenzidine	A121	Extractables

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
p-Dimethylaminoazobenzene	A121	Extractables
7,12-Dimethylbenz(a)anthracene	A121	Extractables
3,3'-Dimethylbenzidine	A121	Extractables
Dimethylcarbamoyl chloride	A144	Acid chlorides
1,1-Dimethylhydrazine	A121	Extractables
1,2-Dimethylhydrazine	A121	Extractables
3,3-Dimethyl-1-(methylthio)-2-butanone,O-((methylamino) carbonyl)oxime[Thiofanox]	A183	Oximes
alpha, alpha-Dimethylphenethylamine	A121	Extractables
2,4-Dimethylphenol	A121	Extractables
Dimethyl phthalate	A121	Extractables
Dimethyl sulfate	A121	Extractables
Dinitrobenzene, N.O.S.	A121	Extractables
4,6-Dinitro-o-cresol (and salts)	A121 A122	Extractables HPLC
2,4,-Dinitrophenol	A121 A122	Extractables HPLC
2,4-Dinitrotoluene	A121	Extractables
2,6-Dinitrotoluene	A121	Extractables
Di-n-octyl phthalate	A121	Extractables

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
1,4-Dioxane	A101	Volatiles
Diphenylamine	A121	Extractables
1,2-Diphenylhydrazine	A121	Extractables
Di-n-propylnitrosamine	A121	Extractables
Disulfoton	A121	Extractables
2,4-Dithiobiuret	A121	Extractables
Endosulfan	A121	Extractables
Endrin (and metabolites)	A121	Extractables
Ethyl carbamate	A121	Extractables
Ethyl cyanide	A252	Cyanides
Ethylenebisdithiocarbamic acid (salts and esters)	--	--
Ethyleneimine	A121	Extractables
Ethylene oxide	A156	--
Ethylenethiourea	A123	HPLC
Ethyl methacrylate	A121	Extractables
Ethyl methanesulfonate	A121	Extractables
Fluoranthene	A121	Extractables

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Fluorine	A137	--
2-Fluoroacetamide	A157	--
Fluoroacetic acid, sodium salt	A121	Extractables
Formaldehyde	A131	Aldehydes
Formic acid	A101	Volatiles
	A121	Extractables
	A133	Carboxylic acids
Glycidylaldehyde	A131	Aldehydes
Halomethane, N.O.S.	A101	Volatiles
Heptachlor	A121	Extractables
Heptachlor epoxide (alpha, beta, and gamma isomers)	A121	Extractables
Hexachlorobenzene	A121	Extractables
Hexachlorobutadiene	A121	Extractables
Hexachlorocyclohexane (all isomers)	A121	Extractables
Hexachlorocyclopentadiene	A121	Extractables
Hexachloroethane	A101	Volatiles
	A121	Extractables
1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-endo,endo-dimethanonaphthalene	A121	Extractables

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Hexachlorophene	A121	Extractables
Hexachloropropene	A101	Volatiles
Hexaethyl tetraphosphate	A121	Extractables
Hydrazine	A101 A141	Volatiles Gases
Hydrocyanic acid	A141 A251	Gases Anions
Hydrofluoric acid	A251	Anions
Hydrogen sulfide	A141	Gases
Hydroxydimethylarsine oxide	A222	Arsenic
Indeno(1,2,3-c,d)pyrene	A121	Extractables
Iodomethane	A101	Volatiles
Iron dextran (complex)	--	--
Isocyanic acid, methyl ester	A101	Volatiles
Isobutyl alcohol	A134	Alcohols
Isosafrole	A121	Extractables
Kepone	A121	Extractables
Lasiocarpine	A160	--

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Lead and compounds, N.O.S.	A227	Lead
Lead acetate	A227	Lead
Lead phosphate	A227	Lead
Lead subacetate	A227	Lead
Maleic anhydride	A121	Extractables
Maleic hydrazide	A121	Extractables
Malononitrile	A121	Extractables
Melphalan	A122	HPLC
Mercury fulminate	A228	Mercury
Mercury and compounds, N.O.S.	A228	Mercury
Methacrylonitrile	A121	Extractables
Methanethiol	A101	Volatiles
Methapyriline	A121	Extractables
Metholmyl	A122	HPLC
Methoxychlor	A121	Extractables
2-Methylaziridine	A121	Extractables
3-Methylcholanthrene	A121	Extractables

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Methylchlorocarbonate	--	--
4,4'-Methylenebis(2-chloroaniline)	A121	Extractables
Methyl ethyl ketone (MEK)	A101 A121	Volatiles Extractables
Methyl hydrazine	A101 A121	Volatiles Extractables
2-Methyllactonitrile	A121	Extractables
Methyl methacrylate	A121	Extractables
Methyl methanesulfonate	A121	Extractables
2-Methyl-2-(methylthio)propionaldehyde-O-(methylcarbonyl) oxime	A183	Oximes
N-Methyl-N'-nitro-N-nitrosoguanidine	A121	Extractables
Methyl parathion	A121	Extractables
Methylthiouracil	A121	Extractables
Mustard gas	A139	Mustards
Naphthalene	A121	Extractables
1,4-Naphthoquinone	A121	Extractables
1-Naphthylamine	A121	Extractables
2-Naphthylamine	A121	Extractables
1-Naphthyl-2-thiourea	A123	HPLC

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Nickel and compounds, N.O.S.	A229	Nickel
Nickel carbonyl	A229	Nickel
Nickel cyanide	A229	Nickel
	A252	Cyanides
Nicotine (and salts)	A121	Extractables
Nitric oxide	A141	Gases
p-Nitroaniline	A121	Extractables
Nitrobenzene	A121	Extractables
Nitrogen dioxide	A141	Gases
Nigrogen mustard (and hydrochloride salt)	A139	Mustards
Nitrogen mustard N-Oxide (and hydrochloride salt)	A139	Mustards
Nitroglycerine	A121	Extractables
4-Nitrophenol	A121	Extractables
	A122	HPLC
4-Nitroquinoline-1-oxide	--	--
Nitrosamine, N.O.S.	A121	Extractables
N-Nitrosodi-n-butylamine	A121	Extractables
N-Nitrosodiethanolamine	A121	Extractables

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
N-Nitrosodiethylamine	A121	Extractables
N-Nitrosodimethylamine	A121	Extractables
N-Nitroso-N-ethylurea	A121	Extractables
N-Nitrosomethylethylamine	A121	Extractables
N-Nitroso-N-methylurea	A121	Extractables
N-Nitroso-N-methylurethane	A121	Extractables
N-Nitrosomethylvinylamine	A121	Extractables
N-Nitrosomorpholine	A121	Extractables
N-Nitrosonornicotine	A121	Extractables
N-Nitrosopiperidine	A121	Extractables
N-Nitrosopyrrolidine	A121	Extractables
N-Nitrososarcosine	A121	Extractables
5-Nitro-o-toluidine	A122	HPLC
Octamethylpyrophosphoramide	A121	Extractables
Osmium tetroxide	A230	Osmium
7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid	A133	Carboxylic acids

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Paraldehyde	A131	Aldehydes
Parathion	A121	Extractables
Pentachlorobenzene	A121	Extractables
Pentachloroethane	A121	Extractables
Pentachloronitrobenzene (PCNB)	A121	Extractables
Pentachlorophenol	A121	Extractables
Phenacetin	A174	--
Phenol	A121 A122	Extractables HPLC
Phenylenediamine	A121	Extractables
Phenylmercury acetate	A228	Mercury
N-Phenylthiourea	A123	HPLC
Phosgene	A138	Gases
Phosphine	A136	--
Phosphorodithioic acid, O,O-diethyl S-((ethylthio)methyl) ester [Phorate]	A121	Extractables
Phosphorothioic acid, O,O-dimethyl O-(p-((dimethylamino)sulfonyl) phenyl)ester [Famphur]	A121	Extractables
Phthalic acid esters, N.O.S.	A121	Extractables

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Phthalic anhydride	A121	Extractables
2-Picoline	A121	Extractables
Polychlorinated biphenyl, N.O.S.	A121	Extractables
Potassium cyanide	A252	Cyanides
Potassium silver cyanide	A232	Silver
	A252	Cyanides
Pronamide	A121	Extractables
1,3-Propane sulfone	A121	Extractables
n-Propylamine	A121	Extractables
Propylthiouracil	A121	Extractables
2-Propyn-1-ol	A134	Alcohols
Pyridine	A121	Extractables
Reserpine	A122	HPLC
Resorcinol	A134	Alcohols
Saccharin (and salts)	A121	Extractables
	A123	HPLC
Safrole	A121	Extractables
Selenious acid	A231	Selenium

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Selenium and compounds, N.O.S.	A231	Selenium
Selenium sulfide	A231	Selenium
Selenourea	A231	Selenium
Silver and compounds, N.O.S.	A232	Silver
Silver cyanide	A232 A252	Silver Cyanides
Sodium cyanide	A252	Cyanides
Streptozotocin	A122	HPLC
Strontium sulfide	A233	Strontium
Strychnine (and salts)	A180	--
1,2,4,5-Tetrachlorobenzene	A121	Extractables
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	A121	Extractables
Tetrachloroethane, N.O.S.	A101	Volatiles
1,1,1,2-Tetrachloroethane	A101	Volatiles
1,1,2,2-Tetrachloroethane	A101	Volatiles
Tetrachloroethene	A101	Volatiles
Tetrachloromethane	A101	Volatiles

HAZARDOUS CONSTITUENTS--ANALYSIS METHOD (Continued)

Compound	Method Number	Description
2,3,4,6-Tetrachlorophenol	A121 A122	Extractables HPLC
Tetraethyldithiopyrophosphate	A121	Extractables
Tetraethyl lead	A227	Lead
Tetraethylpyrophosphate	A121	Extractables
Tetranitromethane	A101	Volatiles
Thallium and compounds, N.O.S.	A234	Thallium
Thallic oxide	A234	Thallium
Thallium(I)acetate	A234	Thallium
Thallium(I)carbonate	A234	Thallium
Thallium(I)chloride	A234	Thallium
Thallium(I)nitrate	A234	Thallium
Thallium selenite	A234	Thallium
Thallium(I)sulfate	A234	Thallium
Thioacetamide	A123	HPLC
Thiosemicarbazide	A123	HPLC
Thiourea	A123	HPLC
Thiuram	A122	HPLC

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Toluene	A101	Volatiles
Toluenediamine	A121	Extractables
o-Toluidine hydrochloride	--	--
Tolylene diisocyanate	A121	Extractables
Toxaphene	A121	Extractables
Tribromomethane	A101	Volatiles
1,2,4-Trichlorobenzene	A121	Extractables
1,1,1-Trichloroethane	A101	Volatiles
1,1,2-Trichloroethane	A101	Volatiles
Trichloroethene	A101	Volatiles
Trichloromethanethiol	A121	Extractables
Tichloromonofluoromethane	A101	Volatiles
2,4,5-Trichlorophenol	A121 A122	Extractables HPLC
2,4,6-Trichlorophenol	A121 A122	Extractables HPLC
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	A122 A133	HPLC Carboxylic acids
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP) (Silvex)	A122 A133	HPLC Carboxylic acids

HAZARDOUS CONSTITUENTS--ANALYSIS METHODS (Continued)

Compound	Method Number	Description
Trichloropropane, N.O.S.	A101	Volatiles
1,2,3-Trichloropropane	A101	Volatiles
O,O,O-Triethyl phosphorothioate	A121	Extractables
sym-Trinitrobenzene	A121	Extractables
Tris-(1-azridinyl)phosphine sulfide	A190	--
Tris(2,3-dibromopropyl) phosphate	A121	Extractables
Trypan blue	A123	HPLC
Uracil mustard	--	--
Vanadic acid, ammonium salt	A235	Vanadium
Vanadium pentoxide	A235	Vanadium
Vinyl chloride	A101	Volatiles
Zinc cyanide	A252	Cyanides
Zinc phosphide	A253	Phosphides

N.O.S. = Not Otherwise Specified.

APPENDIX D

Summary of Method Numbers

Appendix D cross-references each sampling and analysis method to its corresponding Method Number and the page where the method may be found within the text.

SUMMARY OF METHOD NUMBERS

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APPENDIX E

MS - Analytical Ions

Appendix E catalogs the Hazardous Constituents listed in 40 C.F.R. Part 261, Appendix VIII (May 20, 1981) for which GC/MS analysis procedures have been recommended with their appropriate MS analytical ions and corresponding intensities (when available).

MS - ANALYTICAL IONS

Compound	Ions (Intensities)
Acetonitrile	41(100), 40(50), 39(17), 38(5)
Acetophenone	105(100), 77(83), 51(31), 120(25)
2-Acetylaminofluorene	181(100), 180(82), 223(62), 152(37)
Acrolein	56(72), 27(100), 26(54), 55(51)
Acrylamide	27(100), 44(89), 71(72), 55(58)
Acrylonitrile	53(100), 26(93), 52(79), 51(30)
Aldrin	66(100), 263(73), 220(11)
Allyl alcohol	57(100), 29(39), 31(32), 58(26)
4-Aminobiphenyl	169(100), 170(14), 168(11), 84.5(9)
5-(Aminomethyl)-3-isoxazolol	98(100), 41(66), 39(49), 67(23)
Amitrole	28(100), 84(66), 57(28), 29(23)
Aniline	93(100), 66(33), 65(18), 39(18)
Aramite	
Auramine	
Benz(c)acridine	229(100), 228(19), 230(19), 201(10)

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Benz(a)anthracene	228(100), 229(19), 226(19), 114(18)
Benzene	78(100), 77(19), 52(16), 51(15)
Benzene, dichloromethyl-	
Benzenethiol	110(100), 66(38), 39(28), 109(25)
Benzidine	184(100), 185(15), 183(11), 92(8)
Benzo(b)fluoranthene	252(100), 250(25), 253(25), 126(25)
Benzo(j)fluoranthene	252(100), 250(25), 253(25), 126(25)
Benzo(a)pyrene	252(100), 250(25), 253(23), 125(21)
p-Benzoquinone	108(100), 54(99), 82(37), 53(32)
Benzotrichloride	159(100), 161(64), 89(14), 163(11)
Benzyl chloride	91(100), 126(28), 65(9), 92(8)
Bis(2-chloroethoxy) methane	93(100), 63(65), 95(32), 27(22)
Bis(2-chloroethyl) ether	93(100), 63(98), 27(75), 95(32)
N,N-Bis(2-chloroethyl)-2-naphthylamine	
Bis(2-chloroisopropyl) ether	45(100), 43(36), 41(34), 77(19)
Bis(chloromethyl) ether	79(100), 49(47), 81(33), 51(16)
Bis(2-ethylhexyl) phthalate	149(100), 57(54), 169(33), 71(27)

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Bromoacetone	43(100), 15(84), 14(19), 79(13)
Bromomethane	94(100), 96(94), 15(47), 93(21)
4-Bromophenyl phenyl ether	248(100), 250(99), 141(45), 77(32)
Brucine	
2-Butanone peroxide	
Butyl benzyl phthalate	149(100), 91(50), 206(18), 104(12)
2-sec-Butyl-4,6-dinitrophenol (DNBP)	
Carbon disulfide	76,(100), 32(22), 44(17), 78(9)
Carbon oxyfluoride	47(100), 66(55), 28(14), 31(4)
Chloral (as hydrate)	*
Chlordane (alpha and gamma isomers)	373(19), 375(17), 377(10)
Chlorinated benzenes, N.O.S.	112(100), 77(45), 114(33), 51(12)
Chlorinated ethane, N.O.S.	64(100), 28(91), 29(84)
Chlorinated fluorocarbons, N.O.S.	**
Chlorinated naphthalene, N.O.S.	162(100), 164(33), 127(30)
Chlorinated phenol, N.O.S.	128(100), 130(33), 65(24)
Chloroacetaldehyde	*

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Chloroalkyl ethers, N.O.S.	**
p-Chloroaniline	127(100), 65(34), 129(31), 92(20)
Chlorobenzene	112(100), 77(45), 114(33), 51(12)
Chlorobenzilate	
p-Chloro-m-cresol	142(100), 107(80), 144(32), 77(24)
1-Chloro-2,3,-epoxypropane	
2-Chloroethyl vinyl ether	63(100), 27(62), 43(42), 44(38)
Chloroform	83(100), 85(64), 47(37), 35(20)
Chloromethane	50(100), 52(32), 15(21), 49(9)
Chloromethyl methyl ether	45(100), 29(25), 15(22), 49(17)
2-Chloronaphthalene	162(100), 164(33), 127(33), 128(17)
2-Chlorophenol	128(100), 130(33), 65(24), 64(12)
3-Chloropropionitrile	49(100), 54(77), 51(39), 53(26)
Chrysene	228(100), 226(26), 229(21), 114(13)
Coal tars	**
Creosote	**
Cresols	**

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Crotonaldehyde	*
2-Cyclohexyl-4,6-dinitrophenol	
DDD	235(100), 237(66), 165(38), 75(21)
DDE	246(100), 318(83), 316(66), 248(58)
DDT	235(100), 237(72), 165(59), 75(22)
Diallate	
Dibenz(a,h)acridine	279(100), 280(25), 139.5(23), 278(14)
Dibenz(a,j)acridine	279(100), 280(25), 139.5(23), 278(14)
Dibenz(a,h)anthracene	278(100), 139(24), 279(16), 276(16)
7H-Dibenzo(c,g)carbazole	
Dibenzo(a,e)pyrene	302(100)
Dibenzo(a,h)pyrene	302(100)
Dibenzo(a,i)pyrene	302(100)
1,2-Dibromo-3-chloropropane	157(100), 155(78), 75(46), 159(25)
1,2-Dibromoethane	107(100), 109(95), 27(54), 28(11)
Dibromomethane	174(100), 93(72), 95(62), 172(52)
Di-n-butyl phthalate	149(100), 41(28), 29(25), 28(22)

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Dichlorobenzene (meta, ortho, and para isomers)	146(100), 148(62), 111(39), 75(23)
Dichlorobenzene, N.O.S.	146(100), 148(62), 111(39), 75(23)
3,3'-Dichlorobenzidine	252(100), 254(67), 256(10), 126(12)
1,4-Dichloro-2-butene	75(100), 89(48), 53(36), 77(33)
Dichlorodifluoromethane	
1,1-Dichloroethane	63(100), 27(72), 65(33), 83(12)
1,2-Dichloroethane	62(100), 64(33), 27(70)
trans-1,2-Dichloroethene	61(100), 96(80), 98(51), 63(29)
Dichloroethylene, N.O.S.	146(100), 148(62), 111(38), 113(13)
1,1-Dichloroethylene	61(100), 96(80), 98(52), 63(33)
Dichloromethane	49(100), 84(72), 86(44), 51(31)
2,4-Dichlorophenol	162(100), 164(65), 63(65), 98(40)
2,6-Dichlorophenol	162(100), 164(64), 63(29), 126(20)
2,4-Dichlorophenoxyacetic acid (2,4-D)	162(100), 220(78), 164(64), 222(49)
Dichloropropane, N.O.S.	63(100), 62(74), 27(41), 41(34)
1,2-Dichloropropane	79(100), 81(38), 43(27), 49(20)
Dichloropropanol, N.O.S.	

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Dichloropropene, N.O.S.	75(100), 77(33), 110(25), 112(15)
1,3-Dichloropropene	75(100), 39(55), 77(32), 49(26)
Dieldrin	79(100), 108(19), 263(18), 277(18)
1,2:3,4-Diepoxybutane	55(100), 44(91), 43(73), 29(65)
N,N-Diethylhydrazine	
O,O-Diethyl S-methyl ester of phosphorodithioic acid	
O,O-Diethylphosphoric acid, O-p-nitrophenyl ester	
Diethyl phthalate	149(100), 177(28), 150(13), 176(9)
O,O-Diethyl O-2-pyrazinyl phosphorothioate	
Dihydrosafrole	163(100), 164(25), 77(19), 51(12)
Diisopropylfluorophosphate	
Dimethoate	
3,3'-Dimethoxybenzidine	244(100), 184(61), 201(38), 229(21)
p-Dimethylaminoazobenzene	120(100), 225(73), 77(58), 42(38)
7,12-Dimethylbenz(a)anthracene	256(100), 241(70), 257(48), 240(46)
3,3'-Dimethylbenzidine	
1,1-Dimethylhydrazine	60(100), 42(51), 59(45), 45(42)

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
1,2-Dimethylhydrazine	60(100), 42(98), 28(53), 45(52)
alpha,alpha-Dimethylphenethylamine	58(100), 91(7), 59(5), 134(3)
2,4-Dimethylphenol	122(100), 107(90), 121(55), 91(20)
Dimethyl phthalate	163(100), 77(19), 164(10), 194(6)
Dimethyl sulfate	15(100), 29(71), 95(66), 31(66)
Dinitrobenzene, N.O.S.	30(100), 75(75), 168(70), 76(52)
4,6-Dinitro-o-cresol (and salts)	
2,4-Dinitrophenol	
2,4-Dinitrotoluene	165(100), 89(65), 90(26), 63(35)
2,6-Dinitrotoluene	165(100), 89(52), 90(35), 148(22)
Di-n-octyl phthalate	149(100), 57(39), 167(32), 279(2)
1,4-Dioxane	28(100), 29(32), 59(24), 88(22)
Diphenylamine	
1,2-Diphenylhydrazine	77(100), 182(29), 105(23), 93(15)
Di-n-propylnitrosamine	70(100), 42(99), 117(79), 43(65)
Disulfoton	
2,4,-Dithiobiuret	

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Endosulfan	201(100), 283(48), 278(30)
Endrin (and metabolites)	81(100), 263(70), 82(61)
Ethyl carbamate	
Ethyleneimine	42(100), 43(62), 28(59), 15(22)
Ethyl methacrylate	
Ethyl methansulfonate	79(100), 109(78), 97(26), 80(19)
Fluoranthene	202(100), 200(20), 203(18), 101(13)
Fluoroacetic acid, sodium salt	
Formaldehyde	*
Formic acid	
Glycidylaldehyde	*
Halomethane, N.O.S.	**
Heptachlor	100(100), 272(60), 274(46)
Heptachlor epoxide (alpha, beta, and gamma isomers)	355(100), 353(79), 351(60)
Hexachlorobenzene	284(100), 286(80), 282(53), 142(29)
Hexachlorobutadiene	225(100), 227(65), 223(63), 260(38)
Hexachlorocyclohexane (all isomers)	181(100), 183(99), 109(80), 217(78)

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Hexachlorocyclopentadiene	
Hexachloroethane	117(100), 119(95), 199(50), 201(85)
1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-endo, endo-dimethanonaphthalene	
Hexachlorophene	
Hexachloropropene	
Hexaethyl tetraphosphate	
Hydrazine	32(100), 31(47), 29(40), 30(31)
Indeno(1,2,3-c,d)pyrene	276(100), 138(38), 277(26), 274(21)
Iodomethane	142(100), 127(38), 141(14), 15(13)
Isocyanic acid, methyl ester	
Isobutyl alcohol	
Isosafrole	162(100), 104(42), 131(30), 103(28)
Kepone	
Maleic anhydride	26(100), 54(62), 25(61), 28(36)
Maleic hydrazide	
Malononitrile	66(100), 38(34), 39(34), 28(31)
Methacrylonitrile	

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Methanethiol	
Methapyrilene	58(100), 97(71), 72(22), 71(19)
Methoxychlor	
2-Methylaziridine	28(100), 56(80), 57(54), 30(37)
3-Methylcholanthrene	256(100)
4,4'-Methylenebis(2-chloroaniline)	
Methyl ethyl ketone (MEK)	43(100), 29(24), 72(17), 27(16)
Methyl hydrazine	46(100), 45(61), 28(58), 31(41)
2-Methyllactonitrile	
Methyl methacrylate	41(100), 69(83), 100(51), 39(36)
Methyl methanesulfate	
N-Methyl-N'-nitro-N-nitrosoguanidine	
Methyl parathion	
Methylthiouracil	
Naphthalene	128(100), 127(20), 129(18), 64(7)
1,4-Naphthoquinone	158(100), 104(39), 76(34), 102(31)
1-Naphthylamine	143(100), 115(45), 116(25), 144(14)

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
2-Naphthylamine	143(100), 115(38), 144(14), 116(13)
Nicotine (and salts)	84(100), 133(27), 42(20), 162(19)
p-Nitroaniline	138(100), 92(50), 108(33), 65(30)
Nitrobenzene	77(100), 128(55), 51(55), 65(25)
Nitroglycerine	46(100), 30(24), 29(15), 76(9)
4-Nitrophenol	65(100), 139(90), 109(72), 81(33)
Nitrosamine, N.O.S.	**
N-Nitrosodi-n-butylamine	84(100), 57(79), 29(53), 41(52)
N-Nitrosodiethanolamine	
N-Nitrosodiethylamine	43(100), 42(68), 44(60), 56(56)
N-Nitrosodimethylamine	74(100), 42(75), 43(40), 44(10)
N-Nitroso-N-ethylurea	
N-Nitrosomethylethylamine	88(100), 42(93), 43(46), 56(24)
N-Nitroso-N-methylurea	
N-Nitroso-N-methylurethane	43(100), 96(76), 66(28), 79(20)
N-Nitrosomethylvinylamine	
N-Nitrosomorpholine	56(100), 116(55), 86(37), 28(13)

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
N-Nitrosonornicotine	
N-Nitrosopiperidine	42(100), 114(91), 55(56), 56(24)
N-Nitrosopyrrolidine	100(100), 41(61), 42(58), 68(16)
N-Nitrososarcosine	
Octamethylpyrophosphormide	
7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid	
Paraldehyde	*
Parathion	
Pentachlorobenzene	250(100), 252(62), 248(62), 108(41)
Pentachloroethane	117(100), 119(96), 167(95), 95(93)
Pentachloronitrobenzene (PCNB)	
Pentachlorophenol	266(100), 264(62), 268(63), 165(54)
Phenol	94(100), 66(19), 65(17)
Phenylenediamine	
Phosphorodithioic acid, 0,0-diethyl S-((ethylthio) methyl) ester [Phorate]	
Phosphorothioic acid, 0,0-dimethyl 0-(p-((dimethyl-amino)sulfonyl)phenyl) ester [Famphur]	

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Phthalic acid esters, N.O.S.	**
Phthalic anhydride	104(100), 76(84), 50(40), 148(39)
2-Picoline	
Polychlorinated biphenyl, N.O.S.	**
Pronamide	
1,3-Propane sulfone	
n-Propylamine	
Propylthiouracil	
2-Propyn-1-ol	55(100), 39(8), 28(6), 29(5)
Pyridine	79(100), 52(71), 51(36), 50(26)
Resorcinol	
Saccharin (and salts)	183(100), 76(99), 50(72), 120(40)
Safrole	162(100), 131(38), 104(31), 135(26)
1,2,4,5-Tetrachlorobenzene	216(100), 214(79), 218(49), 179(15)
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	322( ), 320( )
Tetrachloroethane, N.O.S.	
1,1,1,2-Tetrachloroethane	83(100), 85(66), 131(7), 133(7)

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
1,1,2,2-Tetrachloroethane	131( ), 133( ), 117( ), 119( )
Tetrachloroethene	166(100), 164(78), 129(64), 131(62)
Tetrachloromethane	
2,3,4,6-Tetrachlorophenol	
Tetraethyldithiopyrophosphate	
Tetraethylpyrophosphate	
Tetranitromethane	
Toluene	92(65), 91(100), 65(12), 51(6)
Toluenediamine	121(100), 122(93), 94(17), 105(13)
Toluene diisocyanate	174(100), 145(40), 28(39), 27(38)
Toxaphene	231( ), 233( ), 235( )
Tribromomethane	173(100), 171(50), 175(49), 93(22)
1,2,4-Trichlorobenzene	180(100), 182(95), 184(30), 145(30)
1,1,1-Trichloroethane	97(100), 99(66), 117(17), 119(16)
1,1,2-Trichloroethane	97(100), 83(95), 99(66), 85(60)
Trichloroethene	95(100), 130(90), 132(85), 97(66)
Trichloromethanethiol	

MS - ANALYTICAL IONS (Continued)

Compound	Ions (Intensities)
Trichloromonofluoromethane	
2,4,5-Trichlorophenol	196(100), 198(97), 200(31), 97(20)
2,4,6-Trichlorophenol	196(100), 198(96), 200(31), 132(28)
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP) (Silvex)	
Trichloropropane, N.O.S.	**
1,2,3,-Trichloropropane	75(100), 39(58), 49(42), 110(37)
0,0,0-Triethyl phosphorothioate	
sym-Trinitrobenzene	
Tris(2,3-dibromopropyl) phosphate	
Vinyl chloride	62(100), 27(64), 64(33), 26(18)

N.O.S. = Not Otherwise Specified.

*Mass spectrum for aldehydes depends upon derivatization method

**Mass spectrum depends on specific compound

APPENDIX F

Volatile Organic Sampling Train

Appendix F contains a paper which describes a laboratory evaluation by Midwest Research Institute (Kansas City, Missouri) of a Volatile Organic Sampling Train (VOST).

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DEVELOPMENT OF A VOLATILE ORGANIC SAMPLING TRAIN (VOST)

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ABSTRACT

The hazardous waste incineration regulations include the requirement that, for selected principal organic hazardous constituents (POHCs), a destruction/removal efficiency (DRE) of ≥ 99.99% must be achieved. In order to calculate meaningful DRE values, reliable sampling and analysis methods must be available. This paper reports on the development and evaluation of a volatile organic sampling train (VOST) for the collection of volatile POHCs from stack gas. The VOST is a method designed by the USEPA as an alternative to the use of integrated gas bulbs and bags. The paper includes data concerning the collection and analysis of four volatile POHCs during the laboratory evaluation, descriptions of the equipment, a description of a field version of the VOST, procedures followed to minimize sample contamination in the field, and conclusions and recommendations from the study.

1.0 INTRODUCTION

The results of previous hazardous waste incineration trial burns have suggested that volatile principal organic hazardous constituents (POHCs) and volatile products of incomplete combustion (PICs) may be important components in the incineration effluents. The sampling technique described in a recent sampling and analysis document (1) for volatile organic compounds involves the collection and analysis of integrated gas bulb and bag samples. However, the authors of that report recognized that the gas bag technique suffers several drawbacks, including the need to position the gas bag in a bulky evacuated sampling box, bag leakage problems, adsorption losses of sample components, contamination problems, and low sensitivity when the bulb or bag is analyzed using a gastight syringe sampling technique.

To address the need to develop a better sampling and analysis technique for volatile POHCs, personnel from the Environmental Protection Agency (EPA) discussed concepts for a volatile organic sampling train (VOST) with several contracted laboratories. One concept was adopted for development to provide a method to collect a sufficient quantity of volatile POHCs to enable calculation of destruction/removal efficiencies (DREs) as high as 99.999% for incinerators whose waste feed contains as little as 100 ppm of a POHC.

MRI was selected by EPA to carry out a laboratory study to develop and evaluate the sampling train concenpt. Following the laboratory evaluation of the VOST (2),

a field version of the VOST was designed and built by MRI, and is currently being evaluated under field sampling conditions.

This paper describes how the laboratory evaluation was performed, presents the results of the evaluation, describes the field version of the VOST, and presents conclusions and recommendations based on the results to date.

2.0 VOST CONCEPT

The VOST concept to be evaluated basically consisted of a system designed to draw sample gas at a flow rate of 1 liter/ min through two traps in series. The first trap contained Tenax and was preceded by a gas cooler/ condenser and followed by an impinger for condensate collection. A second trap containing a section of Tenax and a section of charcoal was located after the the impinger. The purpose of the second trap was to collect very volatile POHCs (e.g., vinyl chloride), which have low breakthrough volumes and may break through the Tenax trap. In addition, the concept involved replacing both pairs of traps with fresh traps at selected intervals (i.e., every 20 min or 20 liters of sample) over a 2-h sampling period. There were two basic reasons for changing the traps at selected intervals:

- At sample volumes of greater than 20 liters, some of the very volatile POHCs may break through both the front and backup adsorbent traps.

- The changing of the traps allows an initial analysis of one pair of traps. Analysis of a single pair of traps lowers the possibility of collecting too much sample and overloading the GC/MS system. However, if the POHCs are not detected or are present at low levels in the single pair, the option exists of combining the contents of the remaining pairs of traps onto one pair of traps with a concomitant increase in sensitivity. The advantage of the seond option for samples with low POHC concentrations is given below.

If a hazardous waste incineration facility is achieving a DRE of 99.999% for a POHC that is present in the waste at a concentration as low as 100 ppm, the resulting concentration of that POHC in the flue gas will be approximately 0.1 $\mu g/m^3$ or 0.1 ng/ liter. Sampling 20 liters of that gas will collect only 2 ng of the POHC on a single pair of traps. Since 2 ng may not be detectable by GC/MS analysis, the concept required collection of several (e.g., five) additional pairs of traps and the desorption of their contents onto another pair of traps, thereby providing a total of 10 ng for GC/MS analysis.

It was anticipated that, when the VOST system is used in the field, one will not know whether pairs of traps should be analyzed individually or if the contents of several pairs should be desorbed onto one pair. That is, if the concentration of a selected volatile POHC in the effluent is low (e.g., 0.1 to 1.0 ng/liter), several pairs may need to be desorbed onto one pair to achieve sufficient analytical sensitivity. However, if the concentration is high, the pair of traps should be analyzed individually, since desorption of the contents of several pairs of traps onto one pair of traps would make the quantity even larger and saturate the GC/MS detector. Therefore, the intent was to use the VOST to collect six pairs of sample traps, but with one pair being analyzed first, individually, to determine the amount of selected POHCs present. Then, if warranted, the contents of some or all of the remaining pairs could be desorbed onto one pair for analysis, or other pairs of traps could be analyzed individually to check the variability in the stack gas composition with time.

The selection of a Tenax front trap and Tenax/charcoal backup trap was based on several factors including the authors' previous experience with adsorbents and information in the literature, primarily from work done at Research Triangle Institute (3). Tenax alone is not a very good adsorber for very volatile organic compounds such as chloromethane and vinyl chloride. Charcoal is a good adsorber for the very volatile organics, but compounds that are less volatile are not easily desorbed from charcoal. Thus the dual trap configuration was considered the most versatile for providing efficient sample collection and recovery of all volatile organics.

The plan was developed to evaluate the VOST concept that consisted of the following:

- Set up an experimental system to generate a wet gas stream prepared with four volatile POHCs at each of four different concentration levels as described in Section 3.1.
- Construct three identical VOSTs that would simultaneously draw gas from the synthetic gas stream.
- Set up equipment for conditioning traps and for thermally desorbing the contents of several pairs of traps onto one pair.
- Set up equipment for analyzing traps by GC/MS.

After the above equipment had been set up and made operational, the plan consisted of carrying out a series of 10 tests. The test runs included: tests at each of four concentration levels, replicate tests at one level, blanks, and a test (also at the replicate level) where the gas contained HCl. The purpose of this last test was to determine if HCl, which is present in many incinerator effluents, had any effect on the analysis results. The order of the tests was randomized to prevent bias from affecting the results. The sequence of the tests in this plan was:

Test	Level (concentration of POHCs in gas)	Comment
1	III (10 ng/ℓ)	Exploratory run to check system
2	0 -	Blank run
3	III (10 ng/ℓ)	
4	I (0.1 ng/ℓ)	
5	II (1.0 ng/ℓ)	
6	IV (100 ng/ℓ)	
7	0 -	Blank run
8	II (1.0 ng/ℓ)	Duplicate of Run 5
9	II-HCl (1.0 ng/ℓ)	Duplicate of Run 5 with HCl in gas
10	0 -	Blank run

The equipment used in carrying out the tests is described in the next section.

3.0 LABORATORY EVALUATION OF THE VOST

This section contains descriptions of the equipment and procedures used in the laboratory evaluation of the VOST including:

3.1 Sample Gas Generator System.

3.2 Sampling Train Design.

3.3 Trap Conditioning Equipment.

3.4 Analytical Procedures.

3.5 Results.

3.6 Summary and Interpretation of Results.

3.1 Gas Generation System

As shown in Figure 1, the gas generation system consisted of 1/2-in. (1.27 cm) stainless steel tubing to carry vaporous N_2 from a liquid N_2 tank through a heater, where the N_2 was heated to about 300°F (149°C). At that point, the N_2 was rendered "wet" by vaporizing deionized/charcoal-filtered water fed through a quartz tube heater. Also near that point, the liquid containing the four POHCs was pumped by a syringe pump (5 ml/h) into the hot N_2 stream where the liquid immediately vaporized to a gas.

The liquid injected by the syringe pump was a solution of the four POHCs, vinyl chloride, carbon tetrachloride, trichloroethylene, and chlorobenzene in methanol.

The concentrations of each of the four POHCs tested are listed in Table 1.

The solution with the highest concentration (Level IV) was prepared first, then aliquots were serially diluted with methanol to prepare the three lower concentration solutions. These same solutions were used as calibration standards for the subsequent analyses.

Following the steam and POHC solution injection point, the gas stream entered a sampling manifold, with a perforated dispersing plate at the inlet. Gases were drawn from this manifold into the three sampling trains. After the manifold, the hot gas (11 to 12 liters/min) passed through a series of impingers (for water

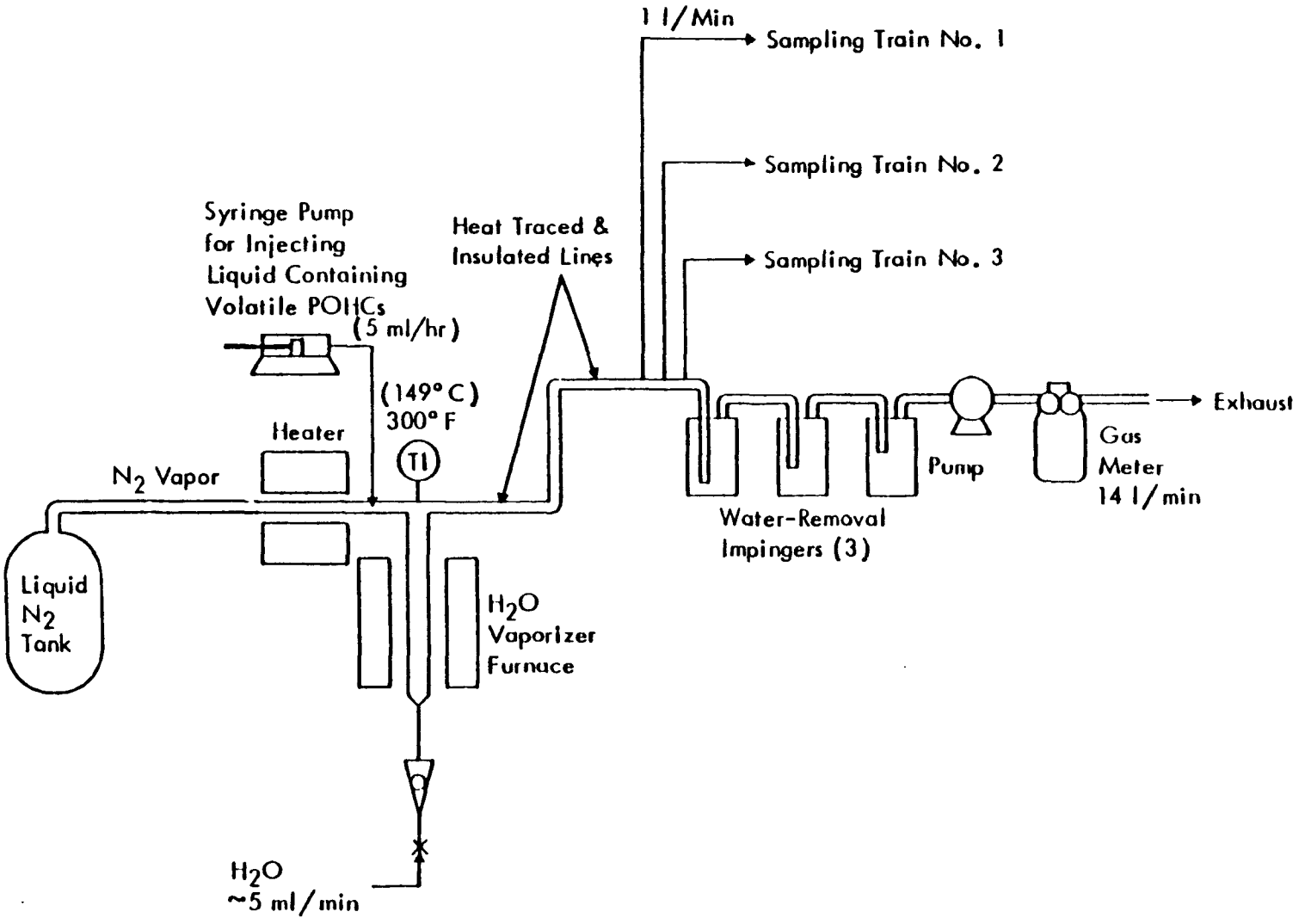

Figure 1. Schematic diagram of laboratory apparatus used to generate and sample a simulated stack gas containing known concentrations of volatile POHCs.

TABLE 1. POHC CONCENTRATIONS TESTED DURING LAB EVALUATION OF THE VOST

Level	Concentration in methanol solution (ng/ml)	Expected conc. in gas stream (ng/ℓ)	Expected amount on each pair of traps (ng)
I	84	0.1	2
II	840	1.0	20
III	8,400	10.0	200
IV	84,000	100.0	2,000

removal) and on through a pump and dry gas meter.

During each of the tests, the gas generation system operated quite well, and all readings were consistent from run to run. The water content of the gas stream ranged from 35 to 37 volume percent, as measured by the impingers and gas meter.

During Run 9, HCl was added to the water at a level of 1.3 g of HCl per liter of water to provide an HCl concentration in the gas of about 0.5 g/Nm^3 (normal cubic meter). This is the HCl concentration estimated to occur in the effluent from an incinerator burning a waste containing 15% Cl and equipped with a wet scrubber operating at the relatively low HCl removal efficiency of 95%.

The gas flow rate in the gas generator system and the POHC syringe pump injector rate were used to compute an "expected value" for the quantity of each POHC in the Tenax traps. It was not feasible within the scope and time frame of this project to quantify the actual concentration of the POHCs in the gas produced by the gas generator system. An independent analysis of the spiked gas stream would have been desirable but very difficult to accomplish; however, the subsequent VOST data gave little or no reason to believe that the actual gas stream concentrations were significantly different than the computed "expected values."

3.2 Sampling Train Design

Figure 2 shows the VOST configuration that was evaluated. The train consisted of:

- A sampling line (1/4-in., 0.64 cm, Teflon tubing in the test system);
- First condenser;
- Tenax trap;
- Impinger (for condensate removal);
- Second condenser;
- Tenax/charcoal trap; and
- Other sampling components (rotometer, pump, dry gas meter).

Except for the Teflon sampling line, most of the components were made of glass, including the traps. However, the fittings at the inlet and outlet of each trap were stainless steel.

When the trains were initially assembled, two problems developed. First, the 5/8-in. (1.58 cm) stainless steel Swagelok fittings for the inlet traps were designed to slip over the glass trap, but some of the traps had an outside diameter slightly larger than the inside diameter of the Swagelok nut. Thus, all the nuts had to be drilled out. Secondly, some of the glass traps were out-of-round. This meant that some traps, when inserted into the sampling train, would not leak-check unless the fittings were tightened with wrenches. Several tubes broke before they could be tightened enough to pass a leak-check. Since checking for leaks and correcting of leaks can take considerable time, the adsorbent traps were redesigned for field use as described in Section 4.0.

Before each run, the gas generation system was started up and allowed to operate for about 1 h. During that time, traps were connected in the three trains and leak-checked. All three trains were then started and operated for 20 min at

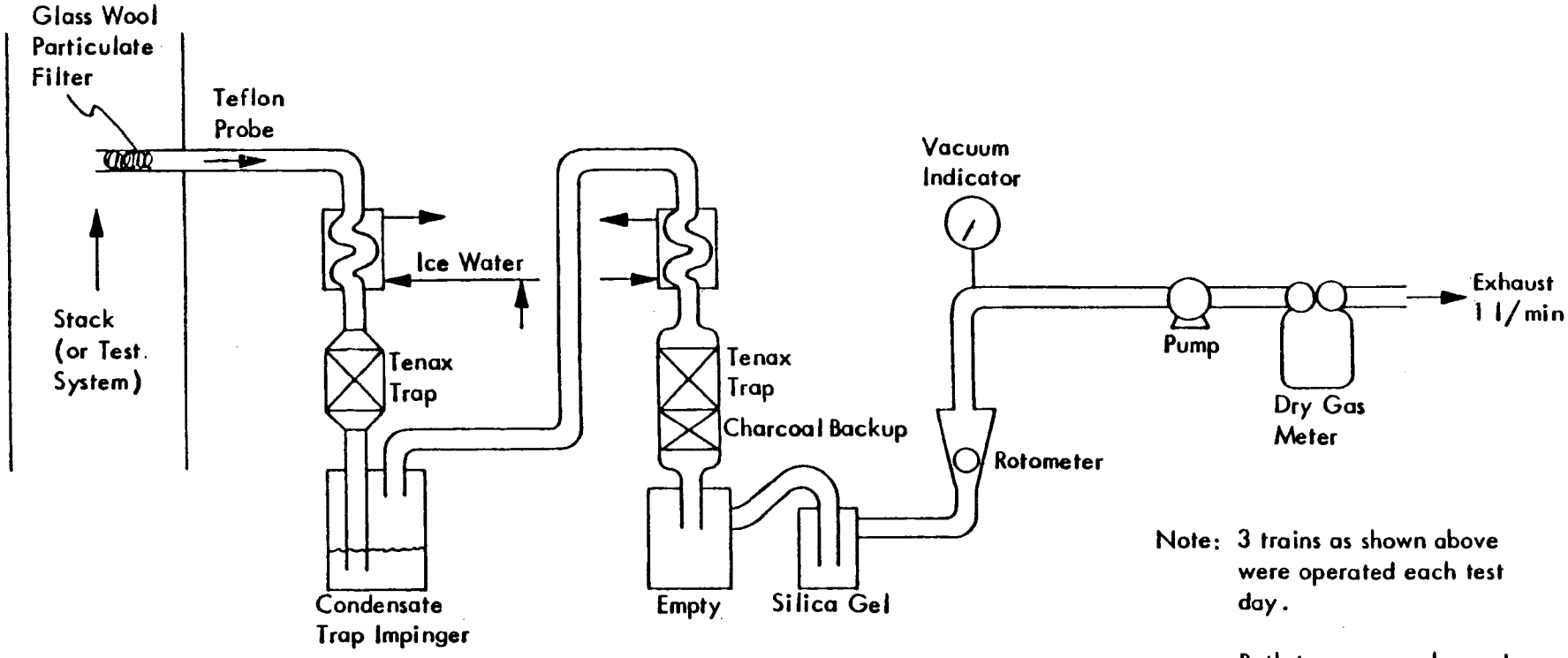

Figure 2. Volatile organic sampling train (VOST).

about the same rate (1 liter/min).* All three sampling trains were then shut off and the traps removed and placed in pre-marked container tubes. Another pair of traps were then inserted in each train and leak-checked before starting the next 20-min sampling period. A run was considered complete after six pairs of traps had been used in each train. During each run, ice water was circulated through the condensers. Thermocouples, located against the surface of the condenser outlet tubes, indicated that the gas temperature entering the first trap was in the range of 60 to 80°F (16 to 27°C). (The train with the longest Teflon sampling tube yielded the lowest temperature.)

Overall, the train configuration caused no particular difficulty, except for the leak-check problem described above. However, using this train configuration to sample a "wet" gas stream saturates the first trap with condensate. This caused no problems in the sampling but did require development of special procedures for analyzing the wet traps, as discussed in Section 3.4.

3.3 Trap Conditioning Equipment

The trap conditioning/desorption apparatus, purchased from Nutech** (Model No. 322), served two purposes for the VOST evaluation. First, it was used to condition traps prior to use, by heating them at 250°C for 4 h with an estimated flow of 30 ml/min of purified nitrogen gas through each trap. Second, it was used to thermally desorb the contents from each of several low-level pairs of traps onto one pair of traps for GC/MS analysis. The purpose of this desorption/adsorption was, in effect, to further concentrate the samples from the sampling train.

A schematic diagram of the conditioning/desorption apparatus is shown in Figure 3, along with the trapping system that was added at the outlet to re-adsorb the contents from the desorbed pairs of traps.

When four traps were being desorbed (which is the capacity of one section of the desorption apparatus), the carrier gas (N_2) exits the desorption chamber hot, but cools rapidly. However, when the traps being desorbed are wet, the cooling is not nearly so rapid because of the steam that must be condensed. Thus, it was necessary to use a condenser at the outlet of the conditioning equipment, in front of the first trap (Tenax). An impinger was also required to remove the condensate before the desorbed gas passed into the second trap. As a result, the re-adsorption system of traps at the outlet of the desorption equipment is equivalent to the sampling train itself. Also, the condensed steam again wets the first trap, so the need to analyze a wet trap still remains.

When using the Nutech conditioning apparatus to desorb several pairs of traps (e.g., five pairs), the conditioner was first heated to its normal operating temperature of 250°C. Four traps were then dropped into the chambers and allowed to remain there for 10 min (with the total N_2 carrier flow of 120 ml/min passing through the four traps). These four traps were then removed and four more traps inserted, repeating the procedure until all five pairs had been desorbed onto the one pair at the outlet. This pair, or any pair analyzed individually without first being desorbed, was then spiked with an internal standard and analyzed using the equipment and procedures described in Section 3.4.

3.4 Analytical Procedures

The analytical procedures described below include cleanup of the Tenax and charcoal prior to packing into traps, preparation of the traps, conditioning of the traps prior to sampling, spiking of the traps with an internal standard following sampling, GC/MS analysis of the traps, and data reduction.

3.4.1 Tenax and Charcoal Cleanup--

The Tenax (35/60 mesh) and SKC petroleum-based charcoal (Lot No. 104) were initially prepared by Soxhlet extraction for 24 h with methanol and then with pentane. The sorbents were then dried in a vacuum oven at 100°C for 6 h prior to loading into empty traps, each engraved with a unique number.

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* Gas flow rates in liters per minute refer to normal conditions of 20°C, 1 atm (dry basis).

** Nutech Corporation, 2806 Cheek Road, Durham, NC 27704.

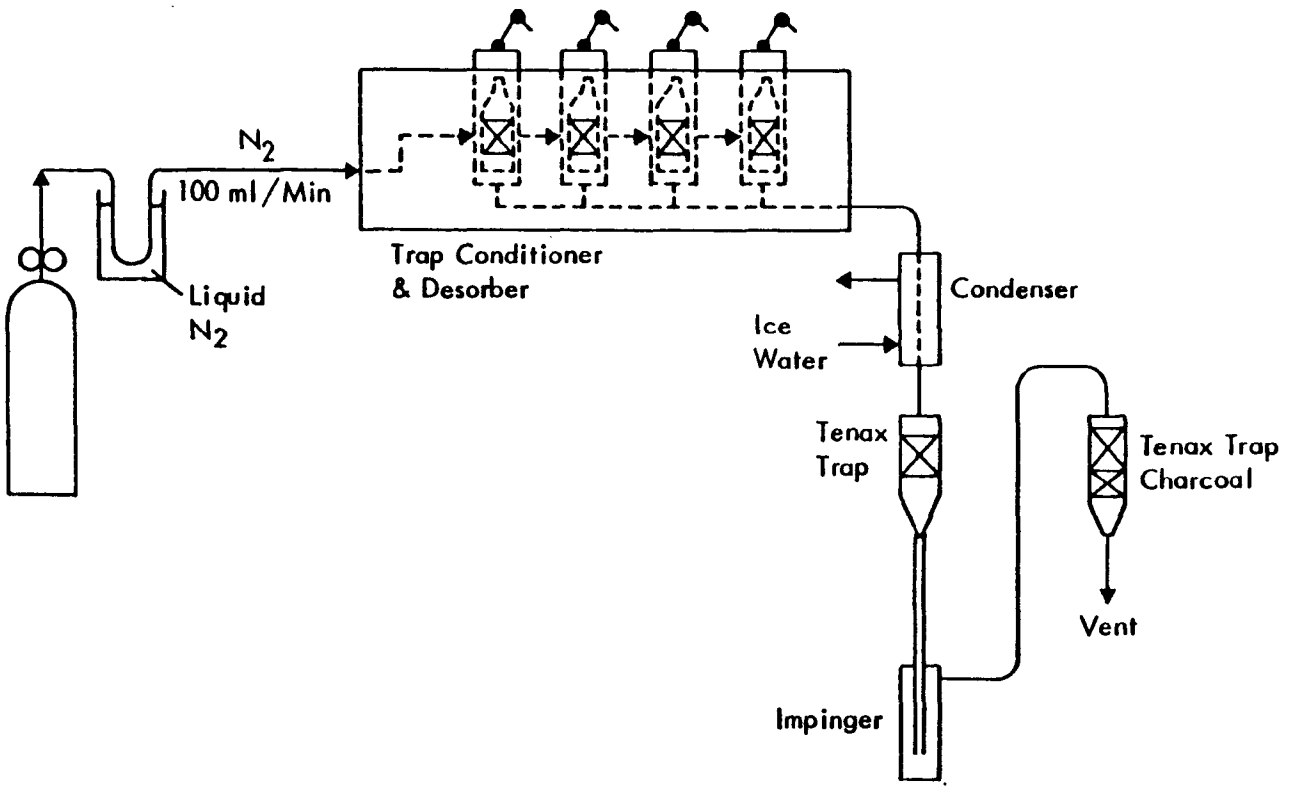

Figure 3. Schematic diagram of trap conditioner/desorption apparatus.

3.4.2 Preparation of Traps--

The 10- x 1.6 cm glass traps with one nippled end (to facilitate removal of the traps from the desorption apparatus with tweezers), available from the Nutech Corporation, were used for the VOST evaluation. A minimum amount of pre-extracted and oven-dried glass wool was used in each of the glass tubes to hold the sorbents in the glass traps. The all-Tenax traps contained about 1.6 g of Tenax, and the Tenax/charcoal traps contained about 1 g of Tenax and 1 g of charcoal (two-thirds Tenax by volume).

3.4.3 Trap Conditioning--

The traps were thermally conditioned prior to use, using the Nutech Model 322 thermal conditioning unit. The conditioning gas (nitrogen or helium) was purified by passing through a U-trap containing a 5-angstrom (5×10^{-8} cm) molecular sieve with the U-trap immersed in liquid nitrogen. The temperature of the conditioning unit was adjusted to 240 to 250°C, and the flow rate of gas through each trap was estimated to be about 30 ml/min. However, only the sum of the flow through four of the traps, which was set at 120 ml/min, could actually be measured with the Nutech conditioning unit. The traps were conditioned for at least 6 h prior to their first use in the VOST evaluation and for at least 2 h more prior to use in sampling. The actual flow through each trap may be lower due to the fact that some of the conditioning gas may flow around rather than through the traps. Also residual pentane was observed during several subsequent analyses of the traps, suggesting that the conditioning step was not completely effective.

Following conditioning, each trap was transferred to a clean 25- x 150-mm screw-cap test tube engraved with the same unique number as engraved on the trap. The traps were then ready for sample collection or spiking experiments.

3.4.4 Spiking of Traps with Internal and Calibration Standards--

Prior to GC/MS analysis, all Tenax and Tenax/charcoal adsorbent trap samples and standards were spiked with 25 ng of perfluorobenzene (PFB) internal standard using the flash vaporization technique in which the spiking solution is vaporized and carried onto the trap with a carrier gas. The glass traps were attached to the injection port (160°C) of a GC with a 5/8-in. (1.58 cm) stainless steel Swagelok nut containing Teflon ferrules. The Swagelok fitting was connected to the GC column connection via a reducing fitting. The helium flow through the traps was set to about 50 ml/min. The gas flow through the trap was turned on and off using the shutoff valve on the side of the Varian 1400 GC.

The spiking solution was loaded and expelled from the syringe using the solvent flush technique to ensure that the standard solution would be completely expelled from the syringe. To use this technique, the needle of a 5.0 µl syringe was filled with clean methanol. The methanol was then expelled leaving methanol only in the syringe needle. Then air was drawn into the syringe to the 1.0 µl mark followed by a 25-ng/µl methanolic solution of the PFB to the 2.0 µl mark. The gas flow was turned on through the trap and the syringe needle inserted through the GC septum port. The contents of the syringe were then slowly expelled over about a 15-s period. At the end of about 25 s, the gas flow through the trap was shut off and the syringe removed. All POHC calibration standards were spiked using exactly the same procedure. The total flow of gas through the traps during spiking was thus only about 25 ml.

3.4.5 GC/MS Analysis of the Traps--

To analyze the traps, the contents of the wet traps (dry traps in the case of method blanks, field blanks, and calibration standards) were thermally desorbed using a stream of carrier gas into a water column (1 to 5 ml); this is a component of the EPA Method 624 purge-trap-desorb GC/MS analysis system. A schematic diagram of the apparatus is shown in Figure 4. The sample trap was dropped into the desorption chamber and desorbed at a flow rate of 100 ml/min for 10 min at 180°C. The desorbed compounds passed into the bottom of the water column, were purged from the water, and then were collected on an analytical adsorbent trap also containing Tenax and charcoal. The compounds were then desorbed from the analytical adsorbent trap into the GC/MS system per EPA Method 624.

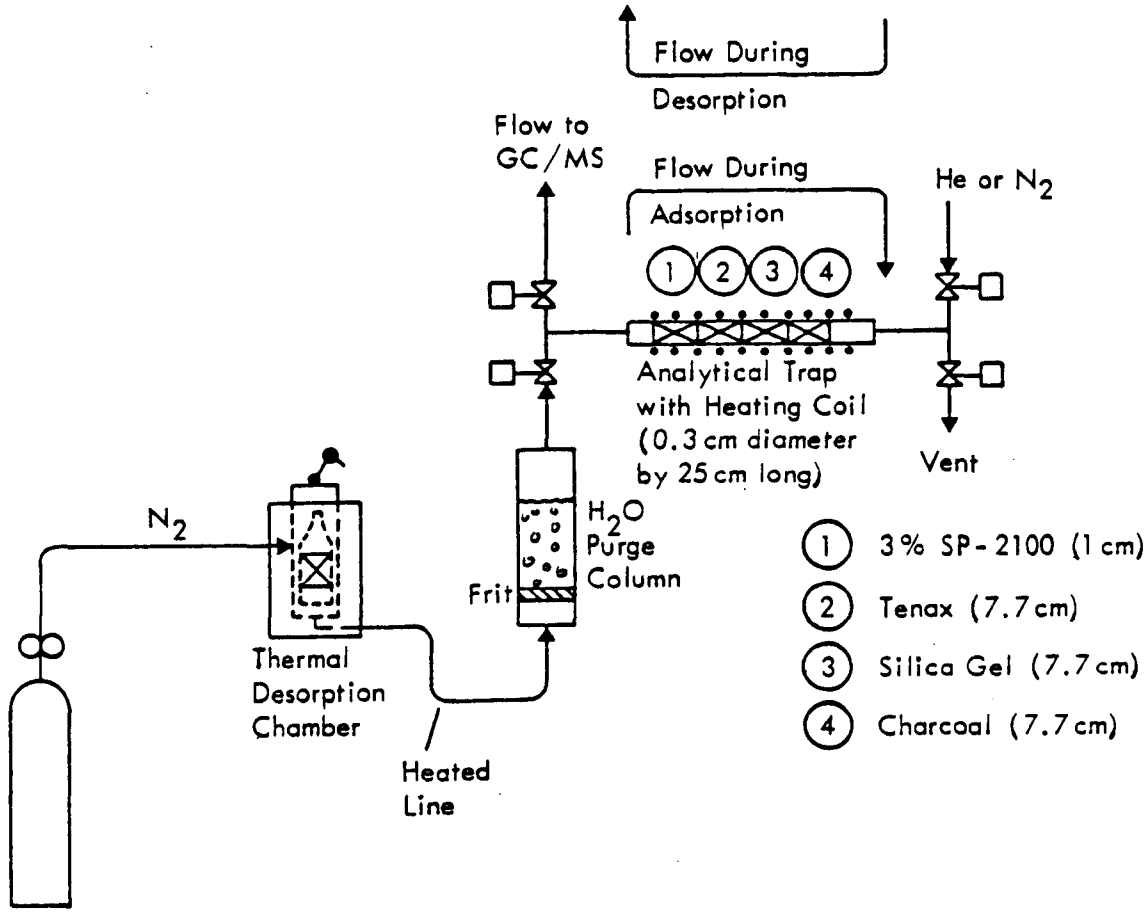

Figure 4. Schematic diagram of trap desorption/analysis system.

The normal routine for analyzing a set of traps from each of the laboratory VOST evaluation runs was to analyze a calibration standard on Tenax, a calibration standard on Tenax/charcoal, and then to intersperse calibration standards about every fourth sample. Blank Tenax and blank Tenax/charcoal traps (conditioned traps spiked with internal standard) were also analyzed when the samples from the blank VOST train were analyzed. The same POHC solution used to spike the wet gas in the VOST runs was used to prepare the calibration standards for quantification of the POHCs on the traps.

The problem of analyzing the wet sample traps was overcome by desorbing the contents of the wet traps into an aqueous purge and trap apparatus. Since the purge and trap technique initially appeared to offer minimal risk of losing or affecting the very small amounts of each compound to be quantified (i.e., 2 to 10 ng of POHC), and was basically consistent with an accepted EPA method, it was used in this evaluation. The Nutech apparatus was initially tested in the normal cryogenic trapping configuration, but the desorbed water froze and clogged the analytical system. Other wet trap analysis techniques were considered but not investigated because of lack of time and possible associated problems.

3.4.6 Data Reduction--

The POHCs in the samples were quantified using the internal standard technique. The area of the masses of m/z 62 for vinyl chloride, m/z 117 for carbon tetrachloride, m/z 130 for trichloroethylene, m/z 112 for chlorobenzene, and m/z 186 for the perfluorobenzene internal standard were used to calculate response factors from analysis of the 8.4- and 84-ng calibration standards according to the equation:

$$\text{Response Factor (RF)} = \frac{(A_S)\ (C_{IS})}{(A_{IS})\ (C_S)}$$

where: A_S = The area of ion for the POHC.
A_{IS} = The area of the ion for the internal standard (m/z 186).
C_{IS} = The amount of internal standard (25 ng).
C_S = The amount of POHC in the calibration standard (generally 8.4 or 84 ng).

The amounts of the POHCs in the samples were then calculated according to:

$$\text{Amount of POHC} = \frac{(A_S)\ (C_{IS})}{(A_{IS})\ (RF)}$$

The reproducibility of the internal standard area counts (m/z 186) was very good with an average variation of only about 10% for a daily batch of samples at a given multiplier setting. There did not appear to have been any particular difference in perfluorobenzene area counts with the type of trap; e.g., wet traps or Tenax/charcoal traps did not give lower area counts than dry traps and Tenax-only traps. This is in contrast to the POHC vinyl chloride which gave higher response on Tenax than on Tenax/charcoal traps during analysis of calibration standards. The reason for this is as yet undetermined. There is no reason to believe that the vinyl chloride broke through the Tenax to the charcoal because only about 15 ml of gas passes through the trap during spiking.

3.5 Results

It was noted in Section 2.0 that a total of 10 runs were made during this evaluation, involving four different concentration levels of the POHCs and three blank runs. After each run, the traps from each of the three trains were analyzed and results reported for the traps as pairs (i.e., Tenax trap plus Tenax/charcoal trap). Not all pairs were analyzed, especially at the higher concentration levels, where it was not necessary to desorb several pairs onto one pair. In most cases, at the lower concentration levels, one pair of traps from each train were analyzed individually, while all remaining pairs from each train were desorbed onto a single pair for analysis. Several calibration standards were analyzed along with the traps from each run in order to be able to quantify a wide concentration range.

Results were initially calculated after each run based on calibration standards analyzed with the samples from each run. After all runs and analyses had been completed, the results were recalculated based on the average mass spectrometric response factor of all the appropriate calibration runs using the internal standard technique described earlier in Section 3.4.6. These response factor data are

shown in Table 2. The data in Table 2 also show transfer efficiencies determined for desorbing several pairs of traps with readsorption onto a single pair. Since the transfer efficiency for vinyl chloride was relatively low (49%), the reported values for vinyl chloride were corrected for this low transfer efficiency. Also, the data for the four POHCs were blank-corrected, as discussed below.

Three blank runs were carried out using the gas generation system and three VOSTs, but without any injection of the solution containing the POHCs into the system. The results for these blank runs are shown in Table 3 and include analyses of single pairs, and several pairs combined onto one pair. As can be seen in Table 2, most of the blank values are relatively low, but are still significant relative to the run at the lowest concentration level where the expected amount of any POHC on each pair was only about 2 ng. In this regard, the blank values for carbon tetrachloride in Runs 7 and 10 are higher than the expected value. Thus, it was not possible to blank-correct the carbon tetrachloride results obtained in the lowest level run (Run 4), which makes it difficult to make any definitive conclusions about using the VOST train for detecting such low levels of carbon tetrachloride.

The problem with the high carbon tetrachloride blanks was evident after Run 7, and therefore another blank run was made (Run 10), after the gas generation system and the trains were purged with vapor from the liquid N_2 tank at room temperature for 24 h. However, the blank carbon tetrachloride values were again found to be high in Run 10. Other blank traps were analyzed which had not been exposed to the gas generation system, but had been exposed to room (laboratory) air, and no POHCs were detected in these blanks (i.e., < 0.5 ng). The absence of carbon tetrachloride in the blanks suggested that the high blank values for carbon tetrachloride resulted from within the gas generation system or the sampling trains and was not a result of any subsequent analytical procedures or contamination from the ambient room air.

Except for the carbon tetrachloride data from the lowest level run, all uncorrected and blank-corrected results were tabulated, with the corrected values being used to compute the results as a percentage of the expected value. These tabulated data are summarized in Table 4. The data in Table 3 provide information on results computed as averages but do not show the range in results. The compounds are discussed individually below.

3.5.1 Vinyl Chloride--

Figure 5 (for vinyl chloride) shows all results, blank-corrected and corrected for the 49% transfer efficiency when transferring the contents of several pairs of traps onto one pair.

The results for vinyl chloride at the 0.1 and 1.0 ng/liter gas phase concentrations appear to be similar, with total recoveries when analyzing single pairs ranging from 48 to 95% of the expected value. When combined pairs were used the recoveries ranged from 48% of the expected value up to 148%. Conversely, at the 10 ng/liter level where only single pairs were analyzed, all except one data point are greater than the expected value, ranging from 100 to 180% of the expected value. This is a rather wide range, but vinyl chloride is very volatile, and it is commonly recognized that analyses for this compound are difficult.

At the highest concentration level (Level IV, 100 ng/liter gas-phase concentration, 2,000 ng/pair of vinyl chloride expected on the traps), the results were consistently low (~ 48% recovery). Although nearly all of the other POHCs were consistently found on the first Tenax trap of any pair, most of the vinyl chloride was found on the backup Tenax/charcoal trap. The data thus suggest that breakthrough or irreversible adsorption of the vinyl chloride occurred at the highest concentration level. Thus in any further testing, one should be aware that this may occur when using the VOST method at high concentrations of vinyl chloride.

3.5.2 Carbon Tetrachloride--

The results for carbon tetrachloride are shown in Figure 6. These data are all blank-corrected except for the data at the lowest concentration level. As a consequence, the data at the 0.1 ng/liter level exhibit some very high values, which undoubtedly are not representative.

TABLE 2. GC/MS RESPONSE FACTOR AND THERMAL DESORPTION COLLECTION EFFICIENCY FOR FOUR VOLATILE POHCs

Compound	Avg RF[a]	σ	% RSD[b]	n[c]	Type of trap	RF[f] following desorption	n	Desorption transfer efficiency
Vinyl chloride	0.140	± 0.042	30	15	T/C[d]	0.069	2	49
Carbon tetrachloride	0.197	± 0.069	35	13	T[e]	0.143	2	73
Trichloroethylene	0.490	± 0.068	14	14	T	0.435	2	89
Chlorobenzene	0.338	± 0.065	19	14	T	0.331	2	98

[a] Mass spectrometric response factor relative to perfluorobenzene.

[b] RSD = Percent relative standard deviation, which equals σ ÷ Mean x 100.

[c] n = Number of determinations (includes 8.4 and 84 ng calibration standards).

[d] T/C = Tenax/charcoal (~ 70:30 v/v) trap.

[e] T = All-Tenax trap (1.6 g).

[f] Contents of calibration standard thermally desorbed onto type of adsorbent trap in previous column.

TABLE 3. TABULATION OF DATA FROM BLANK RUNS

Blank run No.	No. of combined pairs	Amount detected (ng)[a] Vinyl chloride	Carbon tetrachloride	Trichloro-ethylene	Chloro-benzene
		Single pairs data			
2		----------	No single pairs analyzed		----------
7		< 0.5	12.5	0.7	0.8
7		< 0.5	3.6	0.2	0.6
7		< 0.5	3.5	< 0.5	< 0.5
10		< 0.5	1.2	3.4	< 0.5
10		< 0.5	3.7	< 0.5	< 0.5
10		< 0.5	< 0.5	2.0	< 0.5
Avg for single pairs[b]		0	4.1	1.1	0.2
		Combined pairs data			
2	4	5.4	< 0.5	2.3	8.0
2	4	4.8	< 0.5	2.5	6.4
7	5	4.7	35	5.0	8.1
7	5	1.1	49	6.6	10.0
7	5	Lost	17	6.3	4.0
10	5	< 0.5	53	4.8	1.8
10	5	< 0.5	50	2.2	3.6
10	5	< 0.5	54	3.0	6.2
Average per pair for combined pairs		0.5	6.8	0.9	1.3

[a] Amounts calculated based on average response factor determined from all standards (response factor for VC was based on analyzing standards on Tenax/charcoal traps; the other compounds were based on analyzing standards on Tenax traps).

[b] Less than values were assumed to be zero in order to compute an average.

TABLE 4. VOST DATA SUMMARY

Run No.	Expected gas phase concentration of each compound (ng/liter)[a]	No. of cartridge[b] pairs analyzed (i.e., replicates)	No. of cartridge[b] pairs combined for analysis	Average expected value (ng)	Average amount found, in ng, - blank corrected,[d] and (%[d] of average expected value)							
					Vinyl chloride[c]		Carbon tetrachloride[d]		Trichloroethylene		Chlorobenzene	
					Single pairs	Combined pairs	Single pairs	Combined pairs	Single pairs	Combined pairs	Single pairs	Combined pairs
2	0	2	4	0	-	5.1		< 0.5		2.4		7.2
7	0	3	0	0	< 0.5		6.5		0.3		0.5	
7	0	3	5	0		2.9		34		6.0		7.4
10	0	3	0	0	< 0.5		1.6		1.8		< 0.5	
10	0	3	5	0		< 0.5		52		3.3		3.9
4	0.1	2	0	1.9	1.5(79%)		4.2(221%)[d]		1.5(79%)		1.8(95%)	
4	0.1	3	5 (4 in 1 set)	9.1		10.1(111%)		16(176%)[d]		8.8(97%)		9.5(104%)
5	1.0	3	0	19	12(63%)		9(47%)		22(116%)		29(153%)	
5	1.0	3	4	77		37(48%)		68(88%)		83(108%)		101(131%)
8	1.0	3	0	20	17(85%)		11(55%)		23(115%)		21(105%)	
8	1.0	3	4	79		115(146%)		89(113%)		83(105%)		91(115%)
9	1.0 (with HCl)	3	0	20	19(95%)		8(40%)		19(95%)		18(90%)	
9	1.0 (with HCl)	3	4	77		61(79%)		85(110%)		81(105%)		74 (96%)
3	10.0	7	0	193	274(142%)		136(70%)		210(109%)		204(106%)	
3	10.0	-	0	-		-		-		-		-
6	100.0	6	0	2,020	870(43%)		2,180(108%)		2,660(132%)		2,050(101%)	
6	100.0	-	0	-		-		-		-		-

[a] Gas volume in liters refers to dry standard conditions (20°C, 1 atm).

[b] Cartridge pairs refers to one Tenax cartridge and an associated Tenax + charcoal cartridge.

[c] Data for vinyl chloride include correction for 49% transfer efficiency when several pairs are desorbed onto one pair (per Table 1).

[d] All values are blank-corrected except for carbon tetrachloride in Run 4, due to large average blank value (per Table 2).

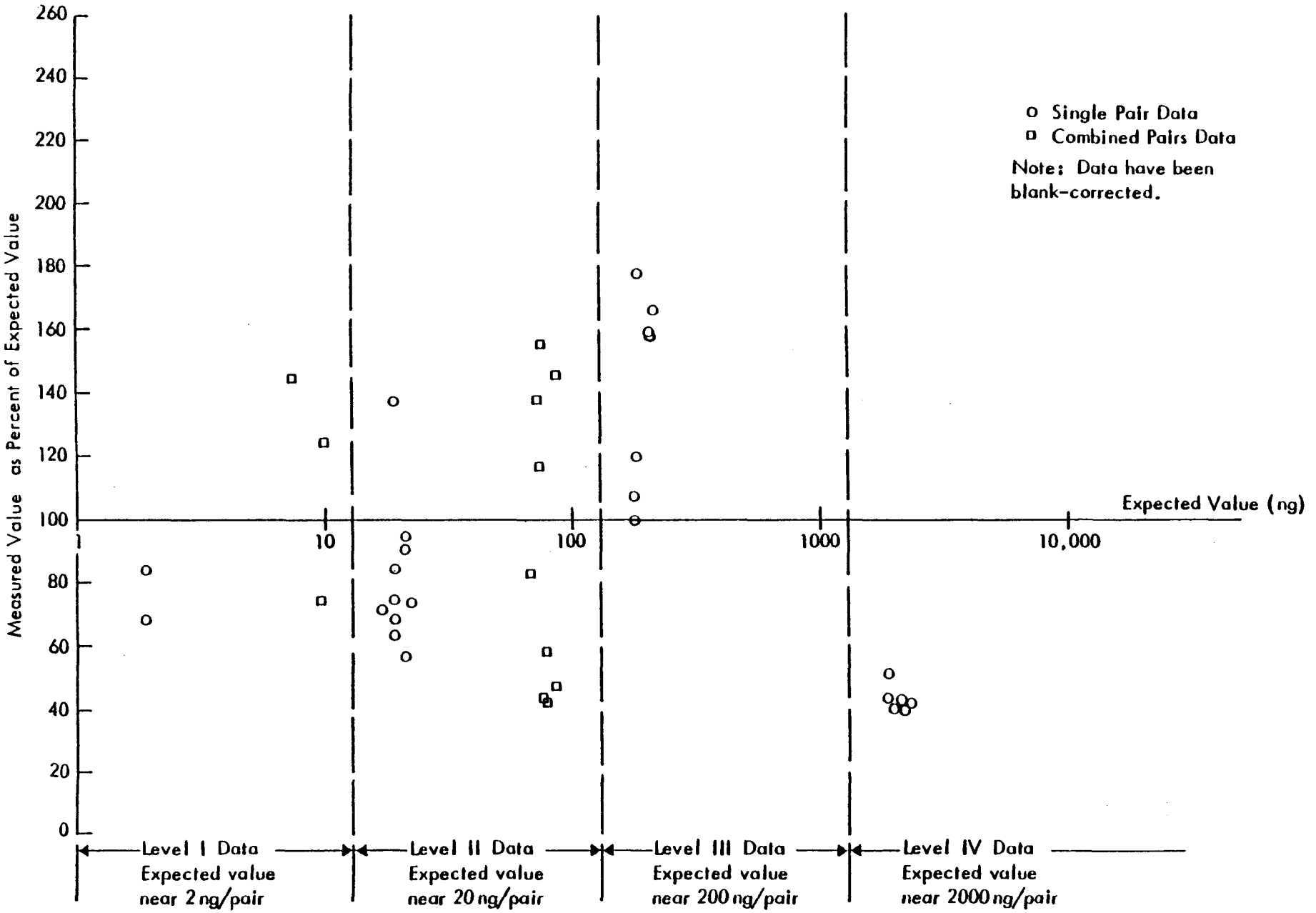

Figure 5. Vinyl chloride test results.

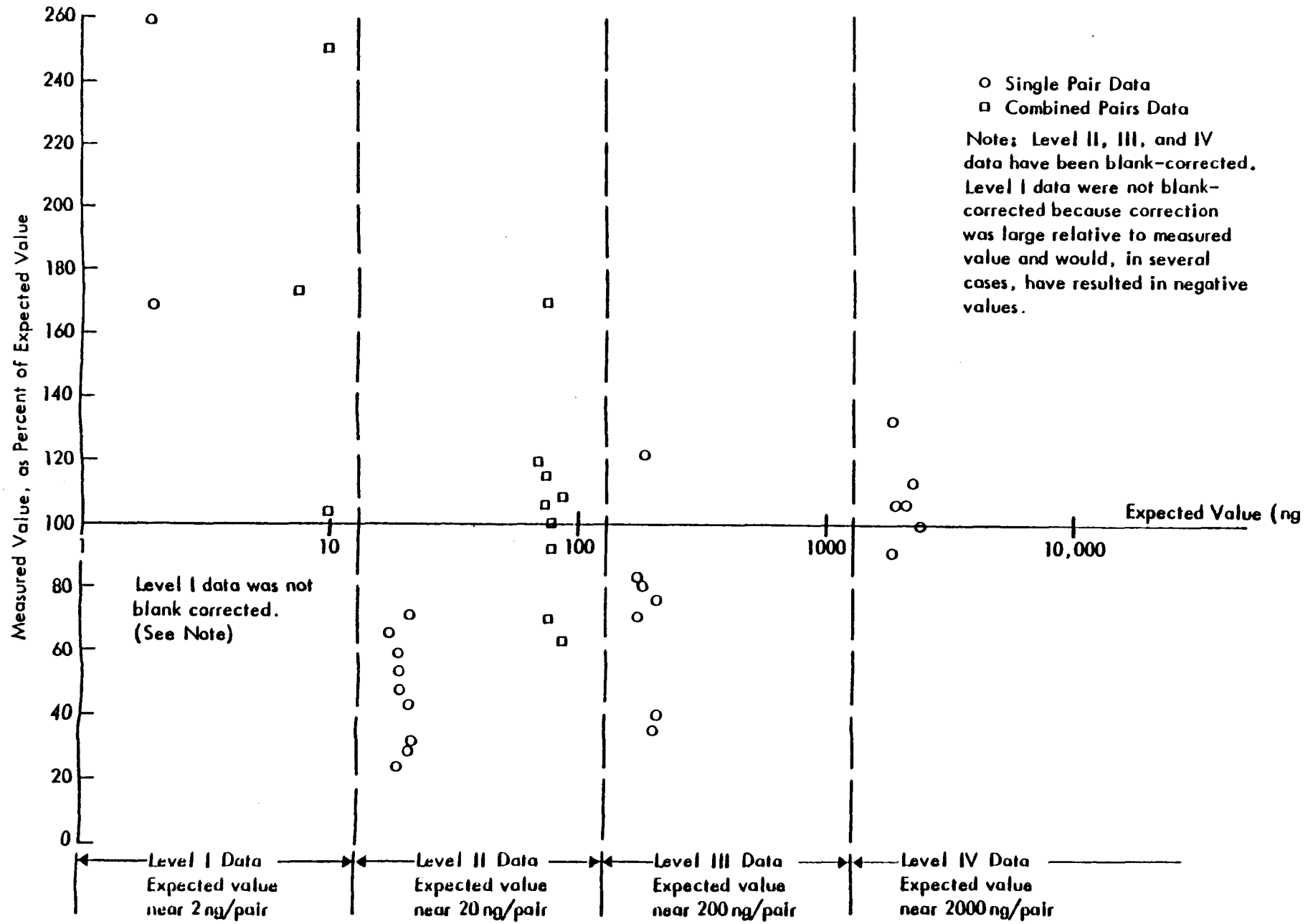

Figure 6. Carbon tetrachloride test results.

Data at the 1.0 ng/liter level are similar to that found for vinyl chloride, in that all data for single pairs are less than the expected value, but data for combined pairs range from 60 to 170% of the expected value. This phenomenon is not as yet explainable, but most probably relates to the quantity present on any trap being analyzed and the characteristics of the purge-trap-desorb and GC/MS analysis method. As originally conceived, the intent would be to rely on results for combined pairs at low levels, which does seem to be supported by the data.

At the 10 ng/liter level, data for all the single pairs, except one, were less than the expected value, ranging from 36 to 120%. Thus, a result for any single pair might be quite low, but it is anticipated that, in any field testing, results would be based on the average of the analysis of several pairs, which in this case would have yielded an average value of 70% of the expected value. It is evident in Figure 6 that, at the highest concentration level (100 ng/liter), all the single pair results were quite close to the expected value.

In summary, the results for carbon tetrachloride do not indicate any major deficiency in the VOST method, except for the relatively high blank values and their effect on results at the lowest concentration level. If these blank values were due to the gas generation system, then high blank values might not be a problem in any field testing. However, if the high blanks somehow resulted from the sampling trains, further work would be needed to determine how trains should be cleaned and prepared prior to each test to minimize blank problems.

3.5.3 Trichloroethylene--

Results for trichloroethylene, given in Figure 7 (blank-corrected), show a much narrower range at all concentration levels than did the results for vinyl chloride or carbon tetrachloride. The extremes varied from 70% of the expected value (at the 0.1 ng/liter level for combined pairs), up to slightly above 140% of the expected value (at the 100 ng/liter level for single pairs). These results appear to be quite good for this compound using the VOST method.

3.5.4 Chlorobenzene--

Results for chlorobenzene, given in Figure 8 (blank-corrected), are not as narrow as for trichloroethylene, but do show decreasing variability with increasing concentration levels. Again, data at the lowest concentration level showed the greatest deviation from the expected value, ranging from 36% up to 173% of the expected value. However, at the next higher concentration level (1.0 ng/liter), data for combined pairs ranged from 88% to about 140% of the expected value. At 10 ng/liter, the results for the single pairs were about the same, ranging from 70% to about 140% of the expected value. As is evident in Figure 8, the range at the highest level was very narrow.

3.6 Summary and Interpretation of Results

The preceding sections have shown that, at the two lowest concentration levels, the results for combined pairs of traps might range from 38 to 173% of the expected value (excluding higher values for carbon tetrachloride at the lowest level, which were not blank-corrected). However, the data presented earlier in Table 4 show that if three trains (or three runs) are used, the average for combined pairs may range from 48% up to 146% of the expected value. At the two highest concentration levels, the average for several pairs analyzed individually ranged from 70% up to 142% of the expected value (excluding a 43% average value for vinyl chloride at the highest concentration level where it appears that breakthrough or irreversible adsorption occurred).

If one assumes, for simplicity of number, that the average value from three tests may span a range of 50 to 150%, it is possible to determine the implications on a subsequent calculation of DRE based on that range, as explained in the two scenarios given below.

In the first scenario, one may be trying to determine DRE for an incinerator that is actually achieving 99.999% for a POHC present in the waste at the low concentration of 100 ppm. As mentioned earlier, the approximate resulting true concentration of that POHC in the stack effluent would be about 0.1 ng/liter. If this gas is sampled over a 2-h period using

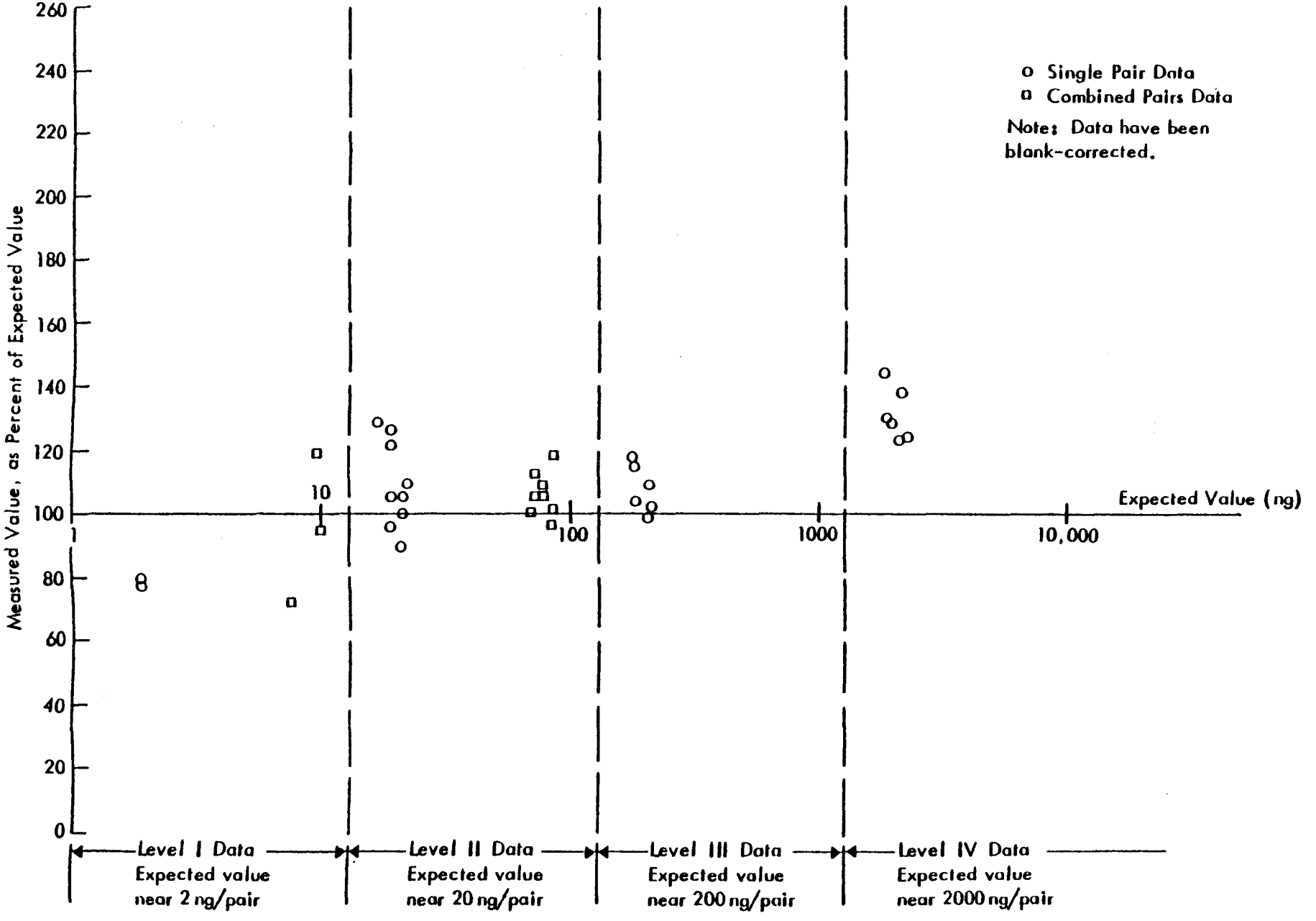

Figure 7. Trichloroethylene test results.

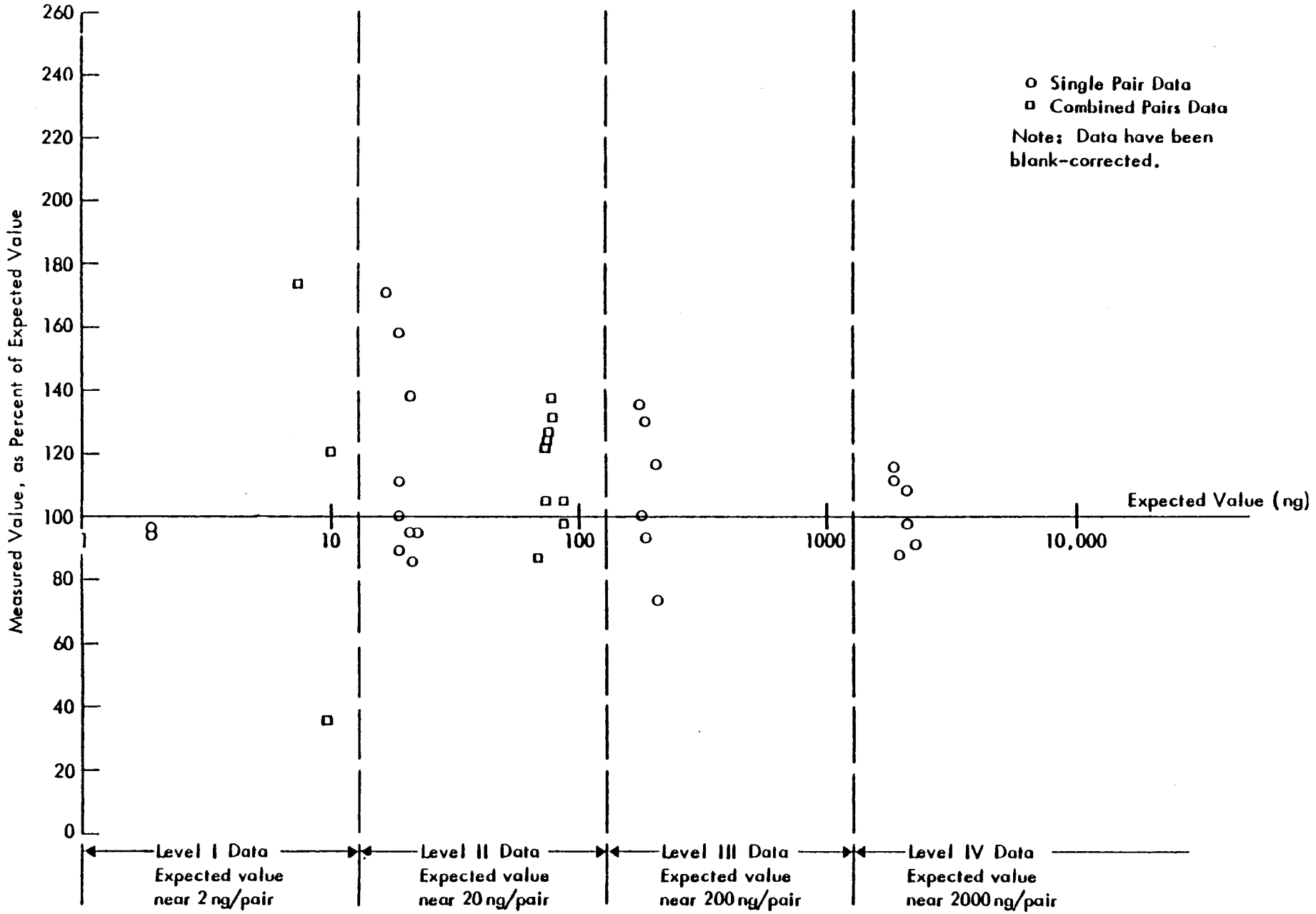

Figure 8. Chlorobenzene test results.

five pairs of traps each time, at 20 min each pair and a flow of 1-liter/min, the results from combining five pairs should be 10 ng. However, if the average for three tests (three runs) at this low concentration ranged from 50 to 150%, the reported value would be between 5 and 15 ng. As a result, the computed DRE would be:

Average amount detected	Computed DRE (%)
5	99.9995
10	99.9990
15	99.9985

In this first scenario it is clear that the sampling/analysis method does allow an accurate determination of DRE, and minimizes the need to report a DRE value as "greater than" 99.99% when it is actually achieving 99.999%.

As a second scenario, the situation might be that the waste again contains 100 ppm of another volatile POHC, but the incinerator is actually achieving a DRE of 99.99%. In this case, the amount of POHC present from combining five pairs of traps should be 100 ng. Since the average for three tests at this level may again range from 50 to 150% of the true value, the reported value might be as low as 50 ng or as high as 150 ng (i.e., 100 ng ± 50). As a result, the computed DRE would be:

Average amount detected	Computed DRE (%)
50	99.995
100	99.990
150	99.985

From the above, it can be concluded that:

- The sampling/analysis method does provide assurance that the computed DRE is accurate to the same decimal place as the true DRE, even if the true DRE is as high as 99.999%.
- The computed DRE could be as low as 99.985% for an incinerator that is actually achieving 99.99%.

This second conclusion is vitally important since current regulations stipulate a DRE of 99.99%. Data obtained in this project make it appear unlikely that a computed DRE would be below 99.985% for an incinerator that is actually achieving 99.99%.

4.0 DEVELOPMENT OF A FIELD VERSION OF THE VOST

Following the successful laboratory evaluation of the VOST described above, the VOST concept was chosen to be evaluated under field sampling conditions along with integrated gas bags. However, the laboratory version of the VOST was not deemed appropriate for field use for the following reasons:

- The difficulty in changing traps under field conditions.
- The lack of ruggedness of the sampling train.
- The high potential for contamination of the outside surfaces of the traps in the hostile environment of the stack and from handling the traps.

As a result of the need for a more rugged VOST with protected traps, several possible VOST and trap designs were considered and evaluated. This paper will only describe the final field version of the VOST which is being used at all trial burns conducted by MRI.

4.1 Trap Design

Figure 9 shows the various components of the field adsorbent traps used in the VOST. The following items should be noted.

- The dimensions of the glass tube remain the same except that neither end is nippled (10-cm x 1.6-cm ID glass tube).
- The amount of Tenax and Tenax/charcoal remains the same.
- The Tenax and charcoal are held in the tubes with a fine-mesh screen held by a C-clip both made from stainless steel. These supporting materials hold the adsorbents more uniformly inside the tubes than the glass wool used during the laboratory evaluation. This results in a lower likelihood of channeling

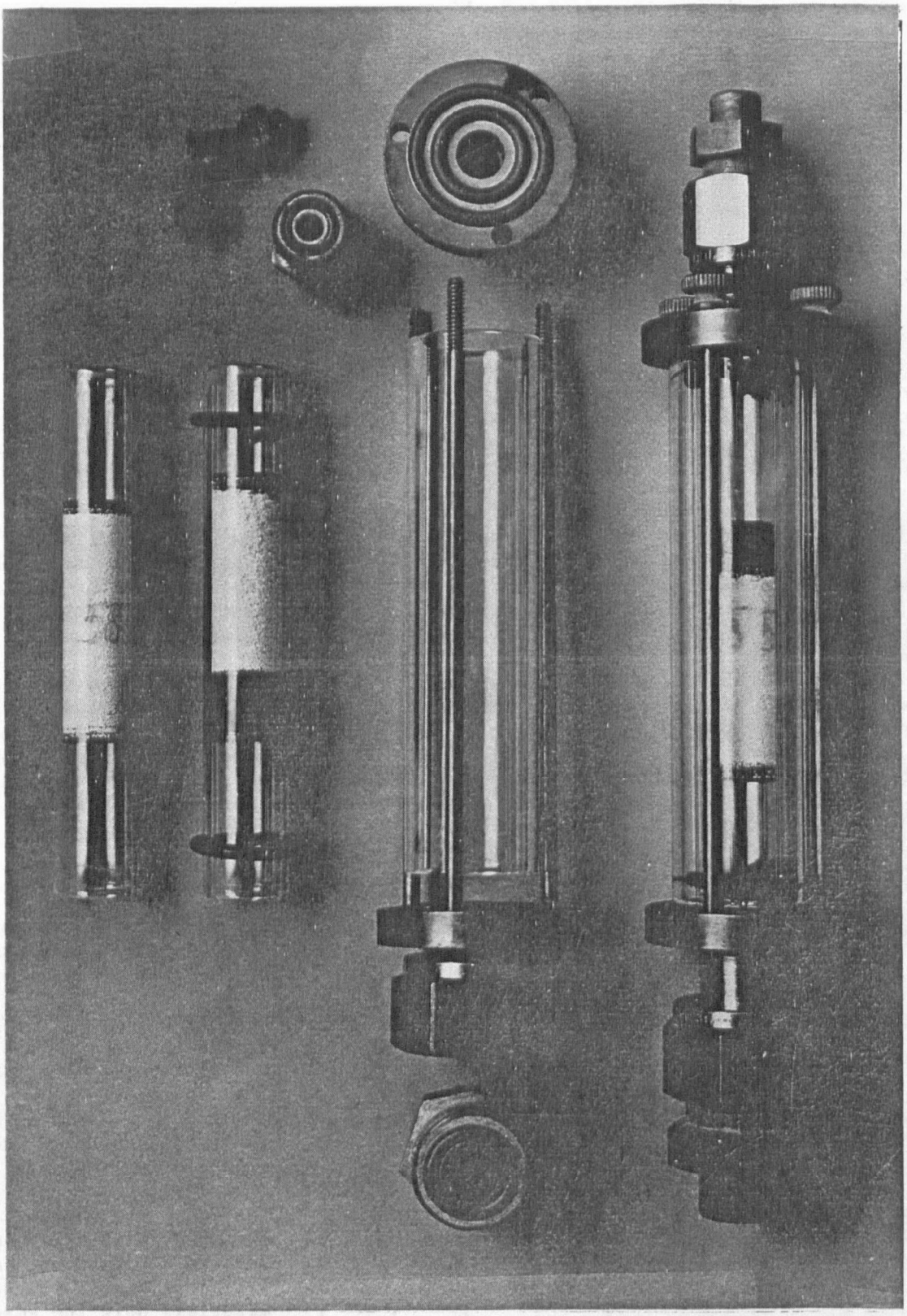

Figure 9. Components of field adsorbent traps for the VOST.

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and lower retention of water in the trap. The stainless steel supports were found not to cause any degradation of volatile POHCs from thermal desorption during analysis.

- The glass tube containing the adsorbents is held within a larger diameter outside tube using Viton O-rings. The purpose of the outside glass tube is to protect the outside of the adsorbent-containing tube from contamination.

- The glass tubes are held in a stainless steel carrier. The glass tubes each butt up against Viton O-rings which are held in machined grooves in each metal end piece. A set of three cylindrical rods are secured into one of the end pieces and fasten to the other end piece with threads and nuts, thus sealing the glass tubes.

- The end pieces, which are fitted with a 1-in. (2.54 cm) female nut, are capped during transport and storage with an end-cap which also seals with a Viton O-ring.

4.2 VOST Design

A photograph of the field version of the VOST is shown in Figure 10. The uppermost section of glass tubing attaches to the probe which is inserted into the stack to collect the sample. The hot wet stack gases, which are drawn into the VOST by the air pump in the lower right-hand part of the photograph, are cooled in the first spiral condenser at the upper left. The bottom portion of the open case is filled with ice water which is continually circulated by a small water pump. The condensed water and stack gas then pass down through the front Tenax trap where most of the organics are adsorbed except those with very low breakthrough volumes; e.g., vinyl chloride. The condensed water collects in the Erlenmeyer flask-shaped impinger and is continually purged by the sampled gas. Any volatile POHCs which pass through the front Tenax adsorbent trap with the water are then purged from the water and pass upward through the Teflon® tube, down through the second spiral condenser and through the backup Tenax/charcoal trap where they are adsorbed. The gas is then dried in the silica gel tube and passes into the dry gas meter for volume measurement. When not in use, the VOST folds up inside the portable case for easy transport.

The field VOST is generally used as described in the laboratory evaluation; i.e., one pair of traps is sampled for 20 min at a flow rate of 1 liter/min. The first trap pair is then removed and a new pair inserted for sample collection. A total of six pairs of traps are collected. The changing of the trap pairs is greatly facilitated by using the field carrier.

A "slow VOST" is also being evaluated during which only two or three pairs of traps are used for sample collection. The slow VOST, which generally samples only 5-10 liters of stack gas sample over a longer sampling period, has the following advantages:

- The lower sample volume reduces the likelihood of breakthrough and serves as a check on breakthrough for the regular VOST.

- A more integrated sample is obtained. This is very advantageous in situations where the stack gas composition changes during the incineration test.

The main disadvantage of the "slow VOST" is its decreased sensitivity.

4.3 Trap Preparation Procedures

During the development and evaluation of the field VOST, it was discovered that the sorbent traps were sometimes severely contaminated with volatile organic compounds. Several possible sources of contamination were identified such as ambient air, contaminated metal carriers, O-rings, and the adsorbents. In order to prevent contamination, a series of stringent trap preparation procedures were tested and adopted which have proved very effective in eliminating the contamination for field sampling with the VOST. These procedures are discussed below.

4.3.1 Preparation of Tenax and Charcoal--

New Tenax and charcoal is Soxhlet-extracted with methanol for 16 h, and dried in a vacuum oven at 50°C prior to packing into tubes. The Tenax and charcoal in

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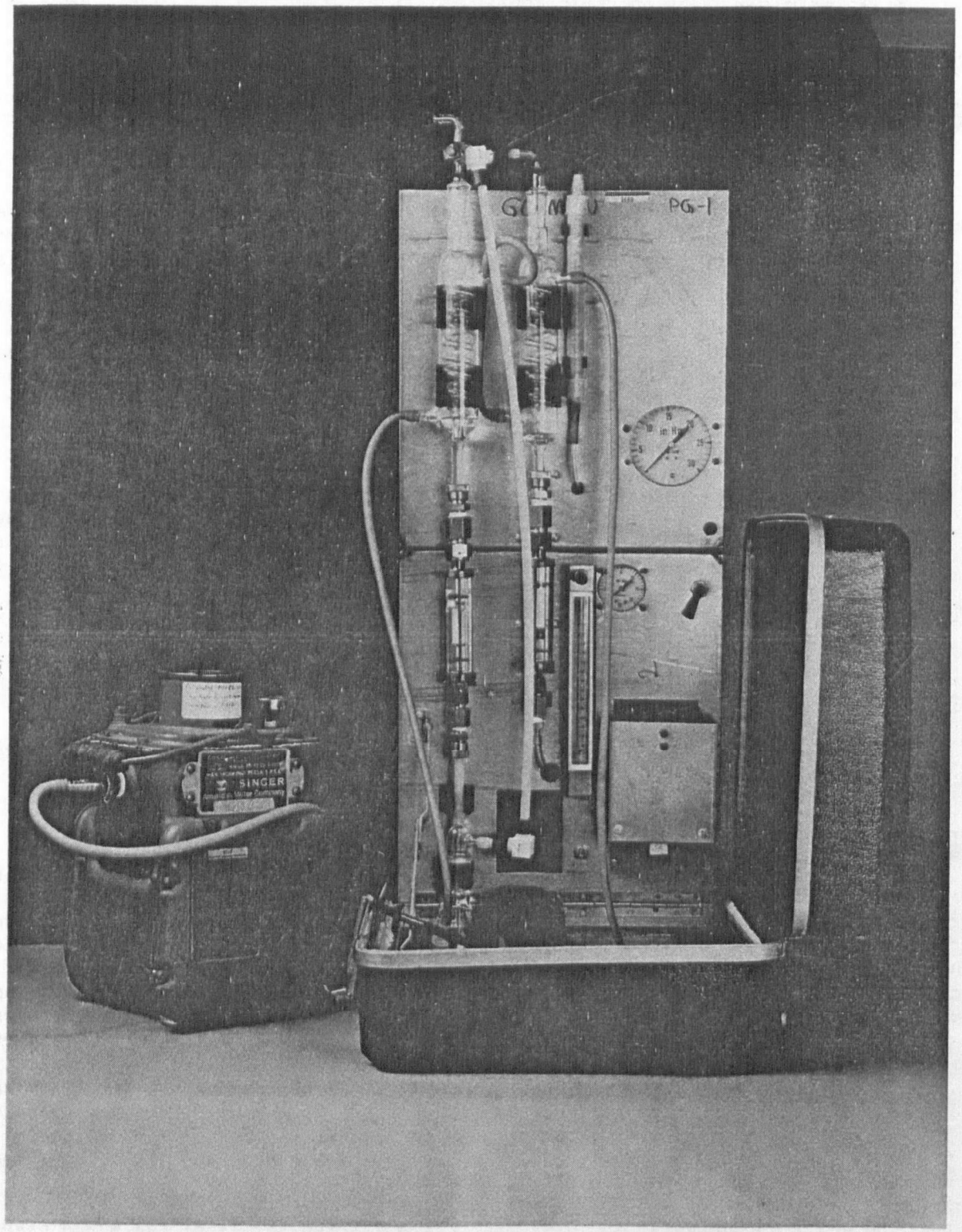

Figure 10. Photograph of the field version of the VOST.

packed tubes are not routinely reextracted following sampling and analysis unless very high concentrations (i.e., micrograms) of sample components are collected.

4.3.2 Preparation of O-Rings--

The Viton O-rings are thermally conditioned in a vacuum oven at 200°C for 48 h prior to use. This procedure removes volatile solvents which may be present in the O-rings and could outgas later.

4.3.3 Preparation of Metal Parts--

The metal parts (including the stainless steel carriers, end plugs, C-clips, and screens) are subjected to sonification in a warm non-ionic soap solution, rinsed with distilled water, air-dried, and heated in a muffle furnace at 400°C for 2 h.

4.3.4 Preparation of Glass Tubes--

The glass tubes are cut from new glass tubing, fire-polished, and annealed.

4.3.5 Packing--

The Tenax and charcoal are packed into the glass tubes in an organic-free laboratory (laboratory air filtered through charcoal).

4.3.6 Trap Conditioning--

The traps are conditioned as described in Section 3.4.3. However, two different conditioning periods are used of at least 4 h each.

4.3.7 Trap Assembly--

The conditioned traps are assembled into the metal field carriers in the same organic-free room where the adsorbents are packed into the glass tubes.

4.3.8 Leak Checking--

The assembled field traps are checked for leaks by removing one of the end caps and attaching the trap to a source of organic-free nitrogen gas at 30 psi (2.1 kg/cm^2). The trap is then immersed in distilled water to check for the appearance of bubbles.

4.3.9 Trap Monitoring--

Following trap assembly and assurance that the traps do not leak, each trap assembly is attached to a manifold (capacity of 10 traps). Organic-free nitrogen is passed through each trap at a flow rate of 30 ml/min while the traps are heated to 190°C. The flow through each trap is sequentially monitored with a flame ionization detector to check for emission of volatile organics from the trap assembly. Most traps show no organic emissions, while others need to remain on the conditioner for several hours until the emissions from the trap are reduced to less than a detectable level (< 2 ppb).

4.3.10 Trap Storage--

When the traps are shown to be clean with the flame ionization detector, they are capped and stored under ice water until they are used for sampling. The traps are also placed back under ice water after sampling until they are analyzed by GC/MS. The ice water serves to keep the traps cold which slows aging of the Tenax; i.e., the gradual transfer of compounds such as benzene and toluene from within the polymeric Tenax matrix to the surface of the Tenax where these compounds can be thermally desorbed during analysis and contribute to high background levels. The water also protects the traps from volatile organic compounds in the ambient atmosphere which could collect on the outside of the trap assembly and contaminate the adsorbents during disassembly just prior to analysis. A summary of the trap preparation procedures is shown in Figure 11.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations based on this evaluation of the VOST are presented below. Some of the conclusions are preliminary and could change upon further evaluation of the VOST. We also expect that the precision and accuracy of the method will improve during further evaluation.

This laboratory evaluation demonstrated that the overall concept for the VOST is valid, and that combining several pairs of traps onto one pair of traps for analysis is advantageous when the POHCs

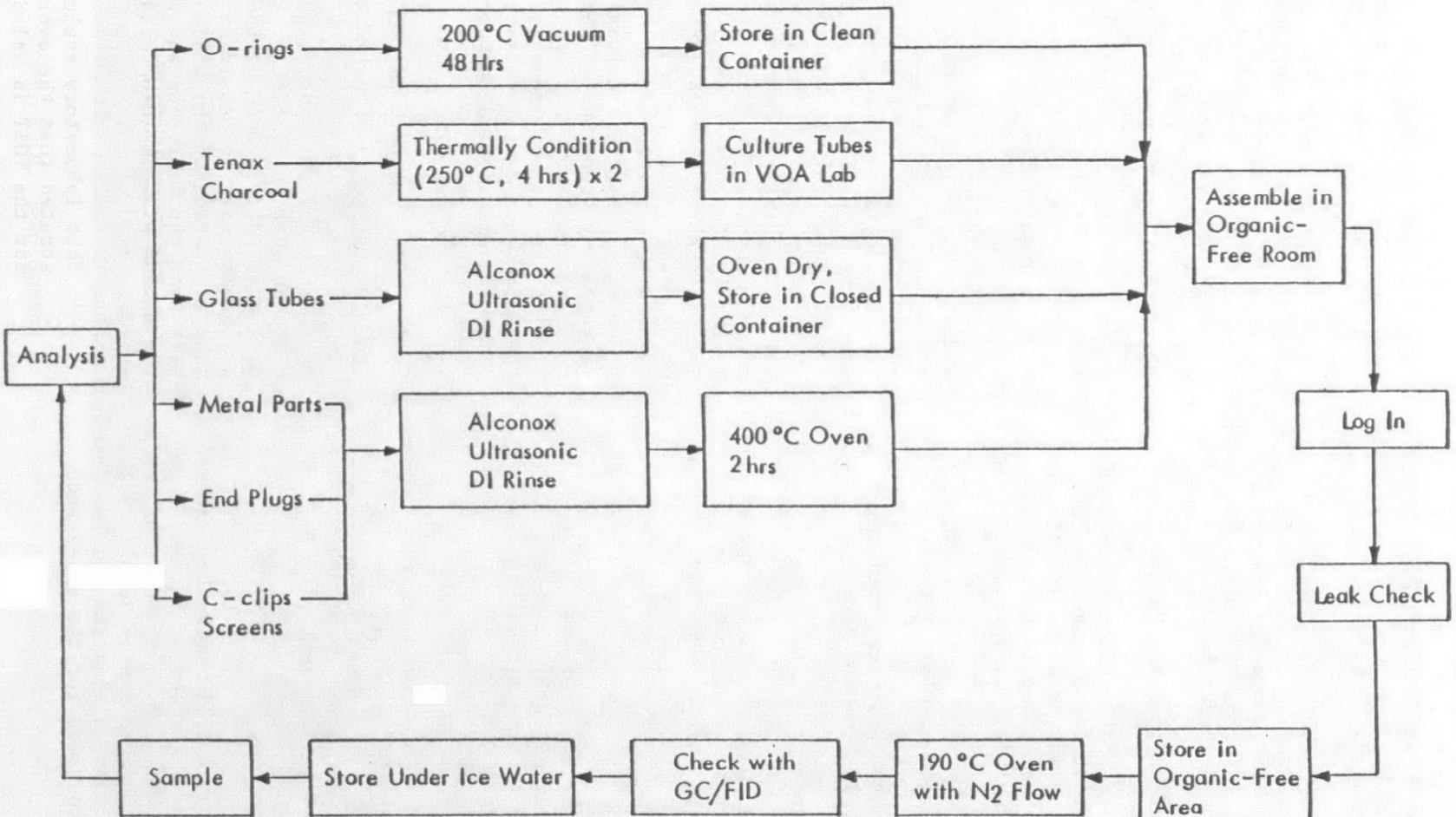

Figure 11. VOST trap cleanup procedure.

are present at low levels. The field work thus far, however, suggests that the levels of volatile POHCs are high enough that combining the contents of several pairs of traps onto one pair is generally not necessary.

- The VOST method does overcome the problem of reporting a DRE value of > 99.99% for an incinerator which is actually achieving 99.999%.

- Results of the laboratory evaluation indicate that a reported value may be as low as 46% or as high as 146% of the expected value (based on the average of three runs when several pairs from each sampling train are combined onto one pair).

- Therefore, for an incinerator that is achieving a DRE of 99.999% (100 ppm concentration of the POHC in the waste), the VOST method does permit determination of DRE to the third decimal place, but with results that could range from as low as 99.9985 to as high as 99.9995.

- The VOST method does not ensure that DRE results can always be accurately computed to the third decimal place. In fact, if an incinerator is actually achieving a DRE of 99.990%, the average results reported for three tests could have a deviation of 99.990 ± 0.005%.

- In this evaluation, results for vinyl chloride and carbon tetrachloride show the most variability, especially at lower concentrations.

- The presence of HCl in the gas being sampled did not appear to have any serious effect on the VOST results.

- The problem of analyzing wet traps can be satisfactorily overcome by desorbing the contents of the sample collection traps into a purge-trap-desorb GC/MS analytical system.

- Stringent trap preparation procedures are required to eliminate the risk of contaminating the traps prior to use.

- Separate traps (blanks) should be exposed to air in the field in order to determine the level of compounds on the traps due to adsorption of the compounds during handling of the traps and their insertion into/removal from the VOST apparatus.

6.0 ACKNOWLEDGMENTS

Much of the work discussed in this paper was funded under contract with the U.S. Environmental Protection Agency (EPA Contract No. 68-01-5915). The work was performed under the direction of Dave Friedman of EPA/OSW and Larry Johnson of EPA/IERL-RTP who provided counsel in all phases of the work.

7.0 REFERENCES

1. Rechsteiner, C., J. C. Harris, K. E. Thrun, D. J. Sorlin, and V. Grady. 1981. Sampling and Analysis Methods for Hazardous Waste Incineration, A. D. Little, Inc., in support of Guidance Manual for Evaluating Permit Applications for the Operations of Hazardous Waste Incineration Units, EPA Contract No. 68-02-3111, EPA/IERL, Research Triangle Park, North Carolina.

2. Jungclaus, G., and P. Gorman. 1982. Draft Final Report, Evaluation of a Volatile Organic Sampling Train, Midwest Research Institute, EPA Contract No. 68-01-5915.

3. Krost, K. J., E. D. Pellizzari, S. G. Walburn, and S. A. Hubbard. 1982. Collection and Analysis of Hazardous Organic Emissions. Anal. Chem., S(4):810-817.

4. EPA Method 624 - Purgeables. 1979. U.S. Environmental Protection Agency, Federal Register 44:69532-69539.

are present at low levels. The field work thus far, however, suggests that the levels of volatile POHCs are high enough that combining the contents of several pairs of traps onto one pair is generally not necessary.

- The VOST method does overcome the problem of reporting a DRE value of > 99.99% for an incinerator which is actually achieving 99.999%.

- Results of the laboratory evaluation indicate that a reported value may be as low as 46% or as high as 146% of the expected value (based on the average of three runs when several pairs from each sampling train are combined onto one pair)

- Therefore, for an incinerator that is achieving a DRE of 99.999% (100 ppm concentration of the POHC in the waste), the VOST method does permit determination of DRE to the third decimal place, but with results that could range from as low as 99.9985 to as high as 99.9995.

- The VOST method does not ensure that DRE results can always be accurately computed to the third decimal place. In fact, if an incinerator is actually achieving a DRE of 99.990%, the average results reported for three tests could have a deviation of 99.990 ± 0.005%.

- In this evaluation, results for vinyl chloride and carbon tetrachloride show the most variability, especially at lower concentrations.

- The presence of HCl in the gas being sampled did not appear to have any serious effect on the VOST results.

- The problem of analyzing wet traps can be satisfactorily overcome by desorbing the contents of the sample collection traps into a purge-trap-desorb GC/MS analytical system.

- Stringent trap preparation procedures are required to eliminate the risk of contaminating the traps prior to use.

- Separate traps (blanks) should be exposed to air in the field in order to determine the level of compounds on the traps due to adsorption of the compounds during handling of the traps and their insertion into/removal from the VOST apparatus.

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7.0 REFERENCES

1. Rechsteiner, C., J. C. Harris, K. E. Thrun, D. J. Sorlin, and V. Grady. 1981. Sampling and Analysis Methods for Hazardous Waste Incineration, A. D. Little, Inc., in support of Guidance Manual for Evaluating Permit Applications for the Operations of Hazardous Waste Incineration Units, EPA Contract No. 68-02-3111, EPA/IERL, Research Triangle Park, North Carolina.

2. Jungclaus, G., and P. Gorman. 1982. Draft Final Report, Evaluation of a Volatile Organic Sampling Train, Midwest Research Institute, EPA Contract No. 68-01-5915.

3. Krost, K. J., E. D. Pellizzari, S. G. Walburn, and S. A. Hubbard. 1982. Collection and Analysis of Hazardous Organic Emissions. Anal. Chem., S(4):810-817.

4. EPA Method 624 - Purgeables. 1979. U.S. Environmental Protection Agency, Federal Register 44:69532-69539.