



## Project Summary

# POHC Analysis Methods for Hazardous Waste Incineration

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**This report describes the evaluation of generalized GC/FID, GC/MS, HPLC/UV, and HPLC/fluorescence analysis methods for measuring principal organic hazardous constituents (POHCs) in various influent and effluent streams of incineration facilities. The report includes summary sheets that list relative retention times, on-column detection limits, molecular weights, relative ion abundances, and wavelengths of detection for the POHCs. Reference chromatograms, calibration curves, mass spectra, key ions and relative abundances, and UV absorption spectra of the POHCs are presented in report appendices.**

*This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

As part of the Resource Conservation and Recovery Act of 1976, the U.S. Environmental Protection Agency 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%.

Approximately 400 compounds (designated POHCs) are included in Appendix

VIII, Part 261, 40 CFR. However, the survey/analysis portion of a waste-characterization scheme often targets specific compounds for determination in incinerator effluent that are not amenable to previously developed methods. Therefore, current research involves the development of specific GC/FID,\* GC/MS, HPLC/UV, and HPLC/fluorescence methods for the determination of several of these compounds. This work involved the evaluation of generalized GC/FID, GC/MS, HPLC/UV, and HPLC/fluorescence methods for determining approximately 200 compounds from this list of POHCs. This report presents preliminary data on methodology for candidate POHCs that represent a variety of compound types, including alcohols, esters, chlorinated aliphatics and aromatics, carboxylic acids, aliphatic and aromatic amines, nitrated aromatics, nitrosamines, hydrazines, nitriles, organosulfur compounds, polynuclear aromatics and heterocyclics, and organometallics.

EPA's manual, Sampling and Analysis Methods for Hazardous Waste Combustion, EPA-600/8-84-002, is a resource document for the preparation and execution of a sampling-and-analysis plan for hazardous-waste incinerators. Report EPA-600/8-84-002 recommends a variety of analytical techniques for determining POHCs. Methods were written to incorporate fused-silica capillary GC/MS and HPLC. These methods were designed to provide satisfactory qualitative and quantitative analyses on a cost effective basis for a variety of waste types and process chemistries. Generalized GC/MS

\* GC = gas chromatography, FID = flame ionization detection, MS = mass spectrometry, HPLC = high performance liquid chromatography, and UV = ultraviolet.

and HPLC techniques were developed to determine as many of the POHCs as possible.

The laboratory work was structured to lead systematically from determining the feasibility of developing generalized test methods to standardizing the resulting methods for selected POHCs. Initially, standard solutions of mixtures of selected POHCs were analyzed to optimize instrumental operating conditions. Then individual chromatograms (GC/FID, GC/MS, HPLC/UV, HPLC/fluorescence) were obtained, calibration curves were established, and detection limits were estimated.

The following tasks supplemented the development of generalized test procedures and, in general, improved EPA-600/8-84-002:

- The evaluation of generalized analysis methods for approximately 100 POHCs by GC/FID and GC/MS.
- The application of a selective GC column and GC/MS using selected-ion monitoring to determine 2,3,7,8-TCDD.
- The evaluation of generalized analysis methods for approximately 100 POHCs by HPLC/UV.
- The evaluation of generalized analysis methods for 13 POHCs by HPLC/fluorescence.
- The development of a derivatization technique for three organometallic POHCs.
- The evaluation of generalized analysis methods for five organometallic POHCs by GC/FID, GC/MS, and HPLC/UV.

## Experimental

### Description of Instruments and General Operating Conditions

The GC/MS generalized test method was developed on a Hewlett-Packard (HP) Model 5985A GC/MS data system. System components included a hyperbolic quadrupole mass filter with a convertible electron-impact (EI) and positive-ion chemical-ionization source and a capillary and jet separator GC/MS interface. Its data system included an H2113 computer, a high-speed printer, a magnetic tape system, a 50-megabyte HP7920M disc-drive system, a communication interface, GC/MS operating software, and an unabridged NBS special library. The supplemental GC/FID work was performed on a HP Model 5840 GC equipped for use with capillary columns.

The work with both the GC/MS and the GC/FID involved capillary-column chromatography with matched, cross-linked fused-silica SE-54 capillary columns 25 m long with a 0.31-mm ID. The initial operating conditions were a compromise of the conditions given for several capillary GC methods in EPA-600/8-84-002. The initial starting column temperature was 40 °C; the temperature was then programmed at 10 °C/min 280 °C for 15 min. Alternate column temperature programs used rates of 20 and 30 °C/min. Injection and detection temperatures were 250 °C. The carrier gas (helium) was maintained at a flow rate through the column of about 2 mL/min. In both the GC/MS work and the GC/FID work, the "splitless" injection technique was employed. Consequently, essentially all of the injected sample reached the column.

The determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) used a fused-silica capillary column capable of separating the 2,3,7,8-TCDD isomer from the other 21 TCDD isomers (Chrompack CP SIL 88, 0.22-mm ID, 60-m length). The initial column temperature was 45 °C for 3 minutes, then programmed to 190 °C at 25 °C/min, then programmed to 240 °C at 5 °C/min, and held at 240 °C for 10 minutes. The injection temperature was 290 °C. Helium at 2 mL/min was used as the carrier gas.

Having established GC operating conditions by the GC/FID procedure, the method was applied to determine the candidate POHCs by GC/MS. The MS was operated in a full mass scanning range (41 to 450 amu) in the EI mode. The scan time was maintained at  $\leq 1$  s to enable the collection of enough scans to characterize each capillary GC peak. The MS was used in the selected-ion monitoring (SIM) mode to determine 2,3,7,8-TCDD. The ions monitored were  $m/z$  257, 320, and 322 for native unlabeled 2,3,7,8-TCDD; 328 for  $^{37}\text{C}_{14}$ -2,3,7,8-TCDD; and 332 and 334 for  $^{13}\text{C}_{12}$ -2,3,7,8-TCDD.

### HPLC Analysis Procedures

The POHCs were grouped into classes of compounds and submitted for HPLC analysis. Initially, standard mixtures of candidate POHCs were analyzed to establish solvent programs suitable for determining a variety of compounds. The UV detector was set to monitor absorbances at 254 nm. Various chromatographic conditions were evaluated and

modified until the evaluation rate and the resolution were optimized.

Ten chromatographic conditions are described in the report. Three columns were used in this work: HC-ODS-SIL-X-1,  $\mu$ Bondapak  $\text{C}_{18}$ , and  $\mu$ Bondapak CN.

In subsequent work, the UV absorption spectra of the candidate POHCs were determined on a Cary Model 17 spectrophotometer to establish an absorption maximum in the range from 190 to 400 nm that would be a suitable alternate wavelength for quantifying each POHC by HPLC/UV. For HPLC/fluorescence, the excitation wavelength was 280 nm for the PAHs (polynuclear aromatic hydrocarbons) and 360 nm for the aflatoxins.

### Derivatization Procedure

Standards were prepared by weighing small amounts (1.0 mg) of the three compounds (benzenearsonic acid, hydroxydimethylarsine oxide, and phenylmercury acetate) into 50-mL centrifuge tubes, adding 1.0 mL of hydroiodic acid (HI) and shaking for 1 minute. The derivatives were extracted into 10 mL of hexane and diluted to make standards.

## Results and Discussion

### GC/FID and GC/MS Analysis

The report summarizes the GC/MS determinations of approximately 100 candidate POHCs. The retention time and on-column detection limit are given for each compound. The compounds are listed in the order of their elution from the GC column. Retention times are relative to that observed for the internal standard, anthracene- $\text{d}_{10}$ . The on-column detection limit was estimated using the calibration curve as suggested in Appendix A of Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA-600/4-82-057. Typical values were between 0.1 and 80.0 ng.

### HPLC/UV Analysis

The report summarizes the HPLC determinations of approximately 100 candidate POHCs. The retention time, on-column detection limit, and wavelength of detection are given for each POHC. The POHCs are listed by group in order of their elution from the HPLC column and subdivided by procedural option. Detection limits were calculated by the same procedure used in GC analyses. Detection limits ranged from 0.001 to 6  $\mu\text{g}$ . The wavelength of detector was 254 nm except where noted. An alternate wavelength was selected from the reference UV spectrum to optimize the detection of the POHCs.

## HPLC/Fluorescence Analysis

The determination of 13 POHCs was completed by HPLC/fluorescence. The retention time, on-column detection limit, and excitation/emission wavelengths are given for each POHC. The POHCs are listed by group in order of their elution from the column and subdivided by procedural option. The on-column detection limit was calculated in the same manner as used for GC/FID and GC/MS. Detection limits ranged from 0.001 to 0.4  $\mu\text{g}$ .

## Conclusions

Generalized GC/FID, GC/MS, HPLC/UV, and HPLC/fluorescence procedures were developed to determine candidate POHCs. Initially, standard solutions of mixtures of selected POHCs were analyzed to optimize instrumental operating conditions. Then individual chromatograms (GC/FID, GC/MS, and HPLC/UV) were obtained, calibration curves were established, and detection limits were estimated. The technical approach in developing and evaluating the generalized instrumental methods is discussed in the report. The chromatograms and data are provided in three report appendices.

Appendix A contains the chromatograms and calibration curves for the GC/FID determinations. Appendix B

shows the mass spectra in addition to the chromatograms and calibration curves for GC/MS determinations. Appendix C contains the UV absorption spectra as well as the chromatograms and calibration curves for HPLC/UV determinations.

A simple derivatization technique allows the determination of benzenearsonic acid, hydroxydimethylarsine oxide, and phenylmercury acetate by the generalized GC/FID and GC/MS procedures. These compounds were recovered quantitatively from sorbents, filters, and water. The derivatization procedure may be useful for other organometallic compounds. Compounds such as selenourea and tetraethyl lead may be determined by the HPLC/UV and GC/FID or GC/MS procedures, respectively, without major modifications of the procedures. The determination of 2,3,7,8-TCDD by the general GC/MS procedure provides a screening analysis and may be applicable for survey/analysis of hazardous waste. However, ultimate selectivity and sensitivity are provided by an isomer-specific GC column and SIM mass spectrometry.

The developed generalized methods are suitable for inclusion in EPA-600/8-84-002. The methods were standardized with selected organic compounds over concentration ranges of interest and showed acceptable precision in determining most of the compounds.

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**Larry D. Johnson** is the EPA Project Officer (see below).

*The complete report consists of three volumes entitled "POHC Analysis Methods for Hazardous Waste Incineration."*

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