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Project Summary

PIC Analysis Methods

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Products of incomplete combustion (PICs) may be formed during the incineration of hazardous wastes. PICs may be defined as compounds in the stack gas of an incinerator but not present in the waste feed at a concentration of 100μg/g. In some instances, the PICs formed may also be constituents of the waste feed, thus confusing the analysis of principal organic hazardous constituents (POHCs). The total amount of hazardous PICs can easily exceed the total of the original POHCs chosen to monitor the trial burn. The compounds may be identifiable as fragments of incineration feed constituents, products of complex recombinations, substitution reactions in the flame or post-flame zone, or compounds that enter the incineration process from other sources.

Study efforts applied previously developed POHC general analysis methods to the analysis of PICs. A large body of the literature on PICs is based on the findings of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in incinerator effluents. Generalized GC/FID and GC/MS analysis methods for PCDDs and PCDFs were evaluated.

The generalized GC/FID and GC/MS procedures were extended to many of these compounds from a list of 121 compounds recently added to the potential POHC list in Appendix VIII, Part 261, 40 CFR.

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

The EPA Methods Manual, "Sampling and Analysis Methods for Hazardous Waste Combustion," EPA-600/8-84-002 (NTIS No. PB84-155845), February 1984, is intended to be a resource document for the preparation and execution of a sampling-and-analysis plan for hazardous-waste incinerators. The Methods Manual recommends a variety of analytical techniques for the determination of POHCs. Methods were written to incorporate fused-silica capillary gas chromatography/mass spectrometry (GC/MS) and high-performance liquid chromatography (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 and HPLC techniques were developed for the determination of as many of the POHCs as possible.

Laboratory work led systematically from the determination of the feasibility of developing generalized test methods to the standardization of the resulting methods for selected PICs and POHCs. Initially, standard solutions of mixtures of selected PICs and POHCs were analyzed to optimize instrumental operating conditions. Then individual chromatograms (GC/FID and GC/MS) were obtained, calibration curves were established, and detection limits were estimated.

The following tasks supplemented the development of generalized test procedures and assisted workers in the area of incineration or combustion of hazardous waste:

- The evaluation of generalized analysis methods for 10 PCDDs and 3 PCDFs by GC/FID and GC/MS.
- The evaluation of generalized analysis methods for 23 non-dioxin

proposed PICs.

- The evaluation of a GC/MS/SIM analysis method for 7 PCDDs and 2 PCDFs.
- The evaluation of generalized analysis methods for 56 POHCs by GC/FID and 58 POHCs by GC/MS from an amendment to Appendix VIII, Part 261, 40 CFR.
- Consultation took place during these work assignments with personnel at LSU; at EPA's Combustion Research Facility in Pine Bluff, Arkansas; at Arthur D. Little, Inc.; and at EPA/HWERL's Center Hill Facility in Cincinnati, Ohio.

Experimental

The GC/MS generalized test method was developed on a Hewlett-Packard Model 5985 GC/MS data system. Components of the instrument include 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 includes an HP2113 computer, a high-speed printer, a magnetic tape system, a 50-megabyte HP7920M disk-drive system, a communications interface, GC/MS operating software, and an unabridged NBS spectral library. The supplemental GC/FID work was performed on a Hewlett-Packard Model 5840 GC that was equipped for use with capillary columns.

The work with both the GC/MS and GC/FID involved capillary-column chromatography with matched, crosslinked fused-silica SE-54 capillary columns 25 m long with a 0.31-mm ID. The initial operating conditions were a compromise of those given for several capillary GC methods in the Methods Manual. The initial starting column temperature was 40 °C; the temperature was then programmed at 10 °C/min to 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 and the GC/FID work, the "splitless" injection technique was employed. Consequently, it was assumed that essentially all of the injected sample reached the column.

Having established GC operating conditions by the GC/FID procedure, the method was then applied to the determination of the candidate PICs and POHCs by GC/MS. The mass spectrometer was operated in a full mass scanning range (41 to 450 amu) in the EI mode. The scan time was maintained at ≤1 s to enable the collection of enough scans to characterize each capillary GC peak. The mass spectrometer was used in the selected-ion monitoring (SIM) mode to determine dioxins and furans.

Development of Analysis Methods

In all, 36 PICs and 56 POHCs were determined by GC/FID, and 36 PICs and 58 POHCs by GC/MS. Retention times and on-column detection limits were determined for each compound. Retention times were measured relative to that observed for the internal standard, anthracene-d_{10}. The on-column detection limit was estimated using experimentally determined calibration curves as suggested in Appendix A of "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater." EPA-600/4-82-057 (NTIS No. PB83-201798). Typical values were 2 to 800 ng. From triplicate determinations of the candidate PICs and POHCs, relative standard deviations (RSDs) were calculated, ranging from 0.2 to 31%. GC/MS determinations were less precise than GC/FID determinations.

Conclusions

Generalized GC/FID and GC/MS procedures were successfully developed for the determination of candidate PICs. A selected-ion monitoring GC/MS procedure for PCDDs and PCDFs was also evaluated. Generalized GC/FID and GC/MS procedures were extended to POHCs from the amended Appendix VIII, Part 261, 40 CFR.

The generalized methods are suitable for the determination of PCDDs and PCDFs. The methods are also applicable to substituted polycyclic aromatic hydrocarbons (PAHs).

The developed generalized methods are suitable for inclusion in the Methods Manual. The methods were standardized with selected organic compounds over concentration ranges of interest and showed acceptable precision in the determination of most of the compounds.

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The complete report, entitled "PIC Analysis Methods," (Order No. PB 87-208 955/AS; Cost: $42.95, subject to change) will be available only from:
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