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Project Summary

Evaluation of POHC and PIC Screening Methods

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The application of a tiered approach to the analysis of source emission samples was evaluated for semivolatile and nonvolatile organic compounds. The analyses illustrate that in many cases a combined approach will be useful. If it is known that most of the toxic compounds of interest are present in the 100-300 °C boiling range then GC/MS analysis will provide specific details and GRAV will give an indication of the amount of high boiling nonvolatile material present. Alternately, HPLC/UV may be needed for the analysis of target POHCs of interest and screening of the extract by TCO and GRAV may be sufficient for the characterization of other materials in the sample. When PICs are to be determined, a chromatographic procedure combined with mass spectrometry will probably be required.

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

Introduction

The analysis of incinerator effluents often focuses on the analysis of one or a few compounds as principal organic hazardous constituents (POHCs) and on products of incomplete combustion (PICs) to provide coverage for other compounds. Comprehensive techniques that allow the analysis of all organic compounds in an effluent do not exist and would be costly to apply. Recent studies have proposed a risk-driven tiered-analysis protocol to characterize combustion effluents. These procedures do not preclude the analysis of targeted POHCs to measure destruction and removal efficiency (DRE) or targeted PICs such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) but supplement them to provide extended coverage to compounds of environmental interest that may not be detected in a directed analysis protocol.

Recent work proposed several standard methods for screening purposes. Seven protocols were proposed for screening purposes:

- Gas chromatography/flame ionization detection (GC/FID) screening for volatile compounds
- GC/MS screening for volatile compounds
- Soxhlet extraction for sample preparation
- Total chromatographable organic (TCO) determination
- GC/MS for semivolatile compounds
- Gravimetric (GRAV) determination
- HPLC/UV screening method

The methods were from EPA SW-846 or from other EPA documents. To these methods we propose to add HPLC/MS as a screening method.

The testing of screening methods in this project has focused on the evaluation of procedures to develop information on the semivolatile and nonvolatile components found in MM-5 sampling train samples. We have applied Soxhlet extraction, GRAV, TCO, GC/MS, HPLC/UV,

and HPLC/MS to the analysis of MM-5 samples obtained from incinerators and the analysis of laboratory-spiked samples to determine the feasibility and applicability of screening techniques.

Technical Approach

The testing of screening protocols for the measurement of organic emissions from incinerators can be divided into three categories: volatile, semivolatile and nonvolatile. Volatile compounds are sampled with bags, canisters, volatile organic sampling train (VOST) and other techniques designed to capture compounds that boil below about 130 °C. Semivolatile and nonvolatile compounds are usually captured with an MM-5 train. This study has concentrated on the semivolatile and nonvolatile categories of organic emissions. Samples were obtained from incinerator tests or were prepared as laboratory-spiked samples.

Results and Discussion

The experiments conducted in this project were tiered to apply the least complicated and least expensive techniques to samples first and then to apply the more specific and thus more complex and costly methods to develop data that would indicate complete coverage of the organic materials in the samples. The procedure usually employed TCO analysis and GRAV analysis prior to GC/MS, HPLC/UV or HPLC/MS.

Gravimetric Analysis

A portion of each sample was taken for GRAV analysis. The values for the MM-5 and ash samples varied from about 1 mg to a high of 83 mg. The laboratory-spiked samples all contained between 1 and 11 mg of GRAV material.

Total Chromatographable Organic Analysis

Each sample was analyzed for TCO with GC/FID. The MM-5 and ash samples ranged from less than 1 mg to about 25 mg of TCO. The TCO levels in the spiked samples were in the 1-to-10-mg range.

The data from the TCO and GRAV experiments indicate that usually a more extensive analysis will be needed to aid in the characterization of emission sources. However, if a source has already been extensively characterized these simple analytical procedures may provide enough information to monitor the emissions of organic compounds into the atmosphere.

Gas Chromatography/Mass Spectrometry (GC/MS)

We analyzed samples by GC/MS with SW-846 Method 8270. Mass-spectrometric analysis can identify compounds in chromatographic peaks to determine if hazardous substances are present. We also analyzed laboratory-spiked XAD-2 resin for compounds of environmental interest. In most instances, recoveries are good and relative percent differences of the duplicates are small. However, compounds such as benzidine and 4,4'-methylenedianiline present problems for analysis by GC/MS at these spiking levels (100 µg, 400 µg, and 1000 µg). Spikes of several polynuclear aromatic compounds (PAHs) were also analyzed by GC/MS.

A simplified version of SW-846 Method 8280 was employed to determine the detectability of PCDD/F in the MM-5 samples. Only two labelled PCDDs were added to the sample extracts to serve as standards; the surrogate standard was $^{13}C_{12}$-2,3,7,8-tetrachloro-*p*-dibenzodioxin and the internal standard was $^{37}Cl_4$-2,3,7,8-TCDD. Matrix interferences made positive identification of PCDD/Fs uncertain. This analysis indicated that when data for PCDD/Fs are required, a simple screening procedure is inadequate. A more complete screen for PCDD/Fs requires extensive and complex sample cleanup and analysis techniques such as those described in Method 8290.

Analysis by GC/MS gives data that can characterize the organic emissions from a source in the boiling range of 0 °C to about 300 °C. The range of compounds investigated in this project was from about 90 °C to 300 °C. Although excellent identification and adequate quantitation of target compounds can be made by GC/MS, the range of coverage is small. Compounds with high boiling points or compounds that are thermally labile will not be detected easily by GC/MS. Further analysis by other techniques is needed to extend coverage to these compounds.

High Performance Liquid Chromatography with Ultraviolet Detection (HPLC/UV)

The MM-5 and ash samples were analyzed by HPLC/UV to determine if compounds that were suitable for measurement by HPLC/UV were present. A few peaks were found in the samples, but identification and thus quantification was not performed.

These experiments indicate that HPLC/UV is useful for the analysis of target compounds where standards are available and interferences are not present. However, screening of high-boiling-point, polar, and thermally labile compounds from emission sources will require a technique that gives more specific identification and allows for interferences to be minimized.

High Performance Liquid Chromatography with Mass Spectrometry (HPLC/MS)

Two approaches were used to examine HPLC/MS analysis. We had a moving belt interface available in our laboratory, and the application of this type of interface to samples that contain PAHs has been demonstrated. Our efforts used PAH and other compounds of environmental interest to explore the use of this interface for screening purposes. We detected compounds of molecular weights from 166 to 278. Interferences from the belt itself precluded compounds of lower molecular weight from this analysis. Investigations of MM-5 samples and laboratory-spiked samples did not give positive results. The measurement of compounds by moving belt liquid chromatography/mass spectrometry (LC/MS) is not amenable to quick or easy screening techniques for environmental analysis. In our second approach we submitted a sample containing eight compounds to Vestec Corporation for analysis by a Model 201 dedicated Thermospray LC/MS coupled to a Compaq 386 computer with Technivent software. This particle-beam interface was also of limited usefulness for the sample that we submitted. Other particle-beam interfaces or Thermospray interfaces may give more usable screening data for the evaluation of emission sources.

The use of HPLC/MS in the characterization of emission sources offers the possibility of extending the coverage of analysis to high-boiling-point, thermally labile, and polar compounds. The techniques are complex, and much development work is needed to bring standard methods for general analysis to routine use.

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The complete report, entitled "Evaluation of POHC and PIC Screening Methods," (Order No. PB93-144137; Cost: $19.50; subject to change) will be available only from
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