



Project Summary

Report on Analytical Methodology for Purgeable and Semivolatile Components in Leachates and Solid Wastes

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Methods to determine purgeable and semivolatile organic compounds in solid wastes were studied. Extraction efficiencies, method quantification limits, and matrix effects were studied for 57 volatile and 142 semivolatile contaminants in a variety of solid waste matrices. Recoveries of spiked compounds were in the 90 to 100% range except for the highly polar materials for which poor recovery could be expected. The quantitation limits were found to be 5 $\mu\text{g/g}$ or less for about 90% of the compounds and 1 $\mu\text{g/g}$ or less for half of the compounds. Some significant matrix effects were detected in two sample type. The effects were both compound and matrix dependent and could not be predicted.

For purgeable compounds, the tetraglyme method gave results comparable to the Speis heated purge and trap method, and was superior to the aqueous dispersion method. Methyl tert-butyl ether was not as efficient as methylene chloride for the extraction of semivolatile organics in some lipophobic wastes. The tetraglyme and methylene chloride extraction methods are recommended for analyzing organics in solid wastes and solid waste leachates.

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully document-

ed in a separate report of the same title (see Project Report ordering information at back).

Introduction

Under the Resource Conservation and Recovery Act, the U.S. Environmental Protection Agency is responsible for assessing the potential hazard of municipal and industrial solid wastes. The organic chemical content of waste is one of the characteristics used to assess the potential hazard associated with waste disposal. In a recent investigation conducted by Battelle-Columbus Laboratories, analytical methodology was developed to determine purgeable and semivolatile organic compounds in solid wastes. Two extraction and gas chromatography/mass spectrometry (GC/MS) methods were developed and applied to a variety of solid wastes in an interlaboratory study. The program described in this report was undertaken to provide additional supporting data related to the application of these methods to the analysis of solid wastes and solid waste leachates, and to demonstrate the methods' effectiveness relative to other widely accepted procedures used to extract and analyze purgeable and semivolatile organic components.

For purgeable compounds, the tetraglyme extraction method is demonstrated and compared to the Speis heated purge and trap method and the aqueous dispersion method. Semivolatile compounds were extracted with methylene chloride or methyl tert-butyl ether

(MTBE). Quantitation by GC/MS, GC with flame ionization detection (GC-FID), and microcoulometric total organic halide (TOX) techniques were investigated. Each method was evaluated by determining the extraction efficiency of the solvent, matrix effects, and method quantification limits.

Purgeable Organic Methods

The three methods compared for purgeable organics were identical in the analysis phase, but differed significantly in the sample preparation and purge technique. The tetraglyme extraction method involved the extraction of 2 grams of waste with 40 mL of tetraglyme and the addition of 1 to 1000 μ L of the extract to a purge tube. The Speis method involved the purge of a neat sample of waste in a sand bath at 80°C. The purge of very small samples was necessary to avoid overloading the chromatographic system by high levels of organics. The aqueous dispersion method involved adding 1 to 5 grams of waste to deionized water to give a dispersion of approximately 1% solids, and adding an aliquot of the dispersion to a purging tube.

Semivolatile Organics

Methylene chloride was used in the neutral sonification extraction method for extracting solid wastes because it is known to be a good solvent for a wide variety of organic compounds. Methylene chloride extracts are readily analyzable by GC/MS, however, they cannot be used with other specific GC detectors such as electron capture, thermionic, or TOX detectors. For those applications, MTBE was proposed as an alternate solvent. Samples of six wastes were spiked and extracted with methylene chloride and MTBE. Aliquots of each extract were dried and the residue weights recorded. The masses of the residues found in the extracts show clearly that MTBE is not as effective as methylene chloride under the conditions used. MTBE was found to be effective for the extraction of lipophilic wastes, but not effective for lipophobic wastes. Recoveries of individual components also varied extensively within a given waste, showing compound dependency of extraction.

Method quantification limits for various semivolatile compounds extracted with methylene chloride were expected to vary depending on the detector sensitivities and the compounds' interaction with the waste matrix. In order to decrease the matrix interactions, the previously described kaolin/diatoma-

ous earth wet mud was used. Aliquots of the mud were spiked with 142 semivolatile organic compounds at three spike levels, over a range of 1 to 25 μ g/g. A fourth spike level of 125 μ g/g was tested for 107 of the more soluble compounds. The spiked samples were extracted, concentrated, and analyzed by GC/MS. Each of the 142 compounds was quantified using the internal standard approach. For 79 semivolatiles, the estimated quantification limit was 1 μ g/g or less, while for another 54 compounds the range was 2 to 5 μ g/g. Higher quantification limits were generally found for the more polar compounds; however, even for the most polar compounds such as phenols, anilines, and nitro compounds, the estimated quantification limits were about 5 μ g/g. The only compounds which could not be quantified at the 10 μ g/g level were thiophenol, 4-bromobenzoic acid, 4-nitrophenol, 2,4-D, 2,4,5-T, and diethylstilbestrol.

In each method, the organics were purged and concentrated on a Tenax trap which was then thermally desorbed. The effluent was analyzed in accordance with EPA Methods 601 and 602. In general, the amounts of organics found by the Speis method were similar to those from the tetraglyme method, but the amounts found by the aqueous dispersion method were often considerably less than the tetraglyme method.

The determination of method quantification limits for the purgeable organics using the tetraglyme method was carried out under conditions selected to avoid strong interaction between the solid matrix and the organic contaminants. An organic-free mixture of kaolin and diatomaceous earth was produced and fully hydrated with organic-free water to form a mud-like sample. Aliquots of the wet mud were spiked with 57 volatile organic compounds at four levels ranging from 1 to 125 μ g/g of waste. Each spiked aliquot was extracted with tetraglyme and analyzed by purge and trap GC/MS. Individual compounds were identified by a computer search technique and quantified by comparison to calibration runs at the same levels. Percent recoveries for the volatile organics from the matrix were $100 \pm 25\%$. The results also indicated that purging efficiency was not affected by addition of up to 4% tetraglyme to 5 mL of water in the purge solution.

Method quantification limits for 28 of the 57 compounds were 1 μ g/g of waste or less, and for another 17 compounds

the quantitation limits were 2 to 5 μ g/g. As expected, the quantification limits were for very polar water-soluble compounds were higher, but most were determined to be less than 25 μ g/g. Only three compounds, epichlorohydrin, dichloroacetonitrile, and vinyl acetate, could not be quantified at the 25 μ g/g level.

Matrix effects due to the coextraction of nonpurgeable compounds were studied to determine what effect the additional compounds have on the purging efficiency. Tetraglyme extracts of nine wastes were analyzed with and without spiking of 12 representative purgeable organics. Extracts were analyzed by GC with photoionization detector (PID) or Hall detector, and also by Dohrmann microcoulometric purgeable organic halogen (POX) analyzer. The methods provided similar results, but were too variable to detect any matrix effect in the GC-PID/Hall system. The POX method provided more precise data, and no significant matrix effects were observed.

Percent recoveries obtained for compounds spiked at the 25 μ g/g level were determined by comparing peak area analyte: internal standard ratios with those obtained from the corresponding calibration solution. The recoveries were $90 \pm 20\%$ for the majority of all compounds.

A study of matrix effects attributed to the total extractable mass was undertaken. Extracts of nine waste materials—both spiked and unspiked—were analyzed by microcoulometric TOX analysis and by GC-FID. For the TOX analyses, spike recoveries were 87 to 99% and were not significantly different from spiked blanks. It was concluded that no significant matrix effects were attributable to the waste matrix. Recoveries of spiked compounds by GC-FID were also generally in the same range. However, in two cases, significant matrix effects were detected. These effects were both compound dependent and matrix dependent and could not be readily predicted.

Discussion of Results

The data demonstrated the applicability of the tetraglyme extraction and methylene chloride extraction methods to the analysis of purgeable and semivolatile fractions of solid waste and solid waste leachates. The tetraglyme extraction method provided results which were comparable to the Speis method for analyzing purgeables and superior to the aqueous dispersion method results. For

semivolatile compounds, the methylene chloride extraction procedure provided excellent recoveries and few significant matrix effects. With few exceptions, notably the very polar, water-soluble compounds, the quantification limits for both classes of compounds were estimated to be less than 5 µg/g of waste.

Therefore, the tetraglyme and methylene chloride extraction procedures are recommended for determining purgeable and semivolatile organic compounds in solid wastes and solid waste leachates.

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Robert W. Slater is the EPA Project Officer (see below).

The complete report, entitled "Report on Analytical Methodology for Purgeable and Semivolatile Components in Leachates and Solid Wastes," (Order No. PB 84-180 157; Cost: \$11.50, subject to change) will be available only from:

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