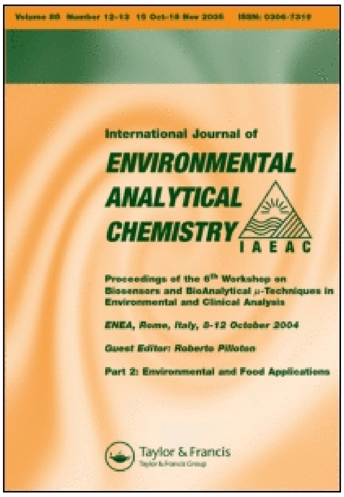

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Maskarinec, M. P. and Harvey, R. W.(1982) 'Screening of Sludges and Solid Wastes for Organic Compounds', International Journal of Environmental Analytical Chemistry, 11: 1, 53 — 60

To link to this Article: DOI: 10.1080/03067318208071561

URL: http://dx.doi.org/10.1080/03067318208071561

Intern. J. Environ. Anal. Chem., 1982, Vol. 11, pp. 53–60
0306-7319/82/1101-0053 $06.50/0

Printed in Great Britain

Screening of Sludges and Solid Wastes for Organic Compounds

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(*Received August 10, 1981*)

A rapid method for the screening for solid and semi-solid environmental materials has been developed. The method employs sequential equilibration for complete extraction of organic compounds. Acidic, basic, and neutral extracts are obtained. All extracts are analyzed directly by gas chromatography using fused silica columns. Thus, qualitative and semi-quantitative information on several classes of organic compounds is obtained with minimal sample preparation. In addition, the fractions obtained are suitable for short-term bioassays, such as the Ames Test. Comparison of this methodology with traditional soxhlet extraction was carried out.

KEY WORDS: Sludges, solid wastes, organic pollutants, sequential extraction, gas chromatography.

INTRODUCTION

Because of incidents involving improper disposal of solid wastes such as Love Canal and Valley of the Drums, analytical chemists have become increasingly aware of the challenges of organic analysis of solid and hazardous wastes. However, unlike the problems of analysis of air and water for organic pollutants, there is wide variability in the matrix itself. Samples may range from crystalline, brick-like solids to semi-solid, watery sludges. Traditional methods of extraction of organic compounds, such as Soxhlet extraction and sonication in an organic solvent, fail to provide

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†Research sponsored by the U.S. Environmental Protection Agency under Interagency Agreement No. DOE 40–1087–80, EPA No. D7–01149, under Union Carbide Corporation's contract W-7405-eng-26 with the U.S. Department of Energy.

adequate recovery of many organic compounds. This is due in part to the wide variability in the water content of solid wastes, and in part to the high adsorptivity of the wastes themselves. In many cases, Soxhlet extraction of sludges which contain fairly high levels of water results in channeling of the organic solvent through the sludge and incomplete contact of the organic solvent with the organic matter contained in the sludge. This problem can be alleviated somewhat by addition of a desiccant such as sodium sulfate to the sludge prior to Soxhlet extraction.[1] However, removal of the interstitial water may well result in a solid matrix which is much more adsorptive than its wet predecessor and much less likely to release organics when Soxhlet-extracted.

The analysis of solid wastes for organic constituents has also been accomplished using three-phase extraction systems.[2,3,4] The sample is made basic and extracted with organic solvent, made acidic and extracted, and the extracts are analyzed. These procedures result in extracts which can be analyzed according to EPA procedures[5] for base-neutral and acidic priority pollutants. However, maintaining the pH of a sludge is technically difficult, and the subsequent extraction may not be predictable. This paper describes methodology for the screening of solid wastes and sludges for organic compounds by sequential extraction with acidic, basic and neutral media. Thus, the pH of the extractant is adjusted and maintained. Analysis of the extracts can be performed directly using fused silica capillary columns.

EXPERIMENTAL

Collection of Samples

Solid waste materials were obtained directly from landfills or treatment plants. The only qualification placed on sample collection was that the source of the waste be somewhat homogeneous such that a relatively large volume of sample could be collected. The solid waste consisted of in the case of site 1, an agricultural chemical sludge; site 2, a tannery sludge; site 3, a pulp and papermill sludge; site 4, a plastics manufacturing sludge; site 5, a groundmill sludge; site 6, a wastewater treatment sludge in which influents came from a variety of chemical industries. The sludges were chosen to provide a variety of physical and chemical matrices and ranged from sandy, high-silica, fairly dry materials to oily, semi-solid materials. All samples were stored in glass bottles at 4°C prior to analysis.

Methods and Apparatus

Soxhlet extraction was carried out on each solid using methylene chloride for a duration of 24 hours as prescribed by EPA methodology.[1] Distilled in glass solvents (Burdick and Jackson, Inc.) were used in all phases of this work, including the aqueous equilibrations.

Gas chromatography was performed using a Hewlett-Packard Model 5736A gas chromatograph with a Model 18835B Grob-type split/splitless injection system. Capillary fused silica columns were obtained from J & W Scientific, Inc. Thirty-m × 0.25 mm i.d. columns coated with SE-52 stationary phase were used. The splitless injection technique was used throughout this work. Quantitation was obtained using a Hewlett-Packard Model 3390A recording integrator. Gas chromatography/mass spectrometry was performed using a Hewlett-Packard Model 5985A gas chromatograph/mass spectrometer/data system in the electron impact mode.

Gravimetric data on the extracts was obtained by application of an aliquot of each extract to a filter pad. The organic solvent was evaporated and the filter pad was weighed on an analytical balance.

RESULTS AND DISCUSSION

Figure 1 shows the analytical scheme developed in this work. The sample, typically 10–20 g, is added to a stoppered flask containing a solution made acidic with HCl. The flask is placed on a wrist-arm shaker and after 4 hours the pH is checked. If the pH is within the range 1.8–2.2, the extraction is continued. Otherwise, the pH is adjusted. The pH is checked after the extraction is finished. The filtered sludge is then added to an aqueous medium adjusted to pH 12 using 6 *N* sodium hydroxide and the same procedure used for extraction of the acids. After filtration, the sludge is neutralized and shaken with a 1:1 mixture of methylene chloride: acetone. The resultant neutral fraction is centrifuged, and the volume of all organic solvents is reduced using a Kuderna-Danish concentrator. The aqueous extracts are adjusted to pH 12 (bases) and pH 2 (acids). Solvent partition is used for removal into methylene chloride.

The isolation procedure has several advantages. The basic compounds are removed from the solid waste in the first equilibration. These are the compounds most likely to undergo chemical decomposition during the isolation procedure. Secondly, the filtration step, which is a key to any analysis of solids due to the possibility of adsorptive losses on the filter,[6] is performed on extracts in which the organic materials are largely ionic in nature and very soluble in the aqueous medium. Finally, the neutral extract is obtained after the sample has been dispersed with NaOH. A solvent system is used which is water miscible, thus providing for complete equilibration of the organic solvent with the solid waste.

Gravimetric data on the extracts is shown in Table I. Comparison of

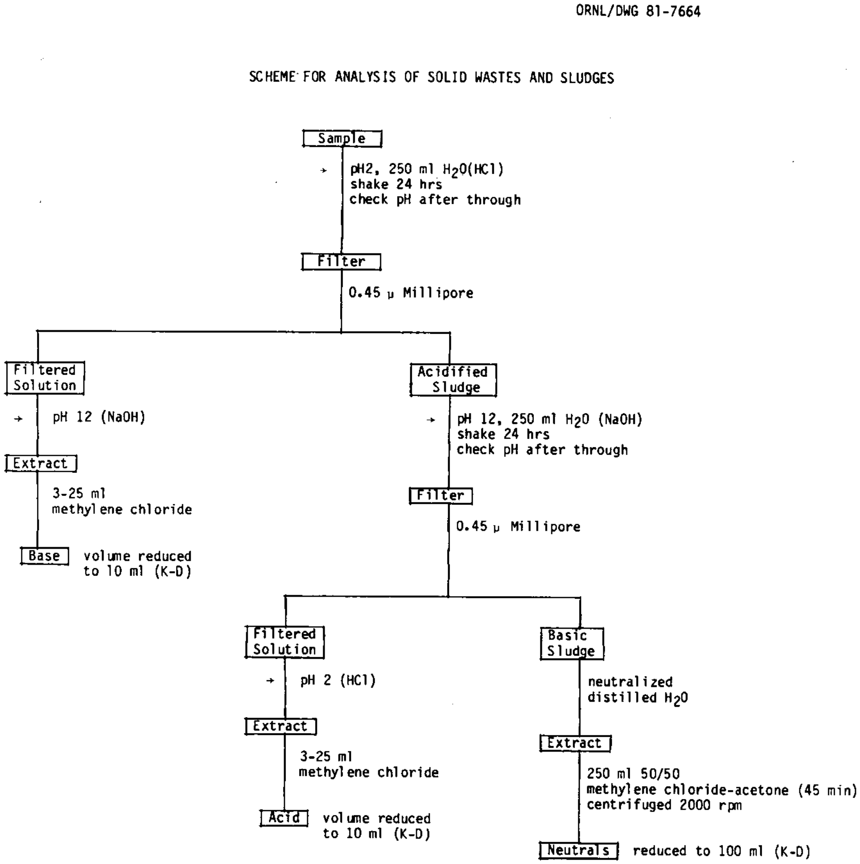

FIGURE 1 Scheme for Analysis of Solid Wastes and Sludges.

TABLE I
Comparison of Soxhlet Extraction with the Sequential Equilibration Scheme: Gravimetric Data on Solid Waste Extracts (mg/g solid)

Site	Acids	Bases	Neutrals	Soxhlet
1	0.74	4.4	38.4	12.1
2	2.4	0.15	14.9	3.0
3	6.5	0.2	24.0	1.3
4	3.5	0.1	58.2	21.0
5	1.6	0.2	26.6	14.2
6	1.0	0.2	60.6	11.2

the sequential equilibration scheme with the Soxhlet extraction on the individual wastes shows that in no case is there more organic material extracted by the Soxhlet than by the sequential equilibration scheme. The magnitude of the difference in the amount of organic material extracted ranges from a factor of 2 to a factor of 50, depending on the waste. The gravimetric data also illustrate the differences in chemical composition between the wastes. For example, site 1, which contains high levels of primary amines, has about 10% of the total weight extracted in the basic fraction: whereas site 2, which contains primarily hydrocarbons, has 99% of the total mass in the neutral fraction.

Comparison of the chromatograms obtained on the fused silica column of the various fractions isolated from site 2 is shown in Figure 2. The Soxhlet extract and the neutral fraction represent equivalent volume injections based on the mass of the solid used in the isolation. The acid fraction and the base fraction have been concentrated by a factor of 20. Qualitative comparison of the chromatograms reveals several interesting things. First, the Soxhlet extract qualitatively compares favorably with the neutral fraction obtained in the sequential equilibration. However, it is to be noted that recovery of the very volatile compounds, those eluting within 10 minutes, is greater in the neutral fraction than in the Soxhlet. Thus, it may be concluded that distillation effects have removed certain very volatile compounds from the Soxhlet extract. Secondly, comparison of the acid, base, and neutral fractions reveals very little carryover from fraction to fraction. Gas chromatography/mass spectrometry was performed on each fraction; and it was noted that the acid fraction contained primarily carboxylic acids, the basic fraction contained only bases, and the neutral fraction contained primarily aliphatic hydrocarbons. Thus, the scheme does effect at least a partial fractionation of the organic content of the original solid waste. Qualitatively, there is not much difference between the material extracted by the Soxhlet extractor and that extracted used the sequential equilibration scheme. However, in all cases enhanced recovery of individual compounds when using the sequential equilibration scheme was noted, particularly in the case of the very polar, water-soluble materials found in the acidic and basic fractions. Finally, Figure 2 clearly illustrates the ability of the fused-silica capillary column to chromatograph even very polar materials.

A further consideration in the assessment of hazard associated with solid wastes is the development of bioassay protocols for solid waste extracts. Perhaps the most widely used short-term bioassay is the Ames mutagenicity test.[7] However, when complex mixtures of organics such as sludge extracts are tested, microbial toxicity is often noted. The superior

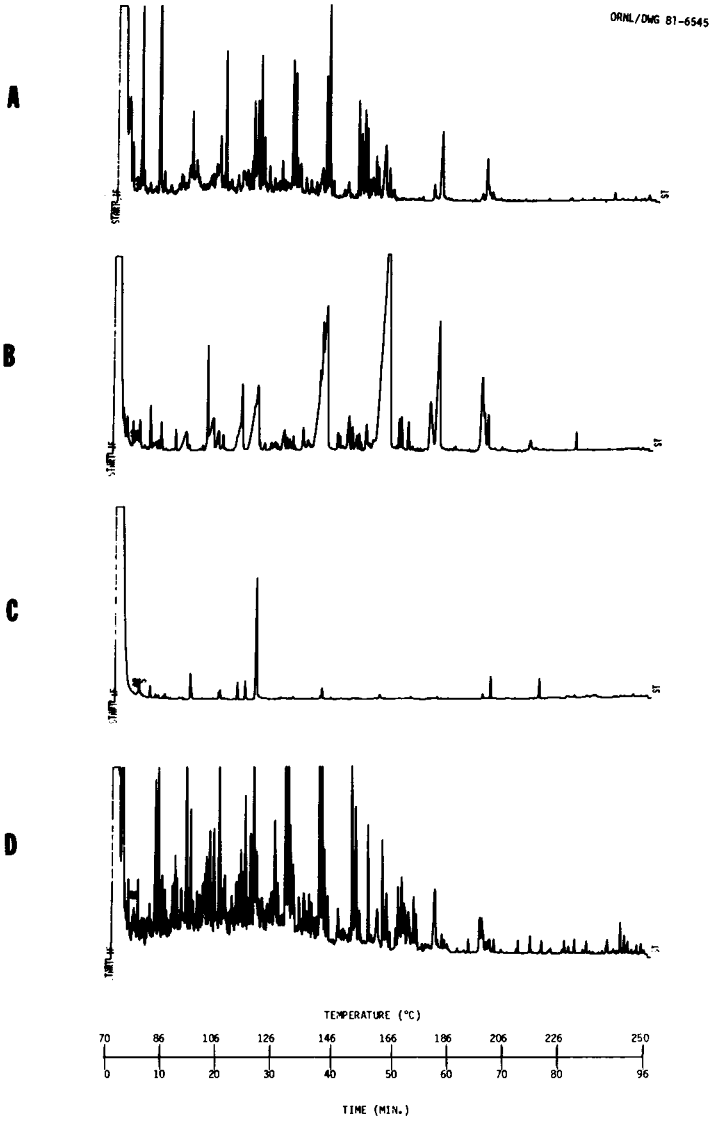

FIGURE 2 Comparison of Sequential Equilibration Scheme with Soxhlet Extraction for Site 2. Soxhlet (A), Acid Fraction (B), Base Fraction (C), and Neutral Fraction (D).

ability of the isolation methodology described here to provide extracts suitable for Ames testing is shown in Table II. While the Soxhlet extracts were usually inactive or toxic, mutagenic activity was detected in the acid and neutral fractions from site 1 as well as in the base fraction of site 5. The toxicity was consistently isolated in the acid fraction. Thus, suitability of this methodology for Ames testing is an additional advantage.

TABLE II
Summary of Salmonella Mutagenesis Bioassays on Solid Wastes from Five Landfills

Site No.	Solid Waste Extractions			
	Soxhlet	Acid	Base	Neutral
1	M, toxic	mildly toxic M TA 98 without activation	NM	M TA 98+100 with activation
2	NM, toxic	very toxic	NM	NM
3	NM	NM	NM	NM
4	NM, toxic	very toxic	NM	NM
5	NM	NM	M TA 98 with phenobarbitaol	NM

M: mutagenic.
NM: non-mutangeic.

The sample obtained from site no. 4 in this work was found to contain primarily phenolic substances, ranging from phenol to methylene bisphenol Therefore, carbon-14 labeled phenol was added to the sludge and extraction carried out by both Soxhlet and sequential equilibration in order to determine on an individual compound the relative efficiency of extraction. While it must be noted that the added phenol is not necessarily in the same physical state within the solid as the indigenous phenol, the measure of recovery is still legitimate. In this case phenol was recovered 65 % by the Soxhlet extractor and 95 % using the sequential equilibration technique. It may be further stated that some phenol was lost in the Soxhlet extraction due to volatility, while this is not a problem in the sequential equilibration since the phenol is extracted in its ionic state. After solvent partition, concentration of the phenol in the Kuderna-Danish was found to result in very small losses on the order of 3 %. Thus, after correction for recovery the quantity of phenol removed from the solid was 98.6 %. While this type of determination was not carried out on all individual compounds nor on all solid wastes, the recoveries might be expected to be similar.

CONCLUSIONS

A screening technique has been developed for the survey analysis of solid wastes for organic compounds. The method is not labor intensive and can be applied to multiple samples. Through the use of an autosampler, gas chromatography can be automated and as many as eight solid wastes can be screened for organic content within one working day. The use of fused-silica columns with their inherent inertness provides an analytical tool which is capable of separating mixtures of widely varying polarities. In addition, isolates may be directly applied to the Ames mutagenesis bioassay. While it was beyond the scope of this work to measure the recovery of each individual compound in each solid waste, in cases where the quantities of individual organics were accurately known and recoveries were determined, the recoveries were excellent.

References

1. "Test Methods for Evaluating Solid Wastes", USEPA SW-846, 1980.
2. "Development of Analytical Test Procedure for the Measurement of Organic Priority Pollutants in Sludge and Sediments", Midwest Research Institute Final Report EPA Contract No. 68–03–2695, June 26, 1979.
3. "Development of Analytical Protocols for Organic Priority Pollutants in Municipal Sludges", Battelle-Columbus Laboratories, Final Report EPA Contract No. 68–03–2624, March 30, 1979.
4. "Presence of Priority Pollutants in Sewage and Their Removal on Sewage Treatment Plants", University of Washington, Annual Report Grant R.806102, July 31, 1979.
5. *Fed. Reg.* **44**, 233, 69540, December 3, 1979.
6. D. K. Brown, C. W. Francis, M. P. Maskarinec and F. W. Larimer, "Toxicity of Leachates", ORNL/TM-7563, June 1981.
7. B. N. Ames, J. McCann and E. Yamasaki, *Mutat. Res.* **31**, 347 (1975).