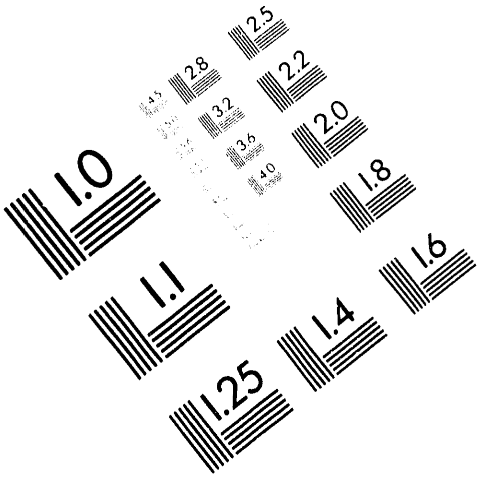

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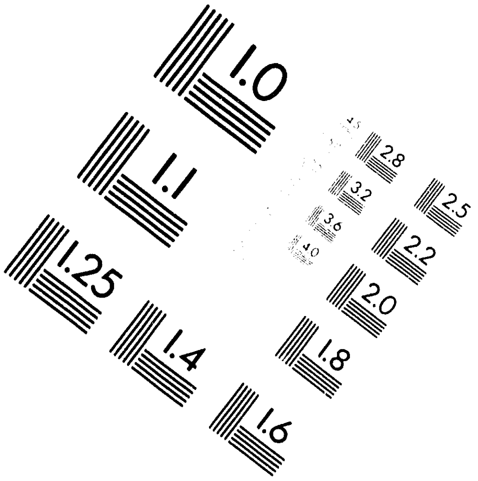

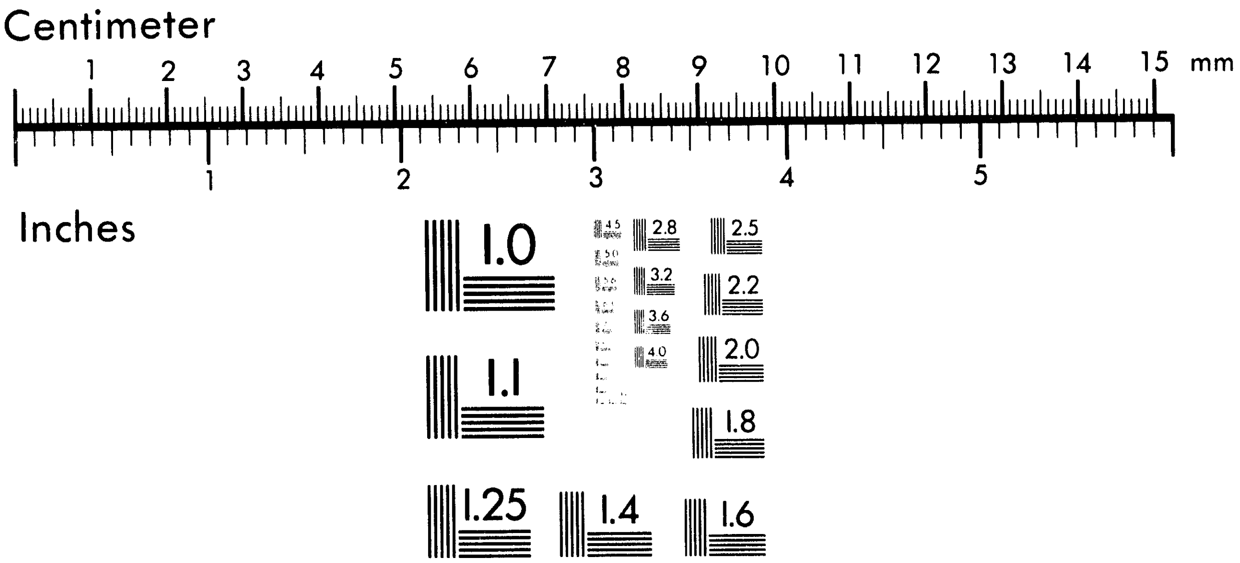

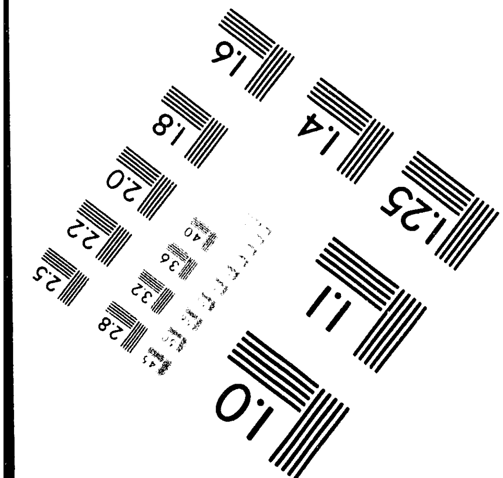

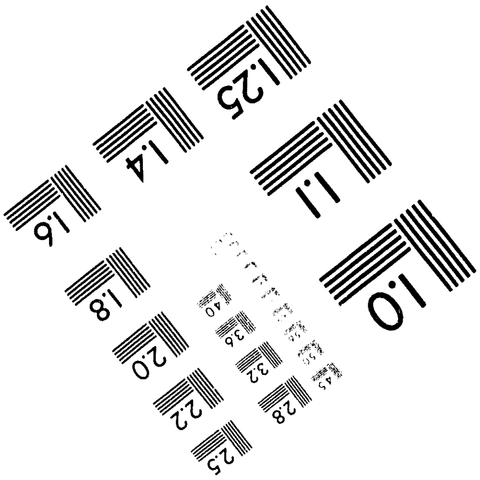

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ANALYTICAL PROCEDURES FOR WASTE MINIMIZATION AND POLLUTION PREVENTION*

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ABSTRACT

Procedures exist for waste characterization, but waste minimization and pollution prevention have not usually played a role in development of these procedures. The U.S. Department of Energy (DOE) expects to require several million characterizations over a 30-year period to accomplish the Department's goals in environmental restoration and waste management. The waste generated by the analytical procedures used for characterizations is a significant source of new DOE waste. We have begun investigating ways to reduce these secondary wastes, focusing on three areas: microanalysis using flow injection; reduction of solvent volume required for dissolution of waste samples for radiochemical analysis; and alternative sample preparation for analysis of organic constituents in waste samples. Preliminary results are reported.

BACKGROUND

The U.S. Department of Energy (DOE) expects to require a large number of waste characterizations over a 30-year period to accomplish the Department's goals in environmental restoration and waste management. Estimates of two million analyses annually are common.[1] The waste generated by the analytical procedures used for characterizations is a significant source of new DOE waste. Success in reducing the volume of secondary waste and the costs of handling this waste would significantly decrease the overall cost of this DOE program.

Selection of appropriate analytical methods depends on the intended use of the resultant data. It is not always necessary to use a "high-powered" analytical method, typically at higher cost, to obtain data needed to make decisions about waste management. Indeed, for some heterogeneous systems, the meaning of "high accuracy" becomes clouded if the data generated are intended as measurements of some property of the system being studied. Among the factors to be considered in selecting the analytical method are the lower limit of detection, accuracy, turnaround time, cost, reproducibility of the method (precision), interferences, and simplicity. Occasionally, there must be tradeoffs among these factors to achieve the multiple goals of a characterization program. The purpose of the work described here is to add "waste minimization" to the list of characteristics to be considered. In this paper we describe an approach and present preliminary results of modifying analytical methods for waste characterization to reduce both the cost and volume of secondary wastes. We expect that, in some cases, tradeoffs may be required to minimize waste while still generating data of acceptable quality for the decision-making process. In other cases, we expect that wastes can be reduced without sacrificing accuracy or precision.

APPROACH

A typical characterization includes the following sequential steps: planning, sample collection, transport, sample preparation and separations, measurement, data analysis, and reporting. Improvements in the planning stage are likely to lead to significant waste minimization because a better definition of what data are required for decisions leads to a more effective sampling scheme. Similarly, there are opportunities for waste minimization during the sampling process. However, we have taken the preparation, separation, and measurement steps as our prime targets because these laboratory-based processes involve chemicals, sometimes hazardous ones, and typically generate significant volumes of waste. Furthermore, we have reason to believe that the waste volume can be significantly reduced by using emerging new technologies. We have chosen to review the analytical procedures in three areas -- sample injection for inorganic analysis, dissolution of waste samples for radiochemical analysis, and sample preparation for analysis of organic constituents. In addition, we are reviewing and evaluating analytical procedures to identify priorities for future work on waste minimization and pollution prevention.

SAMPLE INJECTION FOR INORGANIC ANALYSIS

The determination of the inorganic constituents of environmental and waste samples usually involves the use of multielement techniques such as inductively coupled plasma/atomic emission spectrometry or inductively coupled plasma/mass spectrometry. These techniques provide simultaneous determination of inorganic constituents, such as heavy metals, in aqueous solution. Both techniques use a nebulizer that converts the sample into an aerosol that is injected into the high-temperature plasma. In the standard method, the sample is continuously pumped into a nebulizer having 1% utilization efficiency. However, the combination of a flow injection (FI) technique and a direct-injection nebulizer (DIN) will allow introduction of sample aliquots of less than a milliliter with a 100% utilization efficiency. That is, all of the sample aliquot will be converted to an aerosol for analysis. By using standard solutions, we will examine the sample size requirements and analytical figures of merit for FI-DIN relative to the standard sample introduction arrangement. The elements used for this test will be nickel, cadmium, lead, and uranium. These elements will be studied in a variety of acid and dissolved solid matrices.

DISSOLUTION OF SAMPLES FOR RADIOCHEMICAL ANALYSIS

The rapid and reproducible dissolution of solid samples is an important aspect of performing environmental and waste radiochemical analyses efficiently. However, traditional laboratory techniques[2,3] require either high-temperature fusion or prolonged acid digestion, both of which are time consuming and produce large quantities of secondary wastes.

Recent advances in microwave vessel design have led to systems that use working pressures in excess of 10 MPa (1500 psi). These new systems may allow us to significantly reduce the quantity of acid required and the acid fumes liberated during sample dissolution. Therefore, we are investigating the use of a high-pressure microwave system to replace the traditional method, which involves repetitive acid digestion on a hot plate for the preparation of samples for gross α/β analyses. The preliminary data, contained in Table 1, demonstrate good agreement between the gross α/β measurements on samples prepared by using the hot plate and the microwave dissolution techniques. Compared to the hot plate procedure, the acid volumes required for the microwave procedure are a factor of 20 lower, the analyst time for sample processing is a factor of 2.5 lower, and the turnaround time is a factor of 16 lower.

Table 1. Comparison of Grossα/β Measurements on Samples Prepared Differently

Soil Type	Alpha (pCi/g ± 2σ)		Beta (pCi/g ± 2σ)	
	Hot Plate	Microwave	Hot Plate	Microwave
SRM 4353	22 ± 8	19 ± 8	9 ± 5	7 ± 5
Fernald	12 ± 9	11 ± 9	<8	<10
Mound	25 ± 12	12 ± 10	12 ± 10	20 ± 7
ANL-E	15 ± 7	15 ± 8	14 ± 6	12 ± 6

Moreover, since reactivity increases as pressure increases, a high-pressure microwave system may make it possible to use alternative, nonhazardous solvents for the isolation of certain actinides from soils. We are investigating replacing strong, corrosive acids with milder, nonhazardous complexing agents for removing certain actinides from soils. The preliminary data in Table 2 show that the chemical recovery of ^{239}Pu extracted from soils using several nonhazardous solvents is acceptable for generation of reliable analytical results. Solvents with lower chemical recoveries yield greater sample-to-sample variability for determination of ^{239}Pu and resultant lower accuracy because the correction to measured values is larger.

Table 2. Alternative Solvents for High-Pressure Microwave Dissolution of Soils*

Solvent	^{239}Pu Activity** (pCi/g ± 2σ)	Chemical Recovery (%)
20 mL 1M Citric Acid	0.214 ± 0.020	67
20 mL 1M Sodium Citrate	0.237 ± 0.025	56
10 mL 2M Citric Acid	0.180 ± 0.044	59
10 mL 4M Tartaric Acid	0.257 ± 0.055	55
10 mL 1.5M Sodium Citrate	0.124 ± 0.029	33
10 mL 1.5M Sodium Tartrate	0.218 ± 0.040	68

*Soil used in each test was 1.0 g of SRM 4353 "Rocky Flats Soil #1."
** Accepted value is 0.217 ± 0.016 pCi/g.

Optimum conditions for the dissolution of samples by high-pressure microwave systems will be defined in this project. The use of extraction chromatographic resins in conjunction with microwave dissolution will be applied to the analysis of waste. This combination of techniques should significantly reduce secondary wastes generated during the analysis of selected actinides. Pressure systems will be investigated to allow the use of smaller resin bead sizes, which should reduce solution volumes.

SAMPLE PREPARATION FOR ORGANIC ANALYSIS

Standard U.S. Environmental Protection Agency (EPA) methods for the extraction and analysis of semivolatile organic compounds (SVOCs) in soil and solid waste samples typically use 400 to 500 mL of a solvent such as methylene chloride. Two advanced sample preparation techniques, supercritical fluid extraction (SFE) and microwave-assisted extraction (MAE)[4], have the potential to greatly reduce the amounts of solvent used. We will be studying these two extraction methods to test feasibility of their use and to identify conditions for optimum extraction of priority pollutants from solid matrices.

The effects of major system variables on extraction for both techniques will be studied. Initial samples will be prepared by spiking a semivolatile blank soil with a known amount of the 92 priority pollutants from Method 8270 in EPA's collection of waste analytical methods,[5] along with the normal surrogate standard mixture. The spiking solvent will be evaporated and the sample extracted. After sample cleanup and concentration, analysis and quantitation will be carried out using gas chromatography/mass spectrometry. After the methods have been optimized, the techniques will be used to extract soils with known concentrations of SVOCs, and the results will be compared with the current extraction methods (Soxhlet and sonication).

Microwave-assisted extractions will be carried out with a CEM Corporation MES 1000 microwave extraction system. We will be studying the effects of solvent composition, moisture content, temperature, extraction time, and pulsed versus continuous extraction. It is expected that MAE will use between 30 and 40 mL of solvent per sample. Supercritical fluid extractions will be carried out by using a Suprex SFE/50 instrument. Variables to be considered include CO_2 flow rate, temperature, pressure, solvent modifiers, extraction cell configuration, sample collection technique, moisture content, sample size, extraction time, and static versus dynamic extraction. Since the actual extraction solvent in SFE is CO_2, which is vented to the atmosphere, the technique has the potential to reduce liquid solvent usage to less than 10 mL per sample.

CONCLUSIONS

We conclude that alternative methods exists for sample preparation and analysis that provide data of suitable quality for the decision-making process while simultaneously reducing the amount of secondary wastes produced. Preliminary data show that high-pressure microwave dissolution achieves results equivalent to traditional dissolution methods while significantly reducing the hazardous waste that is generated during sample preparation.

ACKNOWLEDGMENT

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