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Waste Minimization in Analytical Methods*

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Introduction

The U.S. Department of Energy (DOE) will require a large number of waste characterizations over a multi-year period to accomplish the Department's goals in environmental restoration and waste management. Estimates vary, but two million analyses annually are expected.[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 samples taken from some heterogeneous systems, the meaning of "high accuracy" becomes clouded if the data generated are intended to measure a property of this system. Among the factors to be considered in selecting the analytical method are the lower limit of detection, accuracy, turnaround time, cost, reproducibility (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 present results of modifying analytical methods for waste characterization to reduce both the cost of analysis and volume of secondary wastes. Although tradeoffs may be required to minimize waste while still generating data of acceptable quality for the decision-making process, we have data demonstrating that wastes can be reduced in some cases without sacrificing accuracy or precision.

Approach

A typical characterization includes the following sequential steps: planning, sample collection, sample transport, sample preparation (including separations), measurement, data analysis, and reporting. Opportunities for waste minimization exist in the planning stage and in 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 data to show that the waste volume can be significantly reduced by applying 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.

Sample Introduction for Inorganic Analysis

With the promulgation of SW-846 Update II,[2] many of the regulated elements present in environmental and waste samples may be determined by using inductively coupled plasma (ICP) atomic emission spectroscopy, ICP-mass spectrometry (ICP-MS), or a combination thereof. Although these measurement techniques are often capable of achieving instrument detection limits of micrograms per liter or better, normal ICP sample introduction -- continuous pneumatic nebulization (CPN) of a sample solution -- utilizes only 1 to 10% of the sample uptake. The remaining portion of the consumed sample goes directly to laboratory waste, thereby creating a secondary waste stream that would be considered corrosive by standards in the Resource Conservation and Recovery Act, and could also be toxic or mixed radioactive waste. Despite the poor efficiency of the pneumatic nebulization process, dissolution or digestion is the preferred means of preparing bulk solids for ICP analysis. Our objective in this project is to identify and evaluate high-efficiency alternatives for solution introduction that will reduce or eliminate this particular secondary waste stream.

Graphite furnace atomization, hydride generation, and nebulization can all be used to introduce dissolved analytes into an ICP.[3] In the case of furnace atomization and hydride generation, the efficiency with which the analyte is introduced depends in large part upon the chemical properties of the element. The utility of these techniques varies considerably among groups in the periodic table. Solution nebulization, which is a physical means of analyte transport, works well for a broad range of elements and, thus, for a broad range of applications; however, the inefficiency of solution nebulizers was, until recently, the major source of ICP waste. However, development of the direct injection nebulizer (DIN),[4,5] which utilizes 100% of a sample solution by nebulizing it directly into the base of the ICP, has allowed analysts to reduce or eliminate ICP waste.

We compared solution analyses using DIN and CPN. Table 1 summarizes the equipment used and operating conditions. Use of the flow injection (FI) manifold was critical because it facilitated reductions in sample uptake and rinsing between samples. The impact of these reductions is also shown in the last two rows of Table 1. Note that the duration of each spectral integration and the number of repeat integrations were identical for the two systems. The 33% improvement achieved in analysis time using FI-DIN was due principally to the excellent rinseout characteristics of the FI-DIN system. Better rinseout also contributed to the 50% reduction in per sample waste volume; however, the lower consumption of the FI-DIN system was also a factor.

Table 1. Equipment and operating conditions used in this work.

	Continuous pneumatic nebulization	**Flow-injection direct-injection nebulization**
ICP-mass spectrometer	PlasmaQuad II+ with high performance interface (Fisons Instruments, Winsford UK)	
Nebulizer	V-groove (Fisons)	Microneb 2000 (CETAC, Omaha NE)
Spray chamber	Scott double-pass (Fisons)	none
Primary solution pump	Minipuls 3 peristaltic pump (Gilson, Middleton WI)	Model S1100 HPLC pump (CETAC)
Solution consumption (mL/min)	1.0	0.06
Injection loop (mL)	none	0.5
Analysis time (min/sample)	7.5	5.0
Waste volume (mL/sample)	7.1	3.4

Tables 2 and 3 compare important analytical figures of merit that were obtained using each of the sample introduction systems. The data in Table 2, which are based upon nine blank analyses carried out over two days, indicate that the instrumental detection limits achieved with each system are quite similar. However, neither system obviates blank limitations as shown by the comparatively poor detection limits for Ni and Pb. The blank limitations for Ni and Pb also appear to affect the precision of Ni and Pb determinations in dilute aqueous standards and two representative aqueous laboratory wastes (Table 3); however, determinations made using both systems appear to agree well in most instances, even where precision is poor.

The data we have collected thus far suggest that significant reductions in waste volume and analysis time are realized, with little or no compromise in analytical figures of merit, when FI-DIN is used in place of CPN for ICP-MS analyses. These results should also be directly applicable to ICP atomic emission spectroscopy. As we continue to examine the FI-DIN system, we intend to make further comparisons of long-term figures of merit, while also studying the susceptibility of FI-DIN sample introduction to common ICP-MS interferences, i.e., polyatomic ion spectral interferences and sensitivity suppression by matrix elements. We will also examine means of further reducing waste and analysis time by means of different flow injection protocols, i.e., smaller injection loops, shorter rinse times, and changes in valve and pump switching logic.

Table 2. Comparison of ICP-MS 3σ detection limits.

	Instrument detection limit (µg/L)	
Element	**FI-DIN**	**CPN**
Ni	1	0.5
Cd	0.05	0.05
Pb	0.8	0.6
U	0.01	0.003

Table 3. Comparison of analyte concentrations determined in nine ICP-MS analyses.

Sample	Method	Analyte concentration (mg/L)			
		Ni	Cd	Pb	U
10 mg/L Std	FI-DIN	10.1 ± 0.9	10.2 ± 0.1	12 ± 1	10.14 ± 0.04
	CPN	10.2 ± 0.3	10.02 ± 0.09	9.7 ± 0.2	9.4 ± 0.2
Waste sol'n # 37	FI-DIN	0.8 ± 0.2	1.31 ± 0.01	1.8 ± 0.3	3.24 ± 0.03
	CPN	0.79 ± 0.05	1.34 ± 0.03	1.58 ± 0.06	3.06 ± 0.09
Waste sol'n # 40	FI-DIN	0.38 ± 0.03	0.0656 ± 0.0005	0.77 ± 0.06	0.613 ± 0.006
	CPN	0.37 ± 0.09	0.073 ± 0.008	0.72 ± 0.07	0.57 ± 0.02

Soil Dissolution for Radiochemical Analyses

Dissolution is a vital aspect of sample preparation for environmental radiochemical analyses of soils. The traditional laboratory techniques[6,7] of high temperature fusion and prolonged acid digestion are time consuming. In addition, they both generate large quantities of secondary wastes and fume hood emissions. Microwave technology has previously had limited application in the radiochemical laboratory because of constraints on sample size resulting from vessel pressure limitations. However, newer microwave systems incorporating closed vessels can withstand pressures up to 10 MPa (1500 psi). Thus, larger sample sizes can be accommodated. We have achieved shorter processing times and reliable sample digestion while dramatically reducing secondary wastes.

We have used gross α/β measurements to compare the performance of alternative procedures for sample preparation: (1) a high-pressure microwave system and (2) a traditional procedure that uses a hot plate for digestion by repetitive acid treatment. A variety of soil types of potential interest to DOE were selected for testing, including a National Institute of Standards and Technology reference soil from the Rocky Flats Plant (SRM 4353) and several environmental and contaminated soils from selected DOE sites (labeled Con1, Con2, and Con3). Paired, two-tailed *t*-tests indicate no significant differences at the 95% confidence interval in the measurements on samples prepared from the hot plate and microwave digestion procedures for these soils; representative data[8] are shown in Table 4. In addition, the microwave procedure demonstrated good reproducibility and low blank values. In comparison to the traditional hot plate method, 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 sample turnaround time is a factor of 16 lower.

Because reactivity increases as pressure increases, these high-pressure microwave systems may make it possible to use alternative, nonhazardous solvents to leach certain contaminants from soils for analysis. We have also investigated replacing strong, corrosive acids with milder, nonhazardous complexing agents for removing plutonium from soils. While these complexing agents have been successful for the extraction of contaminants such as plutonium, as shown in Table 5, the reagents fail to totally break down the sample matrix and, therefore, are not applicable to matrix constituents such as U and Th.

Table 4. Gross α/β analyses by hot plate and microwave digestion methods.

Soil type	Alpha (pCi/g ± 2σ)		Beta (pCi/g ± 2σ)	
	Hot plate	Microwave	Hot plate	Microwave
SRM 4353	15 ± 5	18 ± 5	14 ± 4	11 ± 3
Fernald	9 ± 7	9 ± 5	<6	10 ± 3
Mound	22 ± 9	13 ± 7	16 ± 6	19 ± 4
Con1	320 ± 34	354 ± 35	31 ± 7	32 ± 7
Con2	174 ± 26	191 ± 26	22 ± 7	23 ± 7
Con3	183 ± 26	202 ± 27	27 ± 8	38 ± 8

Table 5. Alternative solvents for high pressure microwave digestion of soils. Soil utilized was 1 g of SRM 4353 "Rocky Flats Soil #1." Accepted value is 0.217 ± 0.016 pCi ^{239}Pu/g.

Solvent specifications	^{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 1.5M sodium citrate	0.124 ± 0.029	33
10 mL 4M tartaric acid	0.257 ± 0.055	55
10 mL 1.5M sodium tartrate	0.218 ± 0.040	68
10 mL 1M Na_2CO_3-0.1M EDTA	0.201 ± 0.014	45
20 mL 1M Na_2CO_3-0.1M EDTA	0.174 ± 0.032	36
10 mL 2M Na_2CO_3-0.1M EDTA	0.183 ± 0.044	55
20 mL 2M Na_2CO_3-0.1M EDTA	0.189 ± 0.039	62
20 mL 1M citric acid + 1 mL H_2O_2	0.238 ± 0.041	50
10 mL 2M citric acid + 1 mL H_2O_2	0.209 ± 0.037	58

Microwave-Assisted Extraction of Organic Compounds

Standard U.S. Environmental Protection Agency (EPA) methods for the extraction and analysis of semivolatile organic compounds (SVOCs) (also called the "base/neutral/acid fraction") in soil and solid waste samples typically use over 300 mL of hazardous solvents, such as methylene chloride. Microwave assisted extraction (MAE)[9,10,11,12] has the potential to reduce the amount of solvent required to 30 to 50 mL. We have studied the extraction of SVOCs from soil, sediment, and sludge samples using SW-846 Method 8270B[2] for measurement and the MAE technique for preparation of samples. In most cases, the MAE results compare favorably with the conventional extraction techniques while simultaneously allowing for reduced solvent usage.

To test the extraction of all Method 8270B SVOCs, these materials were spiked onto a blank soil (Environmental Resource Associates) and extracted at various temperatures. Three solvents were used: methylene chloride, a 50:50 mixture of methylene chloride:acetone, and a 50:50 mixture of hexane:acetone. With the spiked samples, no obvious trends were seen between extractions carried out at 40, 80, and 120°C. At 40°C, increasing the extraction time from 5 to 20 minutes increases the extraction yields; however, at 80 and 120°C this trend is not observed. No dependence of recoveries on the microwave power setting was observed. Sample water content tends to decrease extraction efficiency for the acetone-containing solvents while increasing the extraction of polar compounds with methylene chloride. Table 6 gives the recoveries of semivolatile organic compounds by class for sonication extraction, Soxhlet extraction, and MAE with four different solvent compositions. More complete data are available elsewhere.[13] Direct comparison with an 18-h Soxhlet extraction procedure using methylene chloride gives very similar results for methylene chloride:water, methylene chloride:acetone, and hexane:acetone. Methylene chloride MAE extractions yield similar results to sonication extractions with methylene chloride. Neither MAE nor sonication with methylene chloride is as efficient as the Soxhlet and MAE procedures with other solvents. A number of compounds are not extracted efficiently (particularly strongly polar materials such as benzoic acid and some amines and pyridines). However, this inefficiency is observed with both MAE and traditional extraction techniques.

Table 6. Comparison of the recoveries of SVOCs using alternative extraction techniques.

Semi-volatile compound class	Compounds in class	Average percent recovery					
		Sonication extraction	Soxhlet extraction	Microwave-assisted extraction			
				CH_2Cl_2	CH_2Cl_2 + H_2O[a]	CH_2Cl_2 + acetone	Hexane + acetone
Alkylphenol	5	67	56	68	69	70	72
Halophenol	10	72	78	79	76	78	82
Nitrophenol	4	46	64	56	76	70	76
Phthalate	6	110	97	97	76	70	74
PAH	20	86	84	82	90	87	93
Halocarbon	13	60	70	70	81	78	82
Ether	6	72	75	72	79	77	80
Ketone	2	67	74	70	84	81	81
Sulfonate	2	66	76	24	73	69	63
Alcohol	1	69	73	72	70	71	71
Carboxylic acid	1	13	61	17	38	41	37
Pyridine	2	1	36	0	54	19	24
Amide	2	57	75	56	85	84	86
Nitrosoamine	5	64	70	60	77	77	83
Aromatic amine	12	41	57	49	71	56	54
Hydrazine	1	73	70	69	79	76	78
Azoamine	1	18	78	20	78	88	96
Nitroamine	5	84	88	86	101	95	96

[a] Water is 10% by weight of sample.

The MAE extractions were carried out on soil CRM103-100 (Lot No. RQ103), which contains 15 certified compounds. This PAH-containing soil sample (Fisher Scientific/Resource Technology Corporation) is from a superfund site located in the western United States. Extraction times of 5, 10, 20, and 40 minutes and temperatures of 40, 80, and 120°C were tested. The optimum time/temperature combination was found to be 20 minutes at 120°C. Under these conditions, the average percent recovery for the certified compounds in the reference material is 90% of the certified values with methylene chloride solvent, 113% with methylene chloride:acetone, and 109% with hexane:acetone. When 10% by weight of water is added to the solid before extraction, the methylene chloride extraction efficiency goes up to 100%, while the other two solvents decrease to around 80%. Addition of sodium sulfate does not improve yields. Experiments with different microwave power settings showed no clear trends.

Recoveries of SVOCs with MAE extraction on two quality control standards (Environmental Resource Associates) were comparable to those for most compounds extracted by traditional techniques. The low recoveries observed could be an indication of either a problem with the MAE technique or a lack of sample stability. Extraction of PAHs from a certified American Petroleum Institute separator sludge (CRM101-100, Fisher Scientific/Resource Technology Corporation) gave compound recoveries well within certified prediction intervals. Extraction of PAHs from NIST SRM 1941a, however, only yields an average recovery of about 50% of the certified value.

Conclusions

We have investigated alternative methods for sample preparation and analysis that minimize the production of secondary wastes. Performance data on samples of interest have shown that these alternative methods yield results of comparable quality to those obtained for traditional methods. Our work has demonstrated that flow injection coupled with direct injection nebulization (FI-DIN) is less wasteful than conventional sample introduction techniques, yet critical analytical figures of merit (precision, accuracy) are uncompromised. Significant reductions in waste volume from radiological analysis have been achieved by preparing samples with a high-pressure microwave system. In addition, we have demonstrated that alternative, non-toxic solvents can be used for radiological analyses without compromising extraction efficiency. Recoveries of semivolatile organic compounds from soil, sediment, and sludge using microwave-assisted extraction compare well with those using traditional extraction techniques. Solvent usage and, thus, waste produced are decreased by an order of magnitude with microwave-assisted extraction.

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