PREPARATION OF POLYETHYLENE SACKS FOR COLLECTION OF PRECIPITATION SAMPLES FOR CHEMICAL ANALYSIS

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METRIC CONVERSION TABLE

For the reader who may prefer to use inch-pound units, conversion factors for terms used in this report are listed below:

Multiply SI Units	*By*	*To obtain inch-pound units*
liter (L)	1.057	quart
megaohm (MΩ)	1.000	megaohm
microgram (μg)	3.52×710^{-8}	ounce, avoirdupois
milliliter (mL)	0.03382	ounce, fluid

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ABSTRACT

Polyethylene sacks are used to collect precipitation samples. Washing polyethylene with acetone, hexane, methanol, or nitric acid can change the adsorptive characteristics of the polyethylene. In this study, simulated precipitation at pH 4.5 was in contact with the polyethylene sacks for 21 days; subsamples were removed for chemical analysis at 7, 14, and 21 days after initial contact. Sacks washed with acetone adsorbed iron and lithium; sacks washed with hexane adsorbed barium, iron, and lithium; sacks washed with methanol adsorbed calcium and iron; and sacks washed with 0.30 *N* nitric acid adsorbed iron. Leaching the plastic sacks with 0.15 *N* nitric acid did not result in 100-percent recovery of any of the adsorbed elements. Washing polyethylene sacks with dilute nitric acid caused the pH of the simulated precipitation to be decreased by 0.2 pH unit after 1 week of contact with the polyethylene and increased the specific conductance by 10 microsiemens per centimeter. Contamination of precipitation samples by lead was observed at approximately 0.1 microgram per liter from contact with precleaned polyethylene sacks. No measurable contamination of precipitation samples by zinc occurred.

INTRODUCTION

The adsorption of trace elements from precipitation samples onto collection surfaces has been of great interest in precipitation monitoring and sampling programs (Chan and others, 1983; Eichholz and others, 1965; Struempler, 1968). The apparent concentration of trace elements can be affected by collection-surface adsorption (Good and Schroder, 1984). The emphasis of this interest in adsorption has been placed on finding a material that does not significantly adsorb trace metals from water samples at the range of 3.0 to 8.0 pH units. Various plastic materials have shown considerably different adsorptive characteristics (Chan and others, 1983; Eichholz and others, 1965; Good and Schroder, 1984); therefore, the focus on material type has overshadowed the importance of cleaning protocols prior to sample introduction into containers. Some studies that have included data on plastic-surface cleaning have demonstrated that nitric-acid cleaning may have a noticeable effect on the plastics' adsorptive properties (Feldman, 1974; Karin and others, 1975; Laxen and Harrison, 1981). Nitric acid also is an effective agent for leaching trace-element contaminants from plastic surfaces and reduces adsorption losses from water samples acidified to pH less than 1.

This report documents the results of experiments to determine: (1) The effects on sample composition resulting from the pretreatment of polyethylene sacks with acetone, hexane, or methanol in combination with either 0.30 *N* or 0.15 *N* nitric acid; and (2) the effects on sample pH and specific conductance resulting from pretreatment of polyethylene sacks with 0.30 *N* nitric acid.

DESIGN OF POLYETHYLENE SACK EXPERIMENTS

Polyethylene was chosen for this study because Chan and others (1983) and Good and Schroder (1984) indicated that polyethylene adsorbed certain trace elements (copper, iron, lead, molybdenum, and vanadium) at pH 4.5, which commonly is the pH of natural precipitation. Good and Schroder (1984) reported that polyethylene adsorbed lower percentages of these five elements and had higher recovery of the adsorbed elements. Plastic sacks were used because they are easy to handle, they are used as precipitation collectors, they are easily obtainable, and they are relatively inexpensive.

Precipitation-Sample Composition

The elements of interest (barium, beryllium, calcium, cadmium, cobalt, copper, iron, lithium, magnesium, manganese, molybdenum, sodium, lead, vanadium, and zinc) are elements that may be found in natural precipitation (Boutron, 1982; Davidson and others, 1981; Jeffries and Snyder, 1981) or that are measurable by inductively-coupled plasma, atomic-emission spectrometry (ICP) (Garbarino and Taylor, 1979). Concentrations of elements that were five times the ICP detection limit were used to simulate concentrations of these elements in natural precipitation.

Adsorption Experiment

The adsorption study was conducted for 21 days, the maximum time predicted that a sample would be in contact with a collector before chemical analysis. Thirty-six polyethylene sacks were treated in the following four steps:

1. Nine sacks were rinsed with approximately 100 mL of acetone; nine were rinsed with 100 mL of hexane, nine were rinsed with 100 mL of methanol, and nine were rinsed with 100 mL of deionized water. The sacks were allowed to stand for 5 minutes with the organic solvent in contact with the sack interior.

2. All 36 sacks were rinsed three times each with approximately 200 mL of deionized water.

3. All 36 sacks were rinsed once with 100 mL of 0.30 *N* nitric-acid solution.

4. All 36 sacks were rinsed three times again, each with approximately 200 mL of 2-MΩ deionized water.

A simulated-precipitation solution was prepared using reagent-grade metals or chemical salts solutions and deionized water. Sixteen liters of 2-MΩ deionized water were collected in a clean linear-polyethylene container, and sufficient element solution was added to obtain the desired concentration for each of the 15 elements of interest. The pH of the resulting solution was adjusted to pH 4.5, using dilute hydroxide, and 500 mL of the solution were added to six sacks of each rinse type. One liter of stock solution was placed into a fluorinated ethylene propylene bottle, and the pH was adjusted to less than 2.0, using nitric acid.

Ten-milliliter samples were withdrawn from each sack on days 7, 14, and 21 after intial introduction of the sample. Samples were analyzed for the 15 elements by ICP. When they were not being subsampled, the sacks containing the samples remained in the dark at room temperature. The stock solution was analyzed by ICP on days 1 and 7, twice in triplicate, and on days 14, 21, and 22 once in triplicate, for a total of 21 analyses.

Leach Experiment

On day 21, to attempt recovery of the absorbed elements, 100 mL of 0.15 *N* high-purity nitric-acid solution were added to the emptied sacks. Each sack was sealed and slowly rotated, coating all the interior surface with the nitric acid. Acid contact was maintained for 24 hours, after which 10-mL samples were removed from each sack and analyzed by ICP.

Contamination Experiment

A separate contamination experiment was conducted concurrently with the adsorption study to determine whether elements leached from the polyethylene sacks might be contaminating the samples. Three sacks of each rinse type were used in this experiment. One hundred milliliters of 0.15 *N* high-purity nitric acid were added to each sack. The 12 sacks were stored in the dark at room temperature for 7 days. The solutions were transferred to clean fluorinated ethylene propylene bottles after 7 days, and were analyzed for lead and zinc by graphite furnace atomic absorption spectrometry (GFAA).

Precipitation-Sample pH and Specific Conductance

Six polyethylene sacks and one 125-mL fluorinated ethylene propylene bottle were treated in the following three steps:

1. Sacks and bottle were rinsed three times each with approximately 200 mL of deionized water.

2. Sacks and bottle were rinsed once with 100 mL of 0.30 *N* nitric-acid solution.

3. Sacks and bottle were rinsed three times each with approximately 200 mL of deionized water.

A simulated-precipitation solution was prepared (at pH 4.5) using deionized water and nitric acid. One hundred milliliters of this solution were added to each of the six sacks. The fluorinated ethylene propylene bottle was filled with the solution, leaving no headspace when capped. The sacks and bottle were stored at room temperature in the dark for 1 week.

Sample pH and specific conductance were determined after 7 days. One determination of pH and specific conductance was made for each of the six samples stored in the sacks, and four determinations of pH and specific conductance were made for the bottled sample.

RESULTS OF POLYETHYLENE SACK EXPERIMENTS

Precipitation-Sample Composition

Adsorption experiment

Target concentrations, representing five times the ICP detection limit for the elements of interest, are shown in table 1. Mean concentrations of each element in the stock solution were calculated; then, these concentrations were used to determine the percent adsorption for each element. Mean concentrations of the stock solution in the fluorocarbon bottle were used to determine the percent adsorption for each element. Adsorptive losses by prerinse type are shown in table 2; only iron was adsorbed, regardless of sack-rinse type.

The iron adsorption observed was similar for all rinse types. Iron losses to the sacks ranged from 71 to 78 percent. The minimum iron loss occurred for sacks rinsed with 0.30 *N* nitric acid. Hexane- and acetone-rinsed sacks adsorbed lithium in identical quantities. Calcium was adsorbed only by methanol-rinsed sacks; barium was adsorbed only by hexane-rinsed sacks.

Rinsing the polyethylene sacks with an organic solvent was expected to remove any organic polymers attached to the plastic surface; rinsing the polyethylene sacks with nitric acid was expected to deactivate adsorption sites on the plastic surface. Combination of these two effects was expected to diminish the adsorption of the elements by the plastic (Good and Schroder, 1984). Good and Schroder (1984) found that polyethylene adsorbed 7 percent of the copper, 44 percent of the lead, and 8 percent of the vanadium after 17 days at a pH of 4.5.

Calcium concentration of the solution in contact with the acetone-rinsed sacks was about twice the calcium concentration determined in the stock solution. This increase was not observed in any other samples regardless of prerinse treatment. Possibly the acetone was contaminated with calcium that remained in the sack interior or the acetone leached calcium from the sacks. Acetone-rinsing the sacks may affect the integrity of the sacks. Some sample leaked from these sacks.

Table 1.--*Chemical determination of stock solution by inductively-coupled plasma, atomic-emission spectrometry*

Element	Micrograms per liter		Relative standard deviation (percent)	Number of determinations
	Target concentration	Mean concentration		
Barium------	10	10	18	21
Beryllium---	2.5	2.7	48	21
Calcium-----	100	103	10	21
Cadmium-----	5	5	51	21
Cobalt------	15	11	38	21
Copper------	50	56	8	21
Iron--------	15	15	36	21
Lithium-----	20	28	43	20
Magnesium---	50	45	4	21
Manganese---	5	5	34	21
Molybdenum--	50	39	56	20
Sodium------	1,000	1,158	8	21
Lead--------	50	56	39	20
Vanadium----	30	28	17	21
Zinc--------	15	18	23	21

Table 2.--*Percent loss of elements adsorbed by polyethylene at pH 4.5 after 21 days as a function of rinse type*

Rinse type	Element	Adsorbed loss	
		Micrograms	Percent
Acetone-------------------	Iron	5.9 ± 1.2	78
	Lithium	8.3 ± 0.7	83
Hexane--------------------	Barium	1.5 ± 0.07	31
	Iron	5.4 ± 1.0	72
	Lithium	8.3 ± 0.8	83
Methanol------------------	Iron	5.8 ± 1.1	77
	Calcium	43.2 ± 16.4	14
Nitric acid---------------	Iron	5.3 ± 1.1	71

Leach Experiment

One hundred milliliters of 0.15 *N* nitric-acid solution were used to recover the ions adsorbed by the polyethylene. Results of this experiment are summarized in table 3. The mass, in micrograms of element adsorbed, was calculated using adsorption data. Percent recovery was defined as the mass leached from the sacks, divided by the calculated mass adsorbed, multiplied by 100. No ions were 100-percent recovered. A more concentrated acid-leaching solution may be more effective at recovering adsorbed elements; however, the nitric-acid concentration used in this study was twice the concentration reported by Good and Schroder (1984).

Contamination Experiment

Concentrations of lead in samples from acetone-rinsed, methanol-rinsed, and deionized-water-rinsed sacks were similar; lead concentrations for hexane-rinsed sacks were three times greater, as shown in table 4. The blank for lead concentration was much lower than that in all of the rinse samples, indicating that lead contamination occurred from polyethylene when it was in contact with 0.15 *N* nitric acid for 7 days. Contamination of the samples by lead was on the order of 0.1 to 0.2 μg/L.

Table 3.--*Recovery of adsorbed elements using 0.15 N nitric acid*

Rinse type	Element	Recovery	
		Micrograms	Percent
Acetone	Iron	1.4 ± 0.3	24
	Lithium	2.2 ± 0.2	27
Hexane	Barium	0.3 ± 0.04	21
	Iron	0.9 ± 0.3	16
	Lithium	2.1 ± 0.3	25
Methanol	Iron	0.8 ± 0.3	14
	Calcium	2.3 ± 1.2	5
Nitric acid	Iron	1.2 ± 0.4	23

GFAA results for zinc indicated that the dilute nitric-acid solution (blank, table 4) contained about 1 μg/L zinc. No measurable contamination of the samples occurred by zinc leached from the polyethylene sacks.

Table 4.--*Chemical concentration in 0.15 N* nitric-acid samples after 7-day contact with polyethylene

[All results are an average of triplicate determinations]

Rinse type	Chemical Lead (micrograms per liter)	 Zinc (micrograms per liter)
Acetone	0.17 ± 0.030	1.38 ± 0.54
Hexane	.64 ± .320	.87 ± .40
Methanol	.18 ± .080	.92 ± .34
Deionized	.20 ± .040	.85 ± .42
Blank	.01 ± .002	1.41 ± .04

Precipitation-Sample pH and Specific Conductance

The dilute nitric-acid solution prepared to have a nominal value of 4.5 pH units was stored in a fluorocarbon bottle, with no headspace, for 7 days. Four replicate determinations of pH had a mean of 4.34 ± 0.03. Four of the six sack samples stored for 7 days had pH values greater than three times the standard deviation of the fluorocarbon-bottle mean value. Mean pH of the six sack samples was 0.2 pH units lower than mean pH of the fluorocarbon-bottle sample.

Four determinations for specific conductance of the fluorocarbon-bottle sample were used to determine the mean and standard deviation. One-half of the sack samples had specific-conductance values greater than three times the mean standard deviation of the fluorocarbon-bottle mean value. The mean specific conductance of the six sack samples was 10 µS/cm greater than the mean specific conductance in the fluorocarbon-bottle sample.

CONCLUSIONS

Iron was adsorbed by polyethylene sacks from a simulated precipitation sample at pH 4.5, regardless of the pretreatment of the sack. Pretreating the sacks with only 0.30 *N* nitric acid was more effective than pretreating the sacks with methanol, acetone, or hexane followed by a 0.30 *N* nitric-acid rinse. Rinsing the polyethylene sacks with acetone appeared to contaminate the sample with calcium and caused iron and lithium to be adsorbed. Methanol rinsing of polyethylene sacks caused calcium and iron to be adsorbed. Rinsing with hexane may have affected the integrity of the polyethylene sacks; some leaking was experienced. Barium, iron, and lithium were adsorbed by the plastic after rinsing with hexane. Polyethylene sacks washed with 0.30 *N* nitric acid and rinsed with deionized water would be acceptable for the collection of precipitation samples containing barium, beryllium, calcium, cadmium, cobalt, copper, iron, lithium, magnesium, manganese, molybdenum, sodium, lead, vanadium, and zinc.

Leaching the polyethylene sacks with 0.15 *N* nitric acid to recover the adsorbed iron or other elements was not effective. Iron was recovered at an average of 19 ± 5 percent from the sacks. Good and Schroder (1984) reported that 30 percent of the adsorbed iron was recovered, using 0.07 *N* nitric acid. Increasing the nitric-acid concentration used to recover the adsorbed iron did not increase the iron recovery. None of the elements adsorbed were quantitatively recovered, regardless of the sack-rinse type.

Contamination of the sample by contact with the pretreated polyethylene sacks was significant for lead, but not for zinc. Determination of lead and zinc in dilute nitric acid that was in contact with the sacks for 1 week indicated trace element contamination was less than 1 µg/L. Hydrogen-ion contamination of precipitation samples in contact with nitric-acid-pretreated sacks was probable; this contamination may result in a pH-unit change of 0.2 in the sample.

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