UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

CONTAMINATION STUDIES AND TESTING PROTOCOL FOR POLYETHYLENE BOTTLES

By L. J. Schroder and H. E. Taylor

Open-File Report 80-165

Denver, Colorado
1980

UNITED STATES DEPARTMENT OF THE INTERIOR

CECIL D. ANDRUS, Secretary

GEOLOGICAL SURVEY

H. William Menard, Director

For additional information write to:

LeRoy J. Schroder
U.S. Geological Survey
Water Resources Division
Mail Stop 407, Box 25046
Denver Federal Center
Denver, Colorado 80225

For purchase, write to:

Open File Services Section
U.S. Geological Survey
Box 25425
Denver Federal Center
Denver, Colorado 80225
(303) 234-5888; FTS 234-5888

CONTENTS

TABLES

CONTAMINATION STUDIES AND TESTING PROTOCOL FOR POLYETHYLENE BOTTLES

By

L. J. Schroder and H. E. Taylor

ABSTRACT

Randomly selected polyethylene bottles were tested for trace element contamination, to determine bottle suitability for use as water-quality sample containers. Polyethylene bottles were leached using nitric acid solutions ranging from 0.2 percent to 5.0 percent by volume, and the leachate was analyzed for seventeen selected ions. Results indicate that contamination from these ions is insignificant, if the analytical technique to be used for sample analysis has a lower reporting limit of not less than 1 microgram per liter. Possibility of sample contamination by 7 anions and silica seems remote after examining a small number of bottles. A testing protocol for polyethylene bottles is presented, whereby sample selection, acceptance or rejection criteria, data analysis, and sampling criteria are documented.

INTRODUCTION

Water-quality samples for chemical analysis are stored and shipped to the U.S. Geological Survey laboratories in polyethylene bottles. Contamination of these sample containers is considered a potential source of inaccuracy in the chemical analysis of water samples. Chemical removal (leaching) of inorganic species from the bottle walls was investigated to ensure that present cleaning techniques are adequate to reduce this potential source of contamination. Bottles used for collecting samples for the determination of major metal ions (calcium, magnesium, sodium, and potassium), anions, and certain nonmetals, are cleaned by rinsing with a small portion of sample before final filling. Sample bottles for samples for determination of trace metal ions are acid-rinsed with 3 percent nitric acid at the laboratories, and subsequently rinsed with the sample before filling.

A pilot study was undertaken to prepare a protocol for future testing for potential contamination of sample bottles. Metal ions leachable from the bottles at various acid concentrations were determined; the difference between acid-rinsed and sample-rinsed bottles with respect to metal-ion contamination was also examined.

SAMPLE SELECTION

The U.S. Geological Survey, Denver Central Laboratory, received 180 cases of 500-milliliter polyethylene bottles, containing 216 bottles per case. At least one, but no more than four bottles, were taken from each case for a total suite of 364 bottles. A subgroup of 109 bottles was randomly selected for testing. Bottles were selected with the aid of a random digit table (Miller and Freund, 1977). Acid leaching was performed on 97 bottles and demineralized-water leaching on 12 bottles.

TEST CONDITIONS

Current practice by the Geological Survey is to rinse sample bottles for trace-metal samples with a dilute nitric acid solution before use. All other inorganic samples use bottles that do not undergo pretreatment in the laboratory. Samples for major and trace metals are preserved with either 1 or 2 milliliters of concentrated (70 percent) nitric acid in the field at the time of sampling. This preservation technique presents an additional possibility for sample contamination by acid leaching of metal ions from the bottle walls. To simulate actual bottle usage, all bottles were rinsed with either a 6.3 percent-by-volume nitric acid solution or demineralized water. Demineralized water served as the control-water sample in all studies. Teflon bottles, fluorinated ethylene propylene (FEP), were soaked for 24 hours in a 10 percent-by-volume nitric acid solution, rinsed with demineralized-water, and subsequently used as control samples or reagent blanks. Teflon was chosen for this purpose because of its low trace-element contamination characteristics.

Acid Leaching

Acid solutions were prepared in 20 liter lots using high-purity (triple-distilled) nitric and hydrochloric acids diluted with demineralized water. Nitric-acid solution concentrations ranged from 0.2 percent to 5.0 percent by volume. One mixed-acid solution was used, containing 0.6 percent-by-volume of both nitric and hydrochloric acids.

Two-tenths percent by volume is the normal preservation concentration for water-quality samples that are to be analyzed for metal ions. Eight bottles were tested at this concentration. It was hypothesized that more concentrated acid solutions (0.6, 1.2, and 5.0 percent) would produce results indicative of the 0.2 percent leach result, but at an accelerated rate. Therefore, only minimal testing at the 0.2 percent concentration was needed. The mixed-acid solution of nitric and hydrochloric acid was tested because of its rapid dissolution characteristics on metal particles that could be embedded in or attached to the container walls. Only minimal tests were performed using the mixed-acid solution because bottle-wall contamination by metallic particles was not expected.

Polyethylene test bottles had approximately 300 square centimeters of surface area in contact with the acid solution. Control-sample bottles (1-liter volume) were filled with 550 milliliters of water-acid mixture to maintain the same surface contact area. Acid-bottle-wall contact time ranged from 42 to 74 days, with no time control for the acid-leaching solution. Time control of the acid-bottle-wall contact time was lost during chemical analysis of the leachate at the National Water Quality Laboratory, Denver, Colo.

Demineralized-Water Leaching

Twelve bottles were rinsed and filled with demineralized water and allowed to stand for 5 days. These samples simulate storage conditions for samples designated by the laboratory as "filtered unacidified" or "FU."

The following table summarizes the acid and demineralized water leaching tests.

Table 1.--*Summary of leaching tests performed during pilot study*

Acid-leaching concentration (percent acid by volume)	Number of acid-rinsed bottles	Number of demineralized water-rinsed-samples	Number of control samples
0	--	12	2
0.2	4	4	2
0.6 nitric acid	18	7	4
1.2 nitric acid	17	8	4
5.0 nitric acid	17	8	4
1.2 nitric and hydrochloric acids	8	4	3

CHEMICAL ANALYSIS

All acid-leach samples were analyzed using a multielement inductively coupled argon plasma optical emission technique (ICP), (Garbarino and Taylor, 1978). Twenty samples were also analyzed utilizing electrothermal atomization (ETA) atomic absorption techniques for copper, lead, and zinc only. These metals were selected for two reasons: (1) their ICP detection limits were higher than desired; and (2) their ubiquitous occurrence. Determinations

were performed for 7 anions using ion-exchange chromatography techniques on 4 of the 12 demineralized water-leach samples (Small, 1975).

TEST RESULTS

Concentrations of barium, beryllium, cadmium, copper, iron, lithium, molybdenum, sodium, strontium, vanadium, and zinc were below the limits of detection for ICP analysis (table 2). Sample bottle pretreatment, either acid rinsing or water rinsing, appeared to have no effect for these metals. Lead concentrations were below the detection limit of 10 µg/L (micrograms per liter) for all but three bottles. ICP analysis indicated that these three samples may contain lead at a concentration of approximately 10 µg/L. These 3 samples were among the 20 samples analyzed by atomic absorption analyses; they are discussed later in this report.

Table 2.--*Analytical detection limits using inductively-coupled plasma emission and electrothermal atomization techniques (ETA) for water analysis*

Element	Detection limits	
	ICP (µg/L)	ETA (µg/L)
Barium	2	----
Beryllium	0.5	----
Cadmium	1	----
Calcium	20	----
Cobalt	3	----
Copper	10	0.2
Iron	3	----
Lead	10	.1
Lithium	4	----
Magnesium	4	----
Manganese	1	----
Molybdenum	10	----
Silicon (SiO_2)	9	----
Sodium	200	----
Strontium	0.5	----
Vanadium	6	----
Zinc	3	0.03

Magnesium and silicon (as silica) results indicate that both species were leached from certain bottles. Reagent blank corrected concentrations for these species ranged from below the lower limits (table 2) up to 43 µg/L. However, all concentrations were well below the normal Central Laboratory reporting limit of 100 µg/L; thus indicating that leaching of magnesium and silicon is apparently not a significant problem.

Manganese results indicated that the majority of sample bottles were suitable for samples with a concentration down to 1 µg/L. One test condition, 1.2 percent nitric acid leach, indicated a single positive reagent blank corrected result of 3 µg/L. Since this concentration is very near the detection limit, an intuitive judgment is that the bottles are probably acceptable for samples with a manganese concentration down to 1 µg/L.

ETA atomic absorption analyses for copper, lead, and zinc demonstrated that all three metal concentrations were less than 1 µg/L, and that there was insignificant leaching of these trace metals from the bottle walls. Therefore, these polyethylene bottles appear to be acceptable for water-quality samples, when the analytical technique has 1 µg/L as the lower limit.

Ion-exchange chromatography (Pyen and Fishman, 1979) results indicated that the bottles were not a source of anion contamination under testing conditions. Bromide, chloride, fluoride, nitrite, nitrate, orthophosphate, and sulfate concentrations were all below the detection limits shown in table 3.

Table 3.--*Analytical detection limits using ion-exchange chromatography techniques for water analysis*

Chemical species	Detection limit (mg/L)
Bromide	0.10
Chloride	.20
Fluoride	.01
Nitrite as N	.02
Nitrate as N	.05
Orthophosphate as P	.06
Sulfate	.20

This pilot study indicates that the polyethylene bottles obtained by the laboratories are an acceptable storage and shipping container for most environmental water-quality samples. Under the testing conditions, the bottles did not contribute significant contamination for the major metals of

calcium, magnesium, and sodium, 14 trace metals, 7 anions, and silica (table 4). Information obtained from the study suggests that these bottles will not be a contamination source for most inorganic constituents at the present Central Laboratory reporting limits (Friedman and Beetem, 1979). The chance of obtaining an analytical result that is greater than the detection limit is shown in table 5. Also, prerinsing the bottles with a dilute nitric acid solution and rinsing the bottles with demineralized water yield the same results. Finally, preserving 500 milliliter water-samples with 1 or 2 milliliters of nitric acid does not leach measurable amount of metals from the bottles. Although the study indicates that the bottles in the lot tested are acceptable, the conclusion that all future bottles will give the same results is invalid. Therefore, a quality-control protocol should be followed to test each new lot or purchase of bottles.

Table 4.--*Summary of analytical results obtained from contamination studies of polyethylene bottles*

Element or chemical species	Number of determinations	Percent greater than detection limit	Percent greater than Central Laboratory reporting limit
Barium	97	0	0
Berylium	97	0	0
Bromide	12	0	0
Cadmium	97	0	0
Calcium	97	0	0
Chloride	12	0	0
Cobalt	97	0	0
Copper	117	0	0
Fluoride	12	0	0
Iron	97	0	0
Lead	117	3.1	0
Lithium	97	0	0
Magnesium	97	13.4	0
Manganese	97	1.0	0
Molybdenum	97	0	0
Nitrite as N	12	0	0
Nitrate as N	12	0	0
Orthophosphate as P	12	0	0
Silicon (SiO_2)	97	19.6	0
Sodium	97	0	0
Strontium	97	0	0
Sulfate	12	0	0
Vanadium	97	0	0
Zinc	117	0	0

Table 5.--*Probability of obtaining a positive result from the contamination studies of polyethylene bottles*

Element or chemical species	Number of determinations	Probability of determination exceeding the detection limit	
		95 percent confidence	99 percent confidence
Barium	97	0.02[1/]	0.05[1/]
Berylium	97	.02	.05
Bromide	12	.22	.31
Cadmium	97	.02	.05
Calcium	97	.02	.05
Chloride	12	.22	.31
Cobalt	97	.02	.05
Copper	117	.02	.04
Fluoride	12	.22	.31
Iron	97	.02	.05
Lead	117	.06	.10
Lithium	97	.02	.05
Magnesium	97	.20	.25
Manganese	97	.03	.06
Molybdenum	97	.02	.05
Nitrate as N	12	.22	.31
Nitrite as N	12	.22	.31
Orthophosphate as P	12	.22	.31
Silicon (SiO_2)	97	.27	.33
Sodium	97	.02	.05
Sulfate	12	.22	.31
Vanadium	97	.02	.05
Zinc	117	.02	.04

[1/] Calculated from Dixon and Massey, 1969.

BOTTLE TESTING PROTOCOL

1. Random Sample

A sample is a small selection from some larger aggregate population about which information is needed. To obtain reliable information about a large aggregate, each member of the sample must be selected at random. Dixon and Massey (1969), Miller and Freund (1977), and Snedecor (1961), discuss techniques of random sampling.

2. Sample Size

Selection of the sample sizes needed to assure acceptable results or to accurately define the population is dependent on magnitude of the level of uncertainty that is acceptable. Walpole (1968) states that sample sizes should be equal to or greater than 30, regardless of the shape of most populations, to obtain a good estimate of the mean. Balsley (1966) and Miller and Freund (1977) give rigorous equations for calculating the appropriate sample size, if sufficient knowledge is available to estimate the acceptable standard deviation and standard error of the mean. Pilot studies may be required to obtain estimates of the mean and standard deviation if prior knowledge of the lot quality is unknown. Using the military standard (Miller and Freund, 1977), lot sizes of 10,000 to 35,000 bottles will require a sample size of 125 bottles be tested.

3. Acceptance or Rejection Criteria

Criteria for acceptance or rejection of a bottle lot must be made prior to bottle testing. A change of criteria, after testing has begun, may introduce bias that will invalidate the evaluation. Careful examination of the conditions for acceptance or rejection of a lot cannot be over-emphasized. Miller and Freund (1977) suggest that a standard plan, such as the "military standard," is totally dependent on criteria set by the user. Sufficient prior knowledge of the bottles being tested will allow reductions in the quantity inspected.

Bottle usage application dictates acceptable concentrations of the leached constituents. If copper is leached to a maximum concentration of 0.4 µg/L, the bottle is acceptable for samples with a copper concentration greater than this maximum. Using similar logic, the maximum acceptable concentration limit can be set at the minimum reporting limits for each individual constituent. U.S. Geological Survey Central Laboratories should use the reporting limits stated in the 1980 Services Catalog (Friedman and Beetem, 1979).

4. Reagents

Reagent-grade acids may contain chemical-species (particularly trace metals) that exceed the concentrations obtained from the leaching process. Consequently, high-purity (triple-distilled or equivalent) acids should be used to reduce the reagent blank and the background obtained from the control samples.

5. Control Samples

Teflon bottles (FEP) are recommended as control samples or reagent blanks for inorganic constituents because of the material's resistance to

chemical attack by acids (Bothner and Robertson, 1975). The inside surface area of these bottles should be approximately the same as the bottles to be tested. Control-sample bottles should be precleaned by soaking in a 10-percent-or-higher nitric acid solution for at least 24 hours. After acid-soaking, the bottles are to be rinsed at least three times with demineralized water. Control samples must be treated identically as the test bottles after the cleaning steps.

6. Leaching Experiment

A minimum of 20 liters of acid solution is prepared, using high-quality demineralized water and high purity acids. Since each prepared solution requires control samples, fewer control samples should be necessary if large volumes of the acid solutions are prepared. Acid stock solutions are to be an order of magnitude more concentrated than those used for sample preservation. It is assumed that increased acid concentrations will accelerate the leaching process, thus representing worst-case situations. The worst-case situation examined in the pilot study was a maximum of 25 times the acid concentration used for sample preservation.

Each acid solution used during the leach experiment is to be monitored with a minimum of two control samples; however, four control samples per acid solution is more desirable. Control samples are to be randomly prepared to verify the homogeneity of the solution. Japanese random dice, a random number table, or similar scheme should be used to select the sampling position of the control samples. If significant differences are found in the analytical results of the control samples, the experiment may be considered invalid. Control samples are analogous to reagent blanks used in the analytical determinations. Laboratory regulations governing reagent blanks are applicable to these samples.

Acid solution contact time with the bottle should approximate a sample-bottle contact time. Contact time must be at least equal to the estimated time required to ship, store, and analyze the sample. Note that short tests may not represent long-term sample storage.

7. Analysis

Multielement analyses can be used as a screening technique. Selected elements possibly may be used as monitors, if more sensitive analytical techniques are required. For example, cadmium and manganese can be analyzed at concentrations as low as 1 µg/L using ICP techniques. Detectable concentration of these elements could be used as a indicator to decide that a particular lot of bottles is unsuitable.

After multielement screening is complete, the data should be reviewed to decide whether or not more sensitive analytical determinations are needed.

Additional determinations, using a more sensitive technique, are normally more costly than multielement screening. The constituent to be analyzed must be carefully selected; analysis of unusual trace metals may yield no additional information. Selection of a ubiquitous metal, such as zinc, will probably give more insight to the acceptability of the bottles.

8. Sampling Plans

Single sampling plans (simply a specification of sample size and the acceptance number to be used) are often the easiest plans to administer in testing the lot-quality of bottles. Single sampling plans (Miller and Freund, 1977, and Dixon and Massey, 1969) are appropriate but may be costly, because of the number of analyses that must be performed.

If prior knowledge of the bottle lot is obtained by either a pilot study or previous data, double or multiple sampling plans are to be used. Advantages of double or multiple sampling are: (1) there is a high probability that a good lot will be accepted, or a bad lot will be rejected, on the basis of initial sampling; therefore, analysis costs will be substantially reduced; and (2) all sample lots can be prepared at the same time with a slight increase in effort. Analysis of the leachate can be kept to a minimum for good or bad lots. Lot quality that can be termed "intermediate" is more difficult to accept or reject than good or bad lots. Using double or multiple sampling, the total sample size required may exceed the equivalent single sampling plan for intermediate lots (Miller and Freund, 1977). However, the advantages of reduced analytical costs and data review make double or multiple sampling the recommended choice.

Table 6 compares single- and multiple-sampling plans for a sample of 140 from a lot. If the single-sampling plan is used, all 140 samples are tested and evaluated before the decision is made to accept or reject the lot. The multiple-sampling plan allows the lot to be rejected if 3 or more samples are defective, after testing and evaluating 20 samples. Acceptance of the lot, after the first 20 samples, is not allowed. Therefore, it is possible that a bad lot may be rejected after evaluating only 20 samples. In the second step of the multiple-sampling plan, the lot is accepted if the combined sample contains at most one defective, and is rejected if four or more are defective; otherwise, sampling continues. This process continues until acceptance or rejection of the lot.

9. Data Analysis

Data obtained from the multielement screening should be considered first. Review of control-sample data should precede review of bottle-leach data. If control-sample contamination is present, it is documented. Reagent impurities may dictate a new test; however, if the impurities are limited in scope or magnitude, retesting may not be required.

Table 6.--*A hypothetical example comparing single-sampling and multiple-sampling plans*[1/]

Sample	Number of samples tested	Combined samples		
		Number of bottles tested	Acceptance number	Rejection number
SINGLE-SAMPLING-----	140	140	7	8
MULTIPLE-SAMPLING				
First----------	20	20	---	3
Second----------	20	40	1	4
Third----------	20	60	3	5
Fourth----------	20	80	3	6
Fifth----------	20	100	5	7
Sixth----------	20	120	6	8
Seventh----------	20	140	7	8

[1/]Data obtained from Miller and Freund, 1977.

The Military Standard 105D (Dixon and Massey, 1969, Grant and Leavenworth, 1972, and Miller and Freund, 1977) is recommended as the acceptance or rejection plan for polyethylene bottles. This plan was designed to encourage producers to supply only acceptable products. Tables listing the sample size to be tested and the acceptance and rejection numbers are available for single, double, and multiple sampling in Grant and Leavenworth (1972, p. 662-677). This plan is based on acceptance quality levels that are grouped as inspection levels I, II, or III. Inspection level I places more risk on the consumer or purchasers than either of the other two levels; however, the cost of quality-control experiments are less for inspection level I than any other level. Three types of inspection (normal, tightened, and reduced) slightly change the risk for the producer or consumer of a good lot being accepted or rejected. Tightened inspection increases the producer's risks that a good lot will be rejected. Reduced inspection increases the consumer's risks that a bad lot will be accepted. The type of inspection only slightly changes the risk (either producer or consumer); normal inspection is most commonly used.

Inspection level I is suggested for bottle testing because the required sample size is 125 or 200 bottles for lot sizes of 10,000 to 150,000. The type of inspection (normal, tightened, reduced) must be chosen from prior knowledge of the lot-quality obtained from a pilot study or other available data. If lot quality is either good or bad, normal inspection will be adequate.

Actual maximum allowable ion concentrations that are used to accept a sample cannot be determined rigorously. The maximum allowable ion concentration recommended is the lower-reporting limit, or three times the detection-limit of the specific technique used to determine the ion. Three times the detection-limit should result in a 95 percent chance that the measured value is a real number. Choice of the maximum concentration is to be made by the testing group because the analytical method used will dictate the detection-limit.

CONCLUSIONS

Data from a pilot-study on an experimental lot of bottles indicate that there is no discernable difference at the 95 percent confidence interval between acid-rinsed and water-rinsed bottles with respect to leachable metal-ion contamination. Current field-preservation techniques, consisting of adding 1 or 2 milliliters of concentrated nitric acid to each water sample, do not induce sample contamination from the bottle. Increasing the nitric acid concentration from 0.2 percent to 5 percent does not noticably increase the metal leaching rate, nor does the use of mixed-acid solutions of nitric acid and hydrochloric at the 1.2 percent level. Testing a small number of samples for leachable anions indicates that anion contamination is insignificant.

Bottle-testing protocol requires that sampling and acceptance or rejection criteria be developed before initial testing begins. Multielement analytical techniques may yield sufficient information to accept or reject a sample lot. Very good or very bad lot quality may be ascertained more easily than intermediate lot quality, and double or multiple sampling plans may reduce testing costs.

REFERENCES CITED

Balsley, H. L., 1966, Introduction to statistical methods: Totowa, N. J., Littlefield, Adams, p. 153-156.

Bothner, M. H., and Robertson, D. E., 1975, Mercury contamination of sea water samples stored in polyethylene containers: Analytical Chemistry, v. 47, p. 592-595.

Dixon, W. J., and Massey, F. J., Jr., 1969, Introduction to statistical analysis: New York, McGraw-Hill, p. 40-42, p. 240-251, p. 276-277, p. 501-504.

Friedman, L. C., and Beetem, W. A., 1979, 1980 Water Quality Laboratory Services Catalog: U.S. Geological Survey Open-File Report 79-667, p. 21-36, 59-66, 73-90.

Garbarino, J. R., and Taylor, H. E., 1979, An inductively-coupled plasma atomic emission spectrometric method for routine water-quality testing. Applied Spectroscopy: v. 33, no. 5, p. 220-222.

Grant, E. I., and Leavenworth, R. S., 1972, Statistical quality control: New York, McGraw-Hill, p. 411-443, p. 662-677.
Miller, Irwin, and Freund, J. E., 1977, Probability and statistics for engineers: Englewood Cliffs, New Jersey, Prentice-Hill, p. 161-162, p. 441-443.
Pyen, Grace, and Fishman, M. J., 1979, Determination of selected anions in water by ion chromatography: U.S. Geological Survey Water Resources Investigations Report 79-101, 36 p.
Small, H., Stevens, T. S., and Bowman, W. C., 1975, Analytical Chemistry, 47, p. 1801.
Snedecor, G. W., 1971, Statistical methods: Ames, Iowa, Iowa State University Press, p. 7, 9, 36, 69.
Walpole, R. E., 1968, Introduction to statistics: New York, Macmillan, p. 156-162.

GPO 854 - 765