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Lead and Cadmium Contamination During Acid Preservation of Water Samples

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Trace analysis of metals in drinking water by atomic absorption spectrophotometry requires operation of instruments near the lower threshold of instrumental sensitivities. When working with such minute quantities, quality control of sample collection and handling is paramount because small amounts of contamination can readily yield misleading results. Drinking water metals analysis conducted in support of ongoing research into the human health effects of elevated drinking water sodium levels revealed one such source of contamination that may have implications for laboratories performing similar analyses.

In the spring of 1977, drinking water samples from 80 different households from a community with a high sodium concentration in the drinking water were obtained. Similarly, drinking water samples from 83 different households from a control (i.e. low sodium) community were likewise obtained. In a subsequent study conducted in the spring of 1978, 77 and 76 water samples from completely different households of the same high and low sodium communities, respectively, were obtained.

In both studies water samples were collected according to standard E.P.A. collection techniques. Two samples of tap water were taken [in separate one-liter polyethylene containers (Cubitainer (R) Hedwin Corporation)] from each household with the first sample consisting of the first water drawn from the household plumbing on the morning of sampling. This water sample was considered to represent a sampling of the household water. The water was then allowed to run until it became cool at which time the second container was likewise rinsed and filled. The latter sample was considered to represent water coming from the service system which connect the household pipes with the community system. All samples from the initial study were preserved by pipetting 5 mL of concentrated acid (ACS grade) into the individual sample containers. Samples in the follow-up study were preserved by emptying 1.5 mL of concentrated nitric acid (ACS grade) contained in an acid ampule (Poly Research Corporation) into the individual sample containers.

Metal levels in both household and service system samples collected during the initial study were analyzed in University of Massachusetts' laboratories. In the subsequent study, analyses of metals from the service system (i.e. second water sample per

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household) samples were conducted at University of Massachusetts' laboratories while the household samples were analyzed by the U.S. Environmental Protection Agency Health Effects Laboratory in Cincinnati, Ohio.

Comparison of data relating to the service system samples revealed strikingly different values for lead and cadmium values between the two studies (Table 1).

TABLE 1

Comparison of Spring 1977 and Spring 1978 Mean Lead and Cadmium Levels as Determined From the Service System Samples

	High Sodium Community		Low Sodium Community	
Metal	1977	1978	1977	1978
Pb mean (ppb)	4.6	19	11	64
Cd mean (ppb)	0.01	2.8	0.01	11
Number of Samples	80	77	83	76

The data indicate that lead and cadmium levels markedly increased in the service system of both communities from Spring of 1977 to Spring of 1978. However, no changes had occurred in either community's water supply or distribution system which might explain the differential found in the levels of the two metals. Since the participating households were similarly distributed throughout both communities in both surveys, it did not seem likely that there was a greater occurrence of lead plumbing in the second group of households surveyed. In an effort to determine why elevated levels of lead and cadmium were present in the second study, an analysis was initiated to determine whether methodology involved in sample collection or handling might have lead to elevated levels of the two metals. Since the most obvious difference in the two sampling techniques was the manner in which the samples were acidified, methods were utilized to determine if use of acid ampules in the second sampling might have caused sample contamination. Similarly sample containers and caps of the container were examined for the interfering presence of lead or cadmium.

METHODS

Four different sets of water samples utilizing sample containers, caps, and acid ampules from the same supply as used for the second survey were prepared as follows:

1. Ten sample containers and caps were soaked in a 1:10 concentrated nitric acid-deionized distilled water [Millipore Super Q (R)]solution for 12 h. After four rinsings of both caps and containers with deionized distilled water, each sample was acidified with the 1.5 mL nitric acid contents of an acid ampule.

2. Four samples were prepared in the above manner, however, individual acid ampules used to preserve samples were also soaked for 12 h in the 1:10 nitric acid solution.

3. Four sample containers soaked for 12 h in a 1:10 nitric acid solution were filled with deionized distilled water and covered with a cap that was not soaked overnight or rinsed with deionized distilled water. Samples were preserved by pipetting 1.5 mL of nitric acid into the containers.

4. Four sample containers, unrinsed and which had not soaked overnight in an acid solution, were filled with deionized distilled water and covered with a cap that had soaked in the acid solution and had been rinsed thoroughly with distilled water. Samples were acidified by pipetting 1.5 mL of nitric acid into the containers.

All samples were vigorously shaken and stood in a darkened refrigerator at 4°C for 12 h.

By the above method, one could determine if contamination was arising from the acid ampules (group 1), the caps used on the sample containers (group 3), or the containers (group 4).

Samples were analyzed for total lead and cadmium directly by atomic absorption spectrophotometry. Electrodeless discharge lamps were used for the analysis. Argon was utilized as a purge gas. 20 μL sample aliquots were introduced into the graphite furnace using a microliter pipet [Eppendorf (R)]with disposable polyethylene tips. Duplicate determinations were made for each sample and an average value determined. Concentrations were determined by comparison of sample atomization signals to a calibration curve constructed from known concentrations of aqueous standards. Standard solutions were prepared from commercially available 1000 ppm lead and cadmium stock solutions (Fisher Scientific). Instrumental parameters used were identical to those used for lead and cadmium analysis in the earlier water studies, as suggested by the manufacturer's method development manual (Perkin-Elmer Corporation, 1975).

RESULTS

Analysis of the first group consisting of 10 samples revealed that acidification of the deionized distilled water with acid ampules introduced sufficient lead and cadmium contamination to result in mean concentrations of 36 ± 23 ppb and 0.92 ± 0.44 ppb for the respective metals. Analysis of the samples from the three remaining groups demonstrated little contamination by lead and cadmium. Lead levels in group 2, 3, and 4 samples were in all cases less than 1.0 ppb and cadmium levels less than 0.04 ppb.

DISCUSSION

The use of the acid ampules did contribute to the elevation of lead and cadmium concentrations in the drinking water samples. Discussions with the manufacturer have verified the fact that the blue line placed on individual ampules to mark the point at which they are to be broken (Figure 1) is made with a lead oxide based paint containing cadmium oxide. Similar inquiries from both the U.S.E.P.A. and the U.S. Geological Survey have resulted in the manufacturer's cessation of production of nitric acid ampules containing any exterior markings (N. Ulmer, E.P.A., Cincinnati, Personal Communication). Breaking the acid ampule over the open sample and vigorously shaking the contents into the sample cause sufficient contaminating paint to get into the sample to result in elevations of lead and cadmium concentration. Should a vial accidently fall into the water sample during the acidification process, the resulting lead and cadmium concentrations can become as high as 96.0 and 48.8 ppb, respectively. Analysis of the nitric acid content of the acid ampules demonstrated it to be relatively free of the interfering presence of lead and cadmium. By carefully extracting the acid from the ampule so as not to bring it into contact with the contaminated paint and diluting this to 1 liter with deionized-distilled water, the resulting lead and cadmium levels were found to be < 1.0 ppb and 0.03 ppb, respectively.

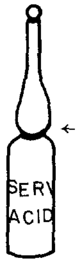

Figure 1: Graphic Illustration of Acid Ampule Used for Sample Preservation. Arrow indicates blue line found to be the source of lead and cadmium contamination.

Based on these findings, it would appear that the elevated levels of lead and cadmium of the second year's survey can be explained at least in part via the contamination of samples by the acid ampules with the lead and cadmium based paint. The laboratory experiment revealed similar lead levels as found in the second field survey while cadmium levels, although elevated, were less than the values obtained in the second survey.

Such variation in the degree of contamination may possibly be explained by the presence of highly variable levels of lead and cadmium in the different lots of ampules and the variation in the extent of contact between the nitric acid and paint during the acidification process.

Laboratories doing similar analyses noting discrepancies in analytical results should re-examine the manner in which samples were preserved. It is recommended that nitric acid ampules used for sample preservation do not contain any potential contamination, especially at the "break off" point of the ampule since this is the greatest area of contact between the acid and the exterior surface of the ampule. Also, it appears that by soaking the ampules in a sufficiently strong acid bath prior to their use, a substantial amount of the contaminating lead and cadmium can be removed. Whether the remaining level of contaminants is sufficient to permit use of the acid ampules would be determined by the goals of individual research studies.

REFERENCE

PERKIN-ELMER CORPORATION: Analytical Methods for Atomic Absorption Spectrophotometry Using the HGA Graphite Furnace. Norwalk, CT: Perkin-Elmer Corporation, 1975.