

Determination of Lead in Potable Waters Using Delves Cup Atomic-Absorption Spectrometer with Signal Integration

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■ A rapid method for the determination of lead in potable water is described. A 50–200- μ l sample is dispensed with 50 μ l of gelatin solution into a stainless steel cup, dried, and inserted into an air-acetylene flame. An automated atomic-absorption spectrometer measures integrated absorbance. The procedure has a detection limit of 5 μ g of lead per liter, with calibration curves linear to 200 μ g of lead per liter. Typical relative standard deviations are 2.5 and 10.2% for 100 and 20 μ g of lead per liter, respectively. When direct calibration was used, most potable water samples showed low recoveries, but use of standard additions avoided this problem. Fifty potable water samples were analyzed using the Delves cup procedure and solvent-extraction atomic-absorption spectrometry. Statistical analysis (Student "t" test) showed excellent correlation between the two procedures.

Although the Delves cup atomization system was originally developed for the determination of lead in blood (1–3), it can be extended to the analysis of lead and other metals in matrices such as air, water, and biological samples. The U.S. Public Health Service Drinking Water Standards specify that the lead level in potable waters should not exceed 50 μ g/liter (4).

American Public Health Association "Standard Methods" (5) cites a colorimetric dithizone procedure and a solvent-extraction atomic-absorption procedure for lead analysis. The former is lengthy and requires considerable manipulative skill. With the latter, the spectrometric measurement is simple, but solvent extraction adds several manipulative steps. In this paper we report a Delves cup procedure in which potable water is analyzed without preconcentration, and signal integration, computations, and quality control procedures are carried out on line by a digital computer.

Instrumentation

The instrumental system has been described in a previous communication from this laboratory (2). Briefly, it comprises a single-beam atomic-absorption spectrometer built from a hollow cathode lamp with dc power supply, burner-Delves cup injector, f/3.5 monochromator, photomultiplier, photon counter, interface, and computer. Insertion of the cup into the flame triggers a delay of 1 sec

during which no measurements are taken (to avoid measuring nonspecific absorption). The system then measures the intensity of transmitted radiation for 200 successive 50-msec periods enclosing the absorption peak. Intensity measurements are converted to absorbance, and the integrated absorbance of the transient lead atomization process is computed. Peak absorbance values are also measured and printed out. The measurement of integrated absorbance allows unmatched cups to be used without any loss in precision (2).

Instrumental Settings. The following instrumental settings were used: slit height, 15 mm; slit width, 50 μ m; lamp current, 8 mA; wavelength, 217.0 nm. A slightly fuel-rich air-acetylene flame was used, with the cup lip about 2 mm below the entrance hole in the absorption tube.

Materials

Reagents. All reagents were prepared from analytical-grade materials.

Standard Solutions. A stock solution containing 100 mg of lead per liter was prepared by dissolving 1.597 grams of lead nitrate in 10 ml of 5M nitric acid and diluting to 1000 ml with deionized water. This solution was diluted further as required.

Samples. Potable water samples were collected from various public water supplies throughout New York State and analyzed for lead using the solvent-extraction atomic-absorption procedure (5). All samples contained less than 10 μ g of lead per liter. They were then spiked at 100 μ g per liter using stock lead solution to bring the lead concentration of the samples to the midpoint of the linear calibration range.

Results

Choice of Sampling Cups. Most work with the Delves system has been carried out using commercially available nickel cups, 0.008 in. thick. With these cups, lead absorption peaks from aqueous samples were broad (about 35 sec). Addition of carbonaceous material produced sharper peaks, presumably by more efficient reduction of lead compounds to atoms. However, thin stainless steel cups (0.005 in. thick manufactured by Arlin Tool Co., Brooklyn, N.Y.) gave sharp peaks (about 10 sec) without addition of carbonaceous material, and these were used for all analyses with aqueous samples.

Barthel et al. (6) reported that aqueous standards cannot be satisfactorily used with nickel cups because migration of the aqueous solution over the edge of the cup pro-

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duces low and erratic readings. We also observed this with stainless steep cups and corrected it by placing 50 μ l of a 1% gelatin solution in each cup before adding samples and standards. The average lifetime of a stainless steel cup under these conditions, after an initial burning off to remove any contamination, is four determinations. Subsequent readings become erratic and irreproducible, apparently because physical changes in the surface of the cup cause the solution to migrate over the edge even when gelatin is used.

Lead in Pure Aqueous Solution. Precision. To determine precision, 100- μ l portions of solutions containing either 100 or 20 μ g of lead per liter were dispensed into prepared stainless steel cups and oven dried at 140°C for 10 min. Repetitive analysis yielded relative standard deviations of 9.9 and 16.0%, respectively, using peak absorbance data and 2.5 and 10.2%, respectively, using integrated absorbance data.

Detection Limit and Calibration Curves. When 200- μ l solutions are used, the detection limit is about 5 μ g per liter (signal-to-noise ratio 2:1). Calibration curves are almost linear in the range 0–200 μ g of lead per liter (Figure 1).

Interferences. The effects of 1000- and 10,000-fold weight excesses of a number of foreign ions on the analysis of 100 μ g per liter lead solutions were studied. The choice of potential interferences was restricted to ions found in the potable water samples: Na^+ , K^+ , Zn^{2+} , Cr^{3+} , Fe^{2+} , Cu^{2+} , Ca^{2+} , Mg^{2+} , and Ni^{2+} as sulfate or nitrate, and SO_4^{2-} , PO_4^{3-} , Cl^- , NO_3^- , and SiO_3^{2-} as the free acid or ammonium salt. None of these ions affected the mean lead signal by more than 5%.

Accuracy. The accuracy of the procedure was evaluated by analyzing aqueous samples of known lead concentration. These had been provided by Dr. P. LaFleur of the National Bureau of Standards as part of a blood lead analysis program and had been analyzed by isotope dilution mass spectrometry—a method accurate to within <0.5%. The samples were analyzed both by the Delves cup procedure with direct calibration and by solvent-extraction atomic-absorption spectrometry. The results show good agreement (Table I), although both atomic-absorption procedures give high results for the low standards.

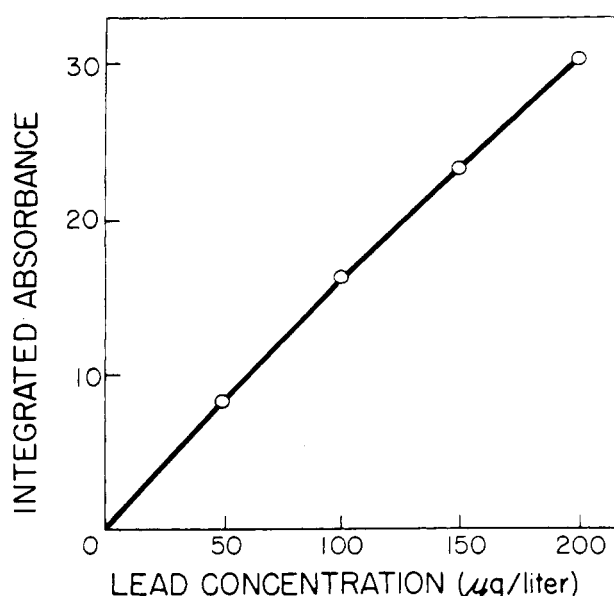


Figure 1. Calibration curve obtained with 50- μ l aliquots of pure aqueous lead standards at 217.0 nm using stainless steel cups

Recovery of Added Lead from Potable Water Samples. Direct Calibration Procedure. When 50 samples were analyzed by the direct calibration procedure, satisfactory results were obtained for some, but in most cases recoveries were significantly low (Table II). The reason for this is not known. Since one possible explanation was *physical*

Table I. Lead Concentration (μ G per Liter) of Six Pure Aqueous Samples as Determined by Three Procedures

| Isotope dilution mass spectrometry | Atomic absorption | |
|---------------------------------------|-----------------------------------|--------------------|
| | Delves cup, direct calibration | Solvent-extraction |
| 49.8 | 52 | 50 |
| 90.8 | 94 | 90 |
| 14.1 | 22 | 23 |
| 14.1 | 15 | 19 |
| 49.8 | 45 | 47 |
| 90.8 | 82 | 86 |

Table II. Lead Concentration Found (μ G/Liter) in 50 Potable Water Samples Spiked to 100 μ G/Liter

| Delves cup procedures | | | |
|-----------------------|------------------------------------|--------------------|--------------------------------------|
| Direct calibration | Direct calibration with added ions | Standard additions | Solvent-extraction atomic absorption |
| 47 | 71 | 106 | 102 |
| 38 | 65 | 98 | 96 |
| 65 | — | 95 | 102 |
| 108 | — | 100 | 120 |
| 33 | 64 | 90 | 88 |
| 96 | — | 95 | 98 |
| 100 | — | 100 | 96 |
| 97 | — | 98 | 94 |
| 52 | 81 | 106 | 100 |
| 47 | 68 | 100 | 104 |
| 40 | 63 | 100 | 95 |
| 55 | 76 | 100 | 102 |
| 37 | 68 | 100 | 93 |
| 64 | 86 | 100 | 108 |
| 91 | — | 94 | 90 |
| 105 | — | 97 | 101 |
| 45 | 72 | 94 | 98 |
| 100 | — | 95 | 99 |
| 70 | — | 102 | 98 |
| 101 | — | 96 | 103 |
| 90 | — | 100 | 94 |
| 60 | — | 98 | 106 |
| 62 | 88 | 95 | 91 |
| 92 | — | 96 | 91 |
| 52 | 78 | 96 | 98 |
| 94 | — | 100 | 95 |
| 98 | — | 92 | 98 |
| 49 | 69 | 100 | 107 |
| 92 | — | 88 | 94 |
| 52 | 81 | 100 | 108 |
| 49 | 71 | 100 | 96 |
| 98 | — | 95 | 97 |
| 81 | — | 100 | 106 |
| 91 | — | 98 | 100 |
| 47 | 69 | 89 | 94 |
| 53 | 90 | 99 | 93 |
| 90 | — | 88 | 97 |
| 42 | 59 | 94 | 98 |
| 98 | — | 90 | 96 |
| 63 | 72 | 92 | 106 |
| 100 | — | 105 | 98 |
| 100 | — | 100 | 102 |
| 57 | 71 | 104 | 98 |
| 51 | 75 | 92 | 96 |
| 59 | — | 100 | 106 |
| 98 | — | 109 | 97 |
| 33 | 52 | 106 | 112 |
| 27 | 59 | 89 | 93 |
| 100 | — | 108 | 98 |
| 94 | — | 99 | 106 |

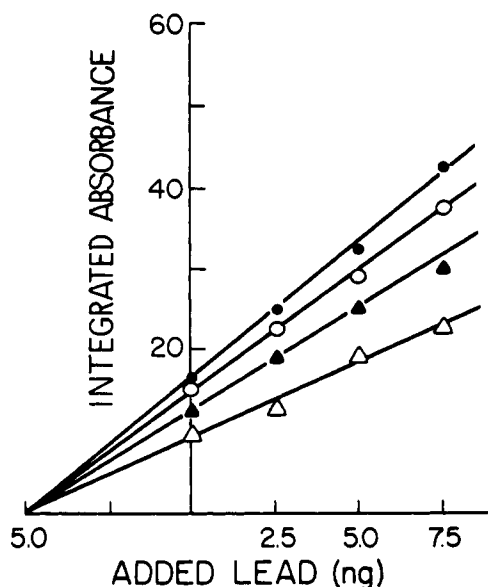


Figure 2. Standard addition curves for the analysis of four 50- μ l potable water samples spiked at 100 μ g/liter

interferences from varying amounts of salt in the cup, a large excess of ions commonly found in water was added to each calibration standard. A 100- μ l portion of a solution containing 500 μ g/ml of all the following ions, Na^+ , K^+ , Cr^{3+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} as the sulfate or nitrate, was added to 50 μ l of sample in the cup prior to drying. Recoveries were significantly improved (Table II) but still unsatisfactory. This phenomenon requires further study.

Effect of Sample Digestion. Digestion of samples in the presence of 30% (w/v) hydrogen peroxide yielded erratic and irreproducible results because froth which formed during oxidation did not collapse back into the base of the cups in a uniform manner.

Method of Standard Additions. The final approach was to use the method of standard additions, which is well suited to analyses in which residual matrix effects occur. The following procedure was developed: Fifty μ l of 1% gelatin, followed by 50 μ l of sample were dispensed into each of four cups and 0, 2.5, 5.0, and 7.5 ng lead as stock solution, respectively, were added. The samples were oven dried at 140°C for 10 min and then analyzed in triplicate. Integrated absorbance was plotted against lead added, and the concentration of lead in the sample was read where the line intercepted the axis. Figure 2 shows typi-

cal curves obtained, and Table II lists the results for all 50 samples.

Statistical analysis of these data (Student "t" test for paired results) showed excellent correlation ($P > 0.1$) with analytical data obtained using the solvent-extraction atomic-absorption procedure (Table II).

Discussion

Although the preliminary studies using pure solutions with known amounts of foreign ions showed no interferences, the method of standard additions is clearly necessary to eliminate interferences in potable water samples. In practice, however, this does not involve much additional work, since the lead content of most real samples is below our detection limit (5 μ g per liter), which in turn is far lower than the maximum permissible level in potable waters (50 μ g per liter). If the lead is "not detectable," standard additions need not be made. (Subsequent to this work, we have developed an on-line computer program for standard additions.)

The high sensitivity of the new method obviates the need for any preconcentration. This advantage, together with the adequate precision and linearity, makes processing much more convenient than by the solvent-extraction atomic-absorption method. A key feature is the use of an automated atomic-absorption spectrometer, which eliminates the most time-consuming step in conventional Delves cup procedures: reading peak heights from chart recorders. The short lifetime of the stainless steel cups is a minor disadvantage of this technique, resulting in slightly higher costs.

The method should be applicable to all of the metals normally determinable in potable waters by the Delves cup technique. In many cases, standard additions may not be necessary to compensate for interferences.

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Received for review February 11, 1974. Accepted December 24, 1974.