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Determination of Lead in Aqueous Samples as the Tetramethyl Derivative by Atomic Absorption Spectrometry

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A new method for the determination of lead in aqueous samples is described. The method involves the extraction of Pb^{2+} into chloroform as the dithiocarbamate complex followed by solvent evaporation and methylation of the residue with methyllithium to form tetramethyllead. The analyte vapor is then trapped on a short column of Porapak Q from which it is eluted into a quartz furnace atomic absorption detector. A relative standard deviation of 6.8% was obtained at the 50 ng/mL level. The working range extends from the detection limit of 5 ng to an upper limit of approximately 200 ng. The results of the analysis of lead-containing Environmental Protection Agency Water Pollution Quality Control Samples are reported.

Metal volatilization techniques provide a number of significant benefits in atomic absorption spectrometry. First, matrix effects can be circumvented. Generally, it is possible to selectively derivatize the analyte while leaving behind the interferences. Second, separation of the analyte from the solvent eliminates the expenditure of thermal energy upon solvent evaporation in contrast to direct aqueous aspiration. Third, due to the thermal instability (*1*) of many volatile metal-containing compounds (compared to their inorganic counterparts), decomposition to the free atoms is facile at relatively low flame or furnace temperatures. Because of the increase in free atom population, the enhancement of atomic emission, absorption, and fluorescence signals is expected. Finally, sensitivity improvement through preconcentration can be obtained when a trapping system is employed in connection with the volatilization scheme. In this manner it is feasible to measure very low analyte concentrations because the volatilized metal compound can be collected from a large solution volume.

A vapor generation technique that has not received significant consideration for many metals is the alkylation of the analyte to form an organometallic species. The alkylated derivatives of most post-transition metals and metalloids are both volatile and stable enough to be trapped and subsequently eluted into a suitable detection system (*2*). Because hydride generation techniques (*3*) cannot be applied to all metals, alkylation may be a possible alternative in many cases, despite the fact that most alkylating agents cannot be used directly with aqueous solutions. The metal whose alkylation has been investigated most thoroughly as an analytical approach is mercury. Mono- and dialkylmercury compounds have been formed from inorganic species and separated by using gas chromatography (*4*, *5*).

The phenylation of dithiocarbamate complexes has been used as a volatilization technique in the determination of As, Sb, Tl, Se, Te, Hg, Bi, and Sn by Schwedt et al. (*6*). Their work utilized metal extraction followed by reaction with phenylmagnesium bromide to form the phenylated metal species. Gas chromatographic separation with flame ionization detection was used.

The work to be described here involves the extraction of lead into chloroform, the evaporation of the solvent, and the methylation of the residue to generate tetramethyllead. The volatile analyte is then collected on a short trapping column prior to subsequent detection via atomic absorption spectrometry.

Lead was selected as a reasonable candidate for study in this extraction/methylation approach. Although lead has been converted to the hydride PbH_4, somewhat specialized reaction conditions were required (*7-9*). A major reason for the choice of lead is the fact that well-developed methodologies exist for the determination of the methylated derivative, $Pb(CH_3)_4$. Used widely as an antiknock additive to gasoline, tetramethyllead has been determined in gasoline itself (*10*, *11*), in the atmosphere (*12-15*), in water (*16*), and in biological samples (*16*). Although continuous detection systems have been utilized (*17*), the general approach involves low-temperature trapping of the lead alkyl compounds and/or a gas chromatographic separation. Of particular interest is an atmospheric trapping method described by Coker (*18*), and used in this work. It is reported that the analyte was retained at ambient temperature on a short column of Porapak Q, a porous polymer. Selective elution of various alkyllead species was then achieved by gradual heating of the column.

Atomic spectrometry lends itself well to the detection of volatile metal-containing compounds (*19*, *20*). While flame atomic absorption spectrometry has been used as a detection system for organolead determinations, it is not as sensitive as absorption methods using furnace atomization (*21*) or as emission techniques utilizing microwave-induced plasmas for excitation (*22*, *23*). The resistively heated quartz furnace described by Chau et al. (*24*) is appealing due to its low cost, ease of operation, selectivity, and sensitivity (subnanogram amounts of organolead compounds).

EXPERIMENTAL SECTION

Apparatus. A Model 82-500 Jarrell-Ash atomic absorption spectrophotometer with a 100-μm entrance slit and a 150-μm exit

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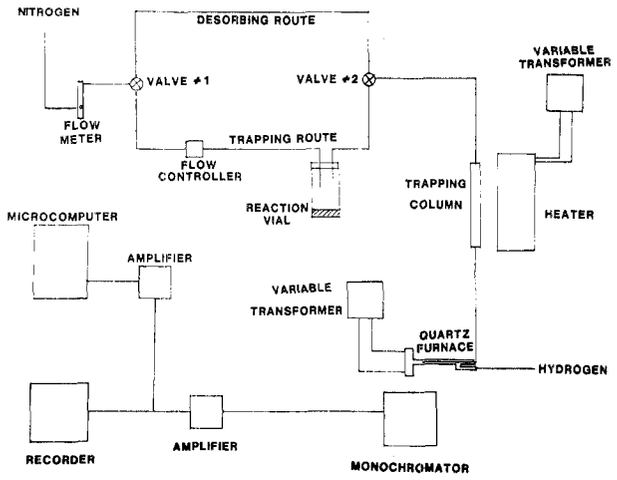

Figure 1. Schematic diagram of the trapping/eluting system.

slit was used. The 1180 groove/mm grating was blazed at 250.0 nm. A lead hollow cathode lamp was operated at a current of 5.0 mA. In order to give suitably rapid instrument response along with a certain amount of noise reduction, a 50-μF capacitor replaced the 1000-μF capacitor in the damping circuitry.

The output from the spectrometer was connected to a Hewlett-Packard Model 17503 A strip chart recorder through a voltage divider which enabled the 10 mV output to be observed on a 1-mV full-scale recorder. The output voltage from the spectrometer was amplified to a suitable level for digitization by the analog-to-digital converter of an Intel 8080 based microcomputer system (*25*). The software, which utilized a signal averaging subroutine, enabled the user to examine the profile of the analyte peak, select integration limits, apply an additional smoothing routine if necessary, and receive the integrated area and peak height. Data acquisition intervals were selected to discriminate against 60-Hz power line noise.

The quartz atomization furnace was essentially the one described by Chau et al. (*24*). A 30 cm long nichrome ribbon with a resistance of approximately 1.4 Ω was powered by a variable transformer providing a steady temperature of 980 °C in the hottest region of the furnace. A calibrated chromel–alumel thermocouple was used to monitor the temperature.

The trapping/eluting system is shown in Figure 1. Connecting lines were 3.2 mm o.d. Teflon tubing with the exception of the lines of 1.6 mm o.d. stainless steel 12 cm in length attached to the trapping column, the 1.6 mm o.d. Teflon tubing leading from the trapping column to the quartz furnace, and the 1.6 mm o.d. stainless steel tubing extending the length of the furnace. The flowmeter, flow controller, and valves 1 and 2 were mounted on a small Plexiglass panel. The trapping column itself was constructed of an 8 cm long piece of stainless steel tubing (6.4 mm o.d., 3.2 mm i.d.). The packing between silanized glass wool plugs consisted of 80–100 mesh Porapak Q (Waters Associates). A household toaster connected through a variable transformer to give a steady 235 °C temperature was utilized as a trapping column heater (*26*). The column was pretreated at this temperature for 3 h prior to initial use.

Small glass screw-cap vials (28 mm × 95 mm) were used both as extraction vials and reaction vials. They were snugly connected to the apparatus by means of a no. 2 rubber stopper attached to the two Teflon lines.

Reagents. The chloroform used in the extractions (Spectroquality, from Matheson, Coleman and Bell), the sodium diethyldithiocarbamate (G.F. Smith Chemical Co.), and the ammonium pyrrolidine dithiocarbamate (Fisher Scientific Co.) were used without further purification. The methylating agents, $LiCH_3$ and CH_3MgBr, were obtained as 1.2 M and 2.7 M solutions in diethyl ether from Aldrich Chemical Co. The additional diethyl ether used (Matheson, Coleman and Bell) was stored over calcium hydride to remove moisture. Distilled water was further purified by ion exchange. Tetramethyllead standards (Ethyl Corp.) were obtained as 80% solutions in toluene.

Procedure. The extraction vials, reaction vials, and volumetric flasks were soaked overnight in 50% nitric acid and rinsed several times with deionized water. Lead standards were prepared by making appropriate dilutions of a 1000 μg/mL lead chloride solution. Dilutions were made immediately before extractions in order to prevent analyte loss through adsorption to glass surfaces. When determinations of the Environmental Protection Agency "Water Pollution Quality Control Samples" were made, the standards were acidified with nitric acid to match the samples.

Into each extraction vial 5.0 mL of chloroform, 5.0 mL of a 0.04 M aqueous solution of chelating agent, and 5.0 mL of either the sample or aqueous lead standard were pipetted. Sodium diethyldithiocarbamate was used as the chelating agent except for these runs utilizing acidified samples, in which case ammonium pyrrolidine dithiocarbamate was used instead. A piece of 1-in. Teflon tape was stretched across the mouth of each vial to prevent contact between the plastic cap and the solutions. The glass threads of each vial were also wrapped with Teflon tape in order to make a leak-proof seal when the cap was tightened. The vials (generally eight at a time) were placed on a mechanical shaker and agitated for 1 h at approximately 275 oscillations/min. Following the extraction and settling of layers, a 1.0-mL aliquot of each chloroform phase was transferred to the corresponding reaction vial. A stream of nitrogen was used to evaporate the chloroform, after which the vials were capped and sealed.

A 1.0-mL aliquot of dry diethyl ether was added to the residue in the reaction vial to redissolve the chelated lead, and the contents were allowed to stand for 10 min. Ten drops of 1.2 M methyllithium solution were added and an additional 10 min of reaction time followed. An occasional manual rotation of the vial ensured contact between the methylating solution and any analyte residue on the sides of the vial. The vial was capped during these periods to prevent the loss of the volatile analyte.

After the reaction period was completed, the vial was securely attached to the apparatus and valves 1 and 2 switched to give a 100 mL/min flow of nitrogen through the trapping route. The trapping column was maintained at room temperature in a beaker of water. The reaction vial was immersed in a bath of 65 °C water in order to speed solvent and tetramethyllead evaporation. As the ether passed through the trap and into the hot furnace it burned, producing large yellow plumes at the ends of the quartz tube. A 50 mL/min flow of hydrogen was maintained through the furnace during all stages of trapping and eluting. After 4 min the trapping column was placed in a bath of boiling water for 1.5 min to elute any ether which had been retained. It was then externally dried for 30 s prior to its insertion into the column heater. At this stage valve 2 was closed, the reaction vial removed, and the trapping column suspended into the toaster. There was no gas flow through the trapping column during the trap heating period. After 3 additional min, valve 1 was switched to allow a 150 mL/min flow of nitrogen through the eluting route to sweep the thermally desorbed tetramethyllead into the atomization furnace. To retard column decomposition due to overheating, it was removed from the toaster immediately after peak elution.

During the 3 min period of trap heating it was necessary for the user to sample both 0% transmittance and base line (100% transmittance) through keyboard commands to the computer. The measurement of analyte absorbance was initiated several seconds before the elution of the analyte peak, and data points were taken every 100 ms. Because peaks were less than 25 s in total width, a 30-s data acquisition time sufficed.

Tetramethyllead standards were used in optimizing various instrumental parameters and in determining the percentage yield of the methylation reactions. In order to subject these standards to the same evaporation and trapping conditions encountered by samples, they were diluted in diethyl ether. A 1.0-mL sample of this solution was pipetted into a vial which was placed on the apparatus and then trapped and eluted in the same manner as samples or standards which had been methylated via methyllithium. The tetramethyllead lead solutions in ether were stable in glass volumetric flasks for several weeks, even at low part-per-billion levels.

RESULTS AND DISCUSSION

The mechanistic aspects of lead alkylation by alkyllithium compounds or by Grignard reagents are not totally characterized. While there is some disagreement concerning the

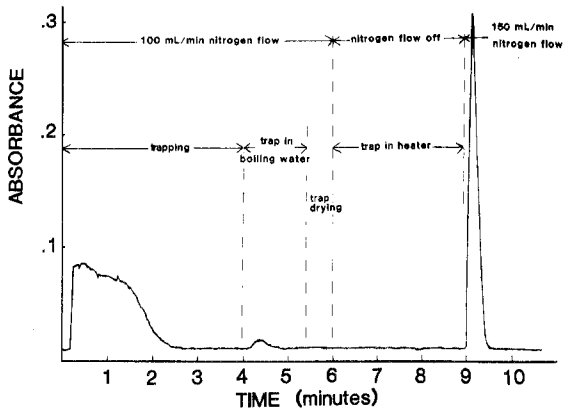

Figure 2. A typical strip chart recording showing the absorbance at the 283.3-nm lead line as a function of time. The sample which was methylated contained 50 ng/mL of Pb^{2+}.

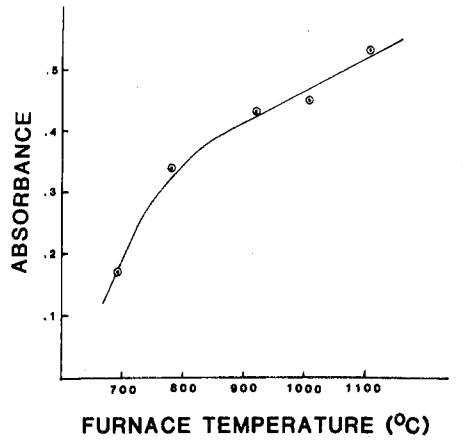

Figure 3. The absorbance maximum as a function of atomization furnace temperature. Each point represents the peak height resulting from 1.0 mL of 33 ng/mL $Pb(CH_3)_4$ standard in diethyl ether.

sequence of steps involved, the net reaction is believed to be as follows (*27*):

with Grignard reagent

$$2PbCl_2 + 4CH_3MgBr \rightarrow Pb(CH_3)_4 + Pb^0 + 2MgBr_2 + 2MgCl_2 \quad (1)$$

with methyllithium

$$2PbCl_2 + 4LiCH_3 \rightarrow Pb(CH_3)_4 + Pb^0 + 4LiCl \quad (2)$$

It is important to notice that due to a disproportionation the maximum conversion of inorganic lead to tetraalkyllead in either case is 50%. While the presently described method of methylating chelated lead species to form tetramethyllead has not been carefully scrutinized, there is reason to believe that the net reactions above hold true. By comparing the signals for tetramethyllead standards to those of inorganic lead that had just been methylated, the authors have found that essentially a 50% conversion was achieved—the percentage theoretically expected.

It is unfortunately not possible to use the methyl Grignard reagent (CH_3–Mg–Br) or methyllithium ($LiCH_3$) directly in aqueous solution as these reagents are strong methyl anion donors which react violently with protic solvents. An attempt was made to evaporate the water from an aqueous sample and directly methylate the remaining residue, but this procedure gave incomplete and irreproducible conversions. This failure was surprising in view of the fact that the standard syntheses of organolead compounds are generally performed via the alkylation of lead halide salts. Although the technique of dithiocarbamate extraction followed by solvent evaporation and subsequent methylation involved more steps, a complete and reproducible yield resulted. In addition, an extraction step serves to minimize the effects of possible interferences found in complex matrices.

Grignard and alkyllithium reactions are generally run in an ether solvent with diethyl ether being the most commonly used. In this work it was necessary to separate the methylated analyte, $Pb(CH_3)_4$, from the solvent because of large molecular signal resulted from the passage of diethyl ether through the atomization furnace. By switching from the 217.0-nm lead line to the somewhat less sensitive 283.3-nm line, we obtained a reduction of the background signal, but further separation was still required. Because the spectrometer was not equipped with automatic background correction, it was necessary to compare the signal at the 283.3-nm line to that obtained at the nonabsorbing 280.2-nm line to differentiate between molecular absorption and true analyte signal.

A variety of trapping column phases were tried including Teflon shavings, Chromosorb 102, and empty Teflon tubing at temperatures ranging from −196 °C to room temperature. At low temperatures diethyl ether (bp = 34.5 °C) was partially retained, while at room temperature a substantial amount of the tetramethyllead was not trapped. Using Porapak Q and a carefully controlled trapping and eluting scheme (see Experimental Section) it was possible to fully separate tetramethyllead from the methylating solvent. As can be seen in Figure 2 the passage of ether vapor gave a large molecular signal which gradually dissipated. The placing of the trap into boiling water caused a small molecular peak as the remaining ether was desorbed but did not cause analyte loss if the heating time was regulated.

A variety of methods were examined for heating the trap to a temperature sufficient to cause analyte desorption. Heating baths of sand or of silicone oil proved inconvenient and dangerous although slightly more rapid than the toaster method described by Chau (*26*) and finally selected. The ideal system should quickly raise the interior of the trapping column to about 235 °C without exceeding 250 °C (and thus causing column deterioration). Despite the lack of elegance the variable transformer-controlled toaster arrangement worked adequately. The interruption of flow gas while the trapping column was heating in the toaster provided for a sharp analyte peak when the flow was reestablished.

It was found that the dimensions of the trapping column (8 cm × 6.4 mm o.d. × 3.2 mm i.d.) were sufficient to give it a capacity of about 100 ng of lead in the form of tetramethyllead. This corresponds to 200 ng of Pb^{2+} from aqueous solution, due to the 50% methylation yield. By eliminating the boiling water step to desorb residual ether, it would be possible to trap larger amounts of analyte without experiencing losses, but a small molecular signal from the solvent would contribute to the total measured peak height or area. The use of a longer or wider column should provide more capacity.

Figure 3 shows the relationship between analyte absorbance (peak height in this case) and quartz furnace atomization temperature. Despite the fact that absorbance increases with furnace temperature, it was decided to use a temperature of approximately 980 °C. In this range the nichrome heating ribbon gave many hours of use, while at higher temperatures it had to be replaced frequently.

A rather substantial lead blank resulted from the methyl Grignard solution. Methyllithium gave a smaller blank signal and was used for subsequent work. Because both of these reagents are highly reactive, a suitable means for removing trace lead impurities could not be found. The attempt to lower blank signals by using very diluted methylating solution proved unsuccessful, with incomplete methylation of analyte resulting even after lengthy reaction periods. Consequently it was determined that 10 drops of 1.2 M $LiCH_3$ solution (in

Table I. EPA Water Pollution Quality Control Samples (in ng/mL, 0.15% Nitric Acid)

sample	exptl value[a]	stated value
1	73 ± 5	80
2	14 ± 4	18
3	226 ± 22	250

[a] Mean value followed by range, duplicate determination.

diethyl ether) gave a small blank signal without the risk of incomplete methylation.

A calibration run was made by using triplicate determinations at concentrations ranging from 0 to 150 ng/mL following the method given above. This plot of concentration (ng/mL) vs. signal (absorbance unit·second) yielded a least-squares slope of 0.0371 ± 0.0012, a y intercept of 0.314 ± 0.069, and a correlation coefficient of 0.9989. The absolute detection limit, defined as the amount of analyte producing a net signal equal to three times the standard deviation of the blank, was found to be 5 ng. Therefore, using the procedure described above, the concentration detection limit was 5 ng/mL. By increasing the aqueous:organic volume ratio in the extraction step or by withdrawing more of the analyte-containing organic phase, it would be possible to substantially lower the concentration detection limit. As was mentioned, it was not possible to exceed 200 ng of analyte because of the trapping column capacity. To study reproducibility, 10 methylation runs of a 50 ng/mL Pb^{2+} aqueous solution were made giving a relative standard deviation of 6.8%. When similar runs were made for an equivalent amount of tetramethyllead standard dissolved in ether, the relative standard deviation was 3.0%. This difference indicates that while some of the overall variation is caused by the methylation procedure, some is inherent in the trapping and detection system employed.

Environmental Protection Agency Water Pollution Quality Control samples were used to test the accuracy of the method. When these samples (0.15% in HNO_3) were run, it was necessary to use ammonium pyrrolidine dithiocarbamate as the chelating agent because sodium diethyldithiocarbamate readily decomposes in acidic solutions (*28*). Ammonium pyrrolidine dithiocarbamate works equally well but is slow to dissolve in water. The EPA determinations were made by using duplicate runs for standards and samples. The values reported in Table I represent the average of the duplicate determinations. The use of a different chelating agent did not significantly change the slope or linearity of the calibration curve. In all sample runs, integrated peak areas were used in preference to peak heights.

CONCLUSION

The work that has been described indicates that an extraction/methylation/trapping procedure is a viable approach to lead determination. The absolute detection limit is adequate for many applications and could be improved considerably by removal of trace lead from the methylating reagents. The use of this scheme in dealing with more complex sample matrices warrants further study. In addition, the extension of the method to a variety of other metals should not prove difficult.

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