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RECEIVED for review June 13, 1985. Accepted August 19, 1985. A. J. Spivack received support from the John and Fannie Hertz Foundation during the period this work was completed. The work was also supported by Grant 830887L-OCE from the National Science Foundation. S. R. Hart's mass spectrometry lab is supported by NSF EAR 83-08809.

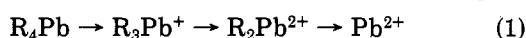
Speciation of Lead and Methyllead Ions in Water by Chromatography/Atomic Absorption Spectrometry after Ethylation with Sodium Tetraethylborate

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This paper describes a novel method for speciation and determination of Me_3Pb^+ and $\text{Me}_2\text{Pb}^{2+}$. The procedure includes *in situ* ethylation by sodium tetraethylborate (NaBEt_4) in water, purging and trapping of alkyllead molecules, and thermal desorption in an electrically heated quartz AAS furnace. The absolute detection limits of Pb for 50 cm^3 are ca. 8.7 pg for Me_3Pb^+ (0.18 pg/cm^3) and ca. 10.5 pg for $\text{Me}_2\text{Pb}^{2+}$ (0.21 pg/cm^3). Major advantages for the technique are avoidance of solvent extraction and sample transfers because ethylation to Me_3EtPb and $\text{Me}_2\text{Et}_2\text{Pb}$ takes place in a closed system. Reaction conditions and apparatus operating parameters were optimized by a Simplex algorithm.

Alkyllead compounds in the environment have more profound physiological effects than inorganic lead because they are more toxic (1). Establishing their concentration is of extreme importance for making a full assessment of the impact of anthropogenic lead input into the environment. Many automobile fuels still contain tetraalkyllead compounds as octane-boosting additives, but such use is diminishing. Studies of organolead compounds in the environment are still hampered by difficulties in speciating their decomposition products. The original molecules are thought to decompose via ionic alkyllead intermediates to inorganic lead (eq 1).



R = Me, Et, and Me-Et combinations

However redistribution, disproportionation, and possible methylation of ionic alkyllead species (2-5) may further complicate decomposition studies (6, 7). The question of whether or not methylation of lead occurs in the environment is controversial, and determination of ionic methyllead compounds in experiments of inorganic lead methylation under model environmental conditions would lead to a better understanding of formation mechanisms. Production of methyllead ions in higher yields than for Me_4Pb is probable, as in the case of tin (8), but most studies determined only volatile products (2, 4, 9).

Determination and speciation of ionic alkyllead species have been done by UV spectrometry (7, 10), differential pulse anodic stripping voltammetry (DPASV) (11-13), gas chromatography with an electron capture detector (GC-ECD) (14), high-performance liquid chromatography with atomic absorption detection (HPLC-AAS) (15), and GC-AAS after hydride generation (16) or butylation (17-20). This variety of techniques suggests a search for methods with good sensitivity, ease of operation, and reliability.

None of the above methods is ideal. UV spectrometric determination after complexation with dithizone is insensitive and often requires peak resolution. Only R_3PbCl compounds, and not R_2PbCl_2 , are volatile enough for direct GC-ECD determination. DPASV determinations require pure aqueous solutions without interfering ions and preferably absence of Pb^{2+} (12). Hydride generation techniques are limited because of alkyllead hydride molecule instability and hydrogen-alkyl exchange. HPLC-AAS can determine a number of ionic alkyllead compounds, but solvent composition, time of operation, and determination of only certain groups of compounds at a time present problems. Butylation to volatile tetraorganolead compounds followed by chromatography with AAS as Pb detector has to date been promising in speciating a variety of ionic alkyllead compounds. However, derivatization

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Table I. Summary of Simplex Optimization Experiments^a

expt no.	peak height ^b	pH	% NaBEt ₄ (w/v)	purge time, min	He flow, cm ³ /min	H ₂ flow, cm ³ /min
1	3.68	4.00	0.10	2.0	80	4
2	4.90	8.00	0.30	12.0	60	20
3	3.42	6.00	0.20	6.0	100	8
4	2.69	2.50	0.60	10.0	120	24
5	2.04	11.50	0.40	4.0	160	16
6	2.19	10.00	0.50	8.0	140	12
7	0.00	0.70	0.28	11.2	40	11
8	2.65	8.80	0.37	5.8	130	15
9	0.34	1.72	0.13	6.3	56	16
10	3.63	7.93	0.41	7.6	119	13
11	2.75	2.57	0.27	9.2	62	13
12	0.00	8.90	^c	4.7	48	^c
13	8.24	4.10	0.43	8.7	102	18
14	2.66	9.44	0.30	5.3	123	12
15	4.83	4.29	0.28	8.2	77	13

^aThis experiment was for 200 pg/50 cm³ Me₃PbCl (as Pb). See Experimental Section for additional details. ^bArbitrary relative units.

^cNegative value.

by butylation involves sample preconcentration and transfers. These lead to losses, restrictions on injected sample size due to co-chromatographing of sample and solvent, and considerable operation time and effort.

This derivatization-purge and trap-AAS procedure is a simpler, less time-consuming, and very sensitive technique for determination of Me₃Pb⁺ and Me₂Pb²⁺ in model studies of environmental samples than those described above. In situ ethylation of aqueous methyllead ion samples by sodium tetraethylborate (NaBEt₄) produced molecular, volatile mixed alkyls of predictable composition. Dynamic purging, cryogenic trapping on a chromatographic packing, mild thermal desorption to an electrically heated quartz furnace, and AAS detection effected their speciation. They eluted according to their boiling points, and their determinations resulted in very low detection limits.

EXPERIMENTAL SECTION

Reagents. Methyllead chlorides and mixed tetraalkyllead compounds were donated by Ethyl Corp. (Baton Rouge, LA). Me₃PbCl was purified by dissolving in deionized distilled water saturated with NaCl and extracting with CHCl₃. Pure crystals occurred after evaporation of the solvent to a quarter of the original volume. Me₂PbCl₂ was recrystallized from dimethylformamide. The ethylating agent NaBEt₄ and MeHgCl were purchased from Alfa Ventron (Danvers, MA). Standards of methyllead chlorides (100 µg/cm³ as Pb) were prepared each day, and stored in darkened volumetric flasks at 4 °C. Aqueous NaBEt₄ solutions were stable for 1 week in similar storing conditions.

Apparatus. The apparatus is a slightly modified form of one used for determination of organotin compounds (21). One modification (Figure 1) is the addition of a four-way valve (Glenco Valves, Anspec, Ann Arbor, MI) switched for trapping-purging or transfer to the quartz furnace aligned in the Perkin-Elmer 503 AAS. The furnace (11 mm i.d., 140 mm length), which was insulated by asbestos string, was heated to 950 °C with Nichrome wire (26 gauge, 10-Ω resistance). Teflon transference lines (1.63 mm i.d.) were kept at 95 °C by use of Nichrome wire (28 gauge, 65-Ω resistance). The empty, U-shaped glass water trap (5 mm i.d., 450 mm length) was kept at -78 °C (dry ice-acetone) and the glass alkyllead compounds' trap (4 mm i.d., 750 mm length), at -190 °C (liquid N₂). The latter, speciating trap was packed with 5.2 g of 10% SP-2100 on Chromosorb W AW-DMCS (80-100 mesh) and was coiled with Nichrome wire (26 gauge, 10 Ω resistance). After removal from liquid N₂, it was heated from -190 °C to 60 °C in 5 min by applying 15 V for selective desorption of alkyllead compounds.

Optimization by Simplex Algorithm. The absorbance signal was optimized for five parameters by using a computer program based on a Simplex algorithm (22), but several modifications were made. Instead of maximization or minimization of a function,

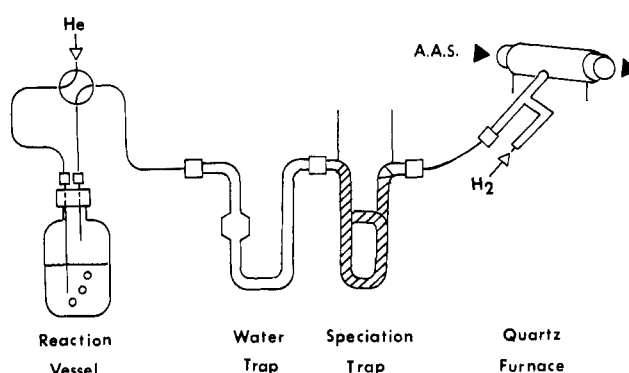


Figure 1. Apparatus for trapping, desorbing, and determining inorganic lead and methyllead ions.

response values were derived experimentally. For the purpose of limiting experiments no major shrinkage was carried out. Instead the next to worst vertex was replaced by a new vertex. The program is capable of dealing with a maximum of 15 parameters provided $n + 1$ vertices (n is the number of parameters) are formed initially. Each vertex represents an experiment with new values for each parameter. In the present study six initial experiments (Table I) were performed with each one carried out for different randomly picked values of each parameter. After each vertex was input (parameter values and absorbance included) a new vertex was calculated giving new values for each parameter. Carrying out the experimental procedure for the new set of values resulted in a new response value. A new vertex was calculated by inputting it into the program. The process is repeated with elimination each time of the worst vertex. The multivariate approach could optimize any experimental system using a minimum number of experiments and avoiding factorial design experimentation.

The parameters investigated in optimization of absorbance signal were initial sample pH, NaBEt₄ concentration, purge time, helium carrier gas flow rate, and hydrogen flow rate. Optimum values after 15 experiments (Table I) were (1) 4.1 initial pH, (2) 3 cm³ 0.43% (w/v) aqueous NaBEt₄, (3) 8.7 min purge time, (4) 102 cm³/min helium flow rate, and (5) 18 cm³/min hydrogen flow rate.

Procedure. Aliquots (50 cm³) of standards containing Me₂Pb²⁺, Me₃Pb⁺, or both were placed in 120-cm³ Hypo-vials, and the pH was adjusted to 4.1. After the vials were capped with crimp-on septa lined with Teflon, 3 cm³ of 0.43% (w/v) aqueous NaBEt₄ was injected. Shaking for 15 min ensured reaction completion, and determinations were effected by purging for 8.7 min and trapping. Desorbing was done by heating from -190 °C to 60 °C in 5 min, and holding the temperature constant until all volatile organolead compounds eluted. Retention times were 2.74 min for Me₄Pb, 3.46 min for Me₃EtPb, 4.27 min for Me₂Et₂Pb, 5.37 min for MeEt₃Pb, and 7.93 min for Et₄Pb. The 217-nm

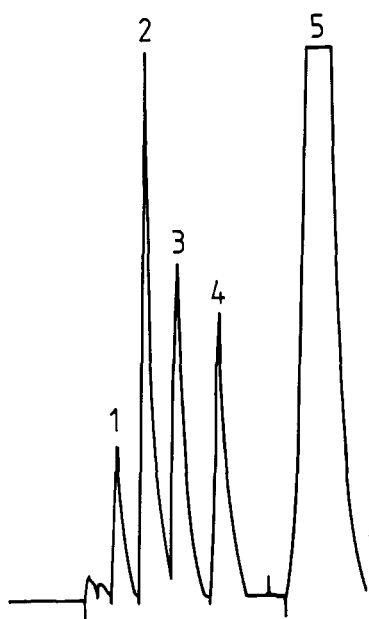


Figure 2. Chromatogram of tetraalkyllead standards (as pg of Pb): (1) Me_4Pb (100 pg), (2) Me_3EtPb (100 pg), (3) $\text{Me}_2\text{Et}_2\text{Pb}$ (100 pg), (4) MeEt_3Pb (100 pg), and (5) Et_4Pb (1000 pg).

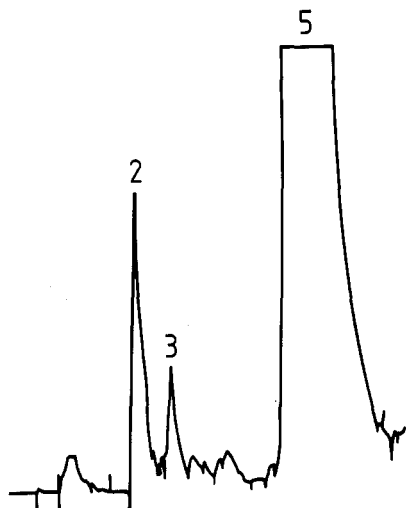


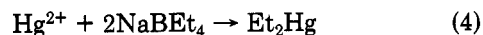
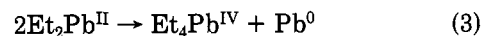
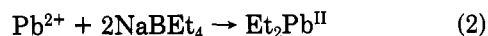
Figure 3. Chromatogram of ethylated derivatives of Me_3Pb^+ , $\text{Me}_2\text{Pb}^{2+}$, and Pb^{2+} (as pg Pb), (2) Me_3EtPb (50 pg), (3) $\text{Me}_2\text{Et}_2\text{Pb}$ (50 pg), and (5) Et_4Pb (3000 pg).

emission line was used throughout the experiments, and the slit width was kept at 1 mm with maximum scale expansion. Mixed tetraalkyllead standards were made in methanol with the last dilution in 50 cm^3 deionized, distilled water, and placed in Hypo-vials. Signals were processed by a Hewlett-Packard 3390 A integrator.

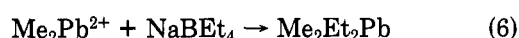
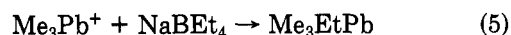
RESULTS AND DISCUSSION

Typical chromatograms of mixed tetraalkyllead standards (Figure 2) and ethylated methyllead ions (Figure 3) show the excellent sensitivity and separation of the method. Precision evaluation of 200 pg of Pb as Me_3Pb^+ or $\text{Me}_2\text{Pb}^{2+}$ resulted in 8.5% relative standard deviation. Linearity of calibration graphs extended from 50 pg to 1 ng Pb. Detection limits of 50- cm^3 aliquots at 3σ blank noise ($n = 10$) were 8.7 pg (or 0.18 pg/cm^3) for Me_3Pb^+ and 10.5 pg (or 0.21 pg/cm^3) for $\text{Me}_2\text{Pb}^{2+}$. Hence, limit of quantitation of 10σ blank noise was 29 pg for Me_2Pb^+ and 35 pg for $\text{Me}_2\text{Pb}^{2+}$ (23). Figure 3 shows that 3 ng of inorganic lead as Et_4Pb always occur as a blank. Any ethyllead compounds present would also form Et_4Pb . Recoveries calculated from mixed alkyllead standards were $87 \pm 4\%$ for Me_3Pb^+ and $72 \pm 8\%$ for $\text{Me}_2\text{Pb}^{2+}$. We observed no alkyl transfer reactions in these experiments.

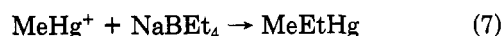
Honeycutt and Riddle (24) first used NaBEt_4 in aqueous solutions to produce Et_4Pb and Et_2Hg from their inorganic salts (eq 2-4). (Some equations are unbalanced and incom-



plete because only organolead and organomercury compounds are of interest here.) Equations 2 and 3 demonstrate why the 3 ng of Pb as Et_4Pb corresponds to 6 ng of Pb^{2+} background. Similarly this study shows that NaBEt_4 reacts with Me_3Pb^+ (eq 5) and $\text{Me}_2\text{Pb}^{2+}$ (eq 6). Preliminary studies show that



determination of MeHg^+ in environmental samples is also feasible after derivatization by NaBEt_4 . The resulting MeEtHg (eq 7) can be quantified by GC or AAS.



Utilization of these reactions for all in situ production of organometallic compounds followed by their purging from aqueous solutions results in a simplified procedure. One can now avoid losses and contamination from solvent extraction of ionic methyllead compounds, derivatization with air- and moisture-sensitive Grignard reagents, and transfer to vessel for preconcentration or solvent evaporation. Also co-chromatographing the sample with its extraction solvent severely limits sample size and thus results in only a small fraction of the sample being used. The present approach requires no concentration techniques, and the entire sample is derivatized, trapped, and determined. This leads to improved detection limits (as Pb) of 0.18 pg/cm^3 for Me_3Pb^+ and 0.21 pg/cm^3 for $\text{Me}_2\text{Pb}^{2+}$ with 50- cm^3 samples, which to our knowledge are the lowest reported.

For the experiments studying methylation of Pb under model laboratory conditions, ethylation by NaBEt_4 should be the method of choice. However, not all alkyllead ions could be determined in this way. The method is inappropriate for mixed ionic methylethyllead species, which may exist in the environment due to anthropogenic input.

ACKNOWLEDGMENT

We thank A. H. Copeland for help with the Simplex algorithm and M. Anderson for writing the computer program.

Registry No. Me_3Pb^+ , 14570-16-2; $\text{Me}_2\text{Pb}^{2+}$, 21774-13-0; Me_4Pb , 75-74-1; Me_3EtPb , 1762-26-1; $\text{Me}_2\text{Et}_2\text{Pb}$, 1762-27-2; MeEt_3Pb , 1762-28-3; Et_4Pb , 78-00-2; NaBEt_4 , 15523-24-7; H_2O , 7732-18-5; Pb, 7439-92-1.

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RECEIVED for review June 3, 1985. Accepted August 19, 1985.
This research was partially supported by National Science Foundation Grant CEE 81-16960.

Determination of Cyanide by Atomic Absorption Using a Flow Injection Conversion Method

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A flow injection method (FIA) has been developed for the determination of cyanide ion by atomic absorption spectrometry (AAS). Aqueous cyanide samples (pH 11.0) are injected into an on-line cupric sulfide packed column, and potassium hydroxide solution (pH 11.0) is used as the carrier. The eluent containing the analyte as cuprocyanide complexes is introduced into the nebulizer of the atomic absorption spectrometer. This novel FIA/AAS method has a sensitivity of 1 ppm cyanide for 0.0044 A and a detection limit also of 1 ppm cyanide. The precision of the technique is better than 2% relative standard deviation at 26 ppm cyanide with a sampling rate of 40-50 samples/h. The effects of flow rate, sample volume, and anionic interference on the FIA/AAS signals are presented. Only citrates were found to interfere significantly (+5% at 20-fold concentration). The conversion method is potentially applicable to other anions.

The resonance lines of most nonmetals occur in the vacuum UV region; hence, these elements do not lend themselves readily to determination by atomic absorption spectrometry (AAS) (1). Christian and Feldman (2) demonstrated a large variety of novel methods for the determination of anions using indirect atomic flame absorption spectrometry; the methods included direct chemical interference and its removal in the flame, solvent extraction or masking of the extraction of an equivalent amount of metal, oxidation or reduction of a metal followed by solvent extraction, and precipitation of a metal. For indirect determination of silicon, Kirkbright et al. (3) formed silicomolybdic acid and extracted it with butanol. The extract was introduced into a nitrous oxide-acetylene flame and the molybdenum measured at 313.3 nm. Phosphate was similarly determined by extraction into an organic solvent as phosphomolybdic acid (4, 5). Bond and O'Donnell (6) de-

termined nitrogen in ammonium salts via the atomic absorption of titanium. They noticed that ammonium salts enhance the absorption of titanium and zirconium in the nitrous oxide-acetylene flame. Westerlund-Helmerson (7) analyzed zinc and lead oxides for chloride by boiling the sample with silver nitrate and nitric acid and dissolving the washed chloride precipitate in ammonia. The silver in the dissolved precipitate was then determined by atomic absorption spectrometry.

The application of flow injection analysis (FIA) to atomic absorption spectrometry has proved to be an efficient way for automating sample preparation and analysis. Olsen et al. (8) developed an on-line FIA preconcentration method utilizing a micro ion-exchange column. Malamas et al. (9) developed an on-line FIA trace-metal enrichment procedure utilizing a column containing 8-quinolinol immobilized on porous glass. Nord and Kalberg (10) applied an FIA extraction procedure to AAS. Lynch et al. (11) applied FIA to metal speciation, utilizing a spectrophotometer and an atomic absorption detector in series. Kamson and Townshend (12) described an FIA application in which an ion-exchange column was used to remove interferences in the determination of calcium by FIA/AAS. A number of investigators applied FIA in combination with atomic absorption spectrometry for metal determinations in blood serum (13-17).

The present study reports a novel approach for anion determination in which an on-line heterogeneous chemical reaction/FIA system, utilizing a column containing cupric sulfide, is used to convert cyanide into a species that can be measured by AAS. Copper(II) is known to acquire powerful oxidizing characteristics in the presence of cyanide, due to the formation of extremely stable cuprocyanide complexes (18). In the present method, cyanide solutions readily dissolve cupric sulfide, and the copper released as soluble cuprocyanide complexes is determined by AAS.

EXPERIMENTAL SECTION

Apparatus. The schematic of the manifold for this study is shown in Figure 1. Sample solutions were injected manually into

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