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Flow injection hydride generation electrothermal atomic absorption spectrometry with in-atomizer trapping for the determination of lead in calcium supplements

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Abstract

Lead hydride was generated from acid solution, containing potassium ferricyanide as an oxidizing agent, by the reaction with alkaline borohydride solution. The effects of reaction conditions (hydrochloric acid, ferricyanide and borohydride concentrations), and the lengths of reaction and stripping coils were studied. The effects of trapping temperature and argon flow rate were also investigated. Under the conditions giving the best peak area sensitivity, the detection limit (concentration giving a signal equal to three S.D. of the blank signal) was 0.12 μg l^{-1} for a 1000 μl injection volume. The detection limit was improved to 0.03 μg l^{-1} when the ferricyanide was purified by passage through a cation-exchange resin. Two calcium supplement materials were analyzed by the flow injection (FI)-hydride generation (HG)-electrothermal atomization atomic absorption spectrometry (ETAAS) method, giving values of 0.55 and 0.66 μg g^{-1}, in agreement with results obtained by previously validated methods. For a 500-mg sample the limits of detection and quantification were 0.006 and 0.02 μg g^{-1}, respectively.

Keywords: Electrothermal atomic absorption spectrometry; Hydride generation; In-atomizer trapping; Lead; Calcium supplements

1. Introduction

The toxicity of lead to humans and animals has been well documented [1] and the need for reliable methods for the quantification of lead in a variety of materials which may lead to the introduction of lead in humans is well understood. Whether there is a safe threshold for lead ingestion is still a topic of debate [2]. As lead is ubiquitous, it is unrealistic to set daily exposure limits which are close to zero, though the need to reduce the lead burden of the population is recognized by several countries [2] and various agencies have prescribed maximum allowable concentrations in air and water. In an effort to establish a practical guideline,

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the Office of Environmental Health Hazard Assessment for California has established [3] a 'no significant risk level (NSRL)' of 0.5 μg day^{-1}.

One possible source of dietary lead is that obtained from calcium supplements. The amount may be 500–1000 mg of calcium (as calcium carbonate) per day. This calcium carbonate comes from a variety of naturally occurring sources. Although there is evidence that the retention of lead varies inversely with the calcium content of the diet [4], the possibility that more than the NSRL could be ingested from the consumption of a few antacid tablets [3] is surely cause for concern. The US Food and Drug Administration has recently proposed lowering the limits of lead allowable in calcium carbonate and other food sources of calcium [5]. Currently the US Pharmacopoeia [6] and the Food Chemicals Codex [7] specify the maximum allowable concentration of lead in calcium carbonate to be 3 μg g^{-1}. Several methods for the analysis of calcium supplements in which the lead is quantified by graphite furnace atomic absorption spectrometry have been developed [5,8–10]. For some of these methods, the sample pretreatment procedure was lengthy. In general for matrix of this sort, a problem with the build-up of calcium deposits on the contact cylinders may be encountered and therefore an alternative method would be preferable. Wolf has developed and validated [3] a method involving leaching with nitric acid, with quantification by ICP-MS. A matrix interference was overcome by allowing up to 20 s after initial sample introduction before the reading was made. Although the solutions were diluted so as to contain between 0.1 and 0.5% dissolved solids, the build up of solids on the spectrometer cones caused a 20% suppression of the signal by the end of a 4-h period. Amarsiriwardena et al. also reported on the results of a procedure in which quantification was by ICP-MS [11]. Calcium supplements were dissolved in nitric acid in a high pressure asher at pressures of up 1770 psi and temperatures of up to 230°C.

Hydride generation (HG) is an increasingly popular procedure for sample introduction in atomic spectrometry [12]. The HG determination of lead has been reviewed by Cámara and Madrid [13]. The in-atomizer trapping procedure, which concentrates the element of interest in the atomizer prior to atomization [14], has a greater relative sensitivity than that of direct introduction of the sample solution into the furnace, as a much larger volume of sample may be processed. HG procedures may be readily automated by the use of flow injection (FI) methodology which, in addition to improved precision and throughput, also has the benefits of decreased reagent consumption and decreased interferences through kinetic masking [15]. However, detection limits for FI-HG procedures are constrained by reagent blank values, and there may be little to be gained from sample volumes of more than 500–1000 μl [16]. Recent developments may be followed in the regular review literature [17].

For all the hydride-forming elements, the generation of the hydride by reaction with borohydride is more efficient from one particular oxidation state of the analyte than from any others. In the case of lead, it has been observed that better performance is obtained in the presence of oxidizing agents, which presumably oxidize the lead to the $+4$ state. Although a number of strong oxidizing agents (such as dichromate, peroxide and peroxodisulfate) have been used to increase the sensitivity, superior results have been obtained with the relatively mild oxidant, ferricyanide [18–22]. Various combinations of oxidants and complexing agents have also been used [12,13]. Brindle et al. [23] have devised a method for the determination of Pb in calcium carbonate by FI-HG with quantification by DC plasma atomic emission spectrometry. By separation of the analyte from the matrix they were able to overcome a spectral interference due to the calcium.

The primary goal of the work described here was to devise a method for the determination of lead in calcium carbonate based on FI-HG. Such a procedure could be interfaced with several instumental detection techniques and would overcome all interference effects of instrumental origin due to the matrix. Secondary goals of the work were to devise a simple sample preparation procedure (shorter than some of the previously published procedures) and to show that external calibration with aqueous standards was feasible. Two sample

materials, representative of the types of calcium supplement currently available in US pharmacies, were analyzed by (a) several electrothermal atomization atomic absorption spectrometry (ETAAS) procedures previously validated and described, and (b) by the proposed FI-HG method with a simple sample preparation in which ETAAS was used for quantification. The determination of lead in a calcium carbonate matrix by FI-HG with quantification by ETAAS with in-atomizer trapping has not, to the authors' knowledge, been reported previously.

2. Experimental

2.1. Apparatus

A standard double-line FI manifold (see Fig. 1) was constructed for a Perkin-Elmer (Norwalk, CT) FIAS-200 FI unit. The manifold was constructed from Teflon® tubing (1 mm i.d.), Perkin-Elmer chemifold fittings and a Perkin-Elmer plastic gas–liquid separator. The sample solution was injected into an acid carrier which was merged downstream with an alkaline borohydride solution. After passage through an open tubular reactor, a stream of argon was merged and, after passage through an open tubular 'stripping' reactor, the reaction zone was delivered to the gas–liquid separator. The optimized manifold specifications were as follows. A tube of 110 mm was used to connect the confluence point of the carrier and the borohydride streams with the argon supply, and a tube of 300 mm was used to connect the argon supply point to the gas–liquid separator. Argon was supplied at 150 ml min^{-1}. Tygon peristaltic pump tubing of internal diameters 1.52, 1.14 and 3.18 mm for the carrier, borohydride and waste lines, respectively. The carrier and borohydride flow rates were 5.6 and 3.6 ml min^{-1}, respectively. The gas–liquid separator and the quartz probe, which was inserted in the graphite tube during generation and trapping of the hydride, were connected by a model MD-250 Nafion® drying tube (Permapure, Toms River, NJ)

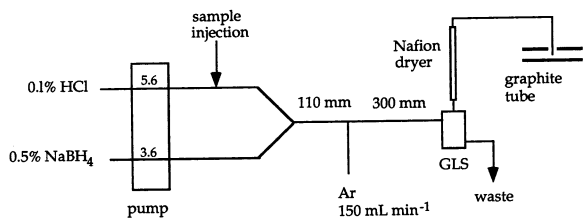

Fig. 1. Double line manifold for hydride generation (HG). The flow rates of the acid carrier was 5.6 ml min^{-1} and of the borohydride reagent was 3.6 ml min^{-1}. The sample injection volume was either 500 or 1000 μl. The gas–liquid separator, GLS, was the Perkin-Elmer part number B019-3772 device containing glass beads. The waste was pumped at a slightly higher rate than the combined liquid introduction rate. The transfer line terminated in a quartz tube which was inserted and withdrawn from the furnace dosing hole under software control at the appropriate time in the cycle.

The hydride was trapped on the interior surface of a transversely heated graphite atomizer in a Perkin-Elmer 4100ZL Zeeman corrected atomic absorption spectrometer fitted with a Perkin-Elmer system II electrodeless discharge lamp operated at 400 mA with detection at 283.3 nm. The instrument was controlled by Perkin-Elmer PEAALABS software (v 7.21) software. Peaks were quantified by area. The interior of the furnace was pre-treated with 120 μg of iridium by the sequential transfer and thermal processing of three 40-μl portions of a 1000 mg l^{-1} iridium solution as described previously [24]. The FI program is shown in Table 1. In the first stage, the valve loop (500 μl unless otherwise specified) was filled with the sample solution. The quartz tipped transfer probe (Perkin-Elmer, Part 509612) was then inserted into the graphite atomizer such that the tip was about 1 mm above the L'Vov platform. The sample was then injected into the carrier steam and carried through the manifold. The hydride was transferred from the gas–liquid separator to the graphite furnace, which had been heated to 300°C. The furnace program is given in Table 2.

2.2. Reagents

Standard Pb solutions covering the range 0–30 μg l^{-1} were prepared by serial dilution of a 1000 mg l^{-1} atomic standard solution. Solutions for

Table 1
FIAS program

Step	Time (s)	Pump 1 (rpm)	Pump 2 (rpm)	Valve	Read
Pre-fill	5	120	0	Fill	
1	25	120	120	Fill	
2	30	0	120	Inject	Y
3	5	120	120	Fill	
4	3	0	0	Fill	

Table 2
Hydride trapping furnace program

Step	Ramp	Hold time (s)	Temperature (°C)	Gas flow (ml min^{-1})	Read
1	1	15	300	250	
2	0	5	1750	0	Y
3	1	3	2100	250	

determination by HG were prepared by adding solid potassium ferricyanide (J.T. Baker, Phillipsburg, NJ, USA and Aldrich, Millwaukee, WI), concentrated hydrochloric acid (Fisher, Fairlawn, NJ) and a standard or sample as necessary to a calibrated flask followed by dilution to volume with deionized, distilled water. Borohydride solution was made by adding the appropriate mass of sodium borohydride granules (Alfa, Ward Hill, MA) and sodium hydroxide (Fisher) to a calibrated flask followed by dilution to volume. Carrier solution was prepared by diluting concentrated hydrochloric acid. Hydrogen peroxide (30% m/v) was used in some of the sample preparation procedures. Stock solutions of ammonium dihydrogen phosphate and magnesium nitrate were used for chemical modification.

2.3. Sample preparation

Samples of two commercially available calcium supplements were obtained from a local pharmacy. Both samples were marketed under the CVS brand name. One sample was a calcium/magnesium/zinc supplement (333 mg Ca, 133 mg Mg and 5 mg Zn per tablet) and the other a calcium supplement based on calcium carbonate from crushed oyster shells (500 mg Ca per tablet). The samples were ground finely in a pestle and mortar. Concentrated nitric acid and 30% hydrogen peroxide (Fisher) were used in the digestion of samples. Three sample digestion and analysis procedures were used.

Method 1 [8]: Approximately 1 g of the ground tablets was heated in a muffle furnace at 450°C for 8–16 h followed by open-vessel, hotplate digestion with 2 ml nitric acid and 5 ml water, and evaporation to near dryness. Up to 4 ml of hydrogen peroxide was then added to remove carbonaceous material and the resulting solution was diluted, after the addition of 1 ml 25% (m/v) ammonium dihydrogen phosphate as a chemical modifier, to 50 ml with water. The furnace program is shown in Table 3. Five lead standards of concentrations between 0 and 30 $\mu g\ l^{-1}$ containing 0.5% ammonium dihydrogen phosphate were used for calibration.

Method 2 (based on EPA method 3050B [25]): Approximately 0.5 g of the ground sample was heated in 20 ml concentrated nitric acid on a hotplate in a covered vessel until a clear solution was obtained. Hydrogen peroxide (1 ml) was added and the solution evaporated to 5 ml prior to dilution to 25 ml. The solutions were filtered prior to analysis. The furnace program is shown in Table 3. Five lead standards of concentrations between 0 and 30 $\mu g\ l^{-1}$ were used for calibration and 5 μl of matrix modifier solution of 0.2% (m/v)

magnesium nitrate and 6% (m/v) ammonium dihydrogen phosphate (as recommended by Perkin Elmer) was used per firing.

Method 3 [9]: 0.5 g of the finely divided sample was heated in a muffle furnace at 425°C for 24 h. The sample was digested in a closed vessel in microwave oven (CEM, Matthews, NC) with 6 ml of concentrated nitric acid at 20% power for 20 min. The solution was cooled, diluted to 25 ml with water and filtered. The furnace program is shown in Table 3. Five lead standards of concentrations between 0 and 30 μg l^{-1} were used for calibration. No modifier was added.

For the determination by FI-HG-ETAAS, 0.5 g of the powdered sample was heated with concentrated nitric acid (20 ml) in a covered container on a hotplate for 1 h. Hydrogen peroxide (1 ml) was added and the solution evaporated slowly to dryness. Water (about 15 ml), 0.75 g potassium ferricyanide, and 0.025 ml concentrated hydrochloric acid were added and the resulting solution filtered and diluted to 25 ml. Five lead standards, of concentrations between 0 and 30 μg l^{-1}, were used for calibration.

All analyses were performed in duplicate and four replicate measurements were made for each standard and sample solution.

2.4. Method development

The various FI-HG parameters were optimized to yield the greatest peak area sensitivity for all of the studies except that of the effect of trapping temperature, for which the figure of merit was highest precision. Four replicate measurements of a 10 μg l^{-1} lead solution were made at each combination of parameter values.

Some preliminary experiments with various oxidising agents (dichromate in lactic acid, and nitirc acid and hydrogen peroxide) were undertaken together with a detailed study of the role of ferricyanide. The concentrations of ferricyanide and acid were considered to be dependent variables and the effects of these were studied by a complete factorial design. Seven different acid concentrations over the range 0.025–3.0% and six different ferricyanide concentrations over the range 0.1–8.0% were investigated. The acid concentration in the carrier was adjusted to be the same as that in the sample. The borohydride concentration was varied between 0.2 (m/v) and 0.8% (m/v), the maximum concentration that could be tolerated without excessive carryover of droplets from the GLS to the atomizer. Three different lengths (110, 300 and 630 mm) of the

Table 3
Furnace program for methods 1, 2, and 3[a]

Step	Ramp	Hold time (s)	Temperature (°C)	Gas flow (ml min^{-1})	Read
1	1	5	140	250	
		50	120		
		20	140		
2	1	10	250	250	
		30	850		
		20	400		
3	1	20	680	250	
		15	20		
		15	20		
4	0	10	1900	0	Y
		5	1900		
		4	1900		
5	1	5	2300	250	
		5	2600		
		5	2400		
6	1	20	20	250	

[a] The methods differ only in the various hold times and temperatures. The values for method 1 are shown first, then those for method 2, and the last figure in a multiple figure entry is for method 3.

Table 4
Peak area values for various oxidant and acid concentrations

Acidic concentration (%v/v)	Oxidant concentration (%w/v)					
	0.1	0.5	1	3	5	8
0.025	0.030	0.082	0.106	0.090	0.067	0.092
0.05	0.046	0.090	0.082	0.119	0.100	0.090
0.1	0.105	0.118	0.118	0.232	0.189	0.131
0.3	0.140	0.144	0.200	0.189	0.180	0.212
0.5	0.162	0.165	0.217	0.186	0.190	0.210
1.0	0.149	0.178	0.190	0.195	0.190	0.202
3.0	0.002	0.006	0.007	0.003	0.001	0.002

reaction coil between the confluence point and the argon addition were investigated. The length of the stripping coil connecting the argon addition point and the gas–liquid separator was varied over the same values. A complete factorial design procedure was also used in the investigation of these two parameters. The argon flowrate was varied between 100 and 200 ml min^{-1}. The flowrates of the carrier and reductant streams were varied by means of the peristaltic pump head rotation rate, which was varied over the range 60–120 rpm, corresponding to flow rates of 3.6–8.0 ml min^{-1} for the carrier stream and 2.4–6.4 ml min^{-1} for the borohydride stream, respectively. The furnace trapping temperature was varied between 20 and 500°C.

An attempt was made to decrease the lead content of the ferricyanide by passage of near saturated solutions through an Amberlite IR20 (Sigma, Milwaukee, WI) cation-exchange resin. The detection limit was estimated from a calibration obtained for standards and a blank to which had been added the appropriate amount of purified ferricyanide solution.

2.5. Method validation

The results obtained by the FI-HG-ETAAS method were compared with those obtained by three previously described, but somewhat different methods, two of which [8,9] had been previously validated by the analysis of reference bone meal (NIST SRM 1486) or animal bone (IAEA CRM H-5) materials. Each method used ETAAS, but differed slightly in the furnace program and the use and nature of chemical modifiers, and differed considerably in the nature of the sample dissolution/digestion procedure. The two materials analyzed were considered to be typical of those previously examined [5,8–11]. Spike recoveries (pre-digestion) for the FI-HG-ETAAS method were calculated for one of each sample type, to which had been added sufficient lead to correspond to approximately 0.5 μg g^{-1} in the solid.

3. Results and discussion

Of the oxidants investigated, ferricyanide was found to be the best. The results of the optimization of the concentrations of acid and oxidant are shown in Table 4. For any given acid concentration, there was a tendency for the signal to increase with oxidant concentration and then decrease, passing though a maximum at around 1–3% (w/v). For a given oxidant concentration, the signal tended to increase and then decrease as the acid concentration was increased, passing through a maximum between 0.1 and 1.0% (v/v). Concentrations of 0.1% (v/v) acid and 3% (m/v) oxidant were chosen. The peak area signal was relatively insensitive to borohydride concentration over the range 0.2–0.8% (m/v) with a slight maximum at 0.5%, the value selected as optimum. The greatest sensitivity was obtained with a mixing coil of 110 mm and a stripping coil of 300 mm. For the concentrations of acid and borohydride selected, the pump rotation speed did not change

the peak area significantly, and a value of 80 rpm was selected corresponding to values of 5.6 and 3.6 ml min^{-1} for the carrier and borohydride streams, respectively. The signal increased significantly as the argon flow rate was increased from 50 to 150 ml min^{-1}. Above this value the signal was independent of argon flow and thus a value of 150 ml min^{-1} was selected. The sensitivity did not vary significantly with trapping temperature, but the greatest precision was obtained at 300°C.

For an injection volume of 1000 µl the equation of the calibration line fitted by least squares regression was $A = 0.050C + 0.071$, where A is peak area (absorbance seconds) and C is concentration in µg l^{-1}. The characteristic mass was 88 pg. As the characteristic mass for conventional introduction is about 30 pg, it may be concluded that the generation, stripping and trapping processes are only about 30% efficient. The limit of detection, calculated as the concentration corresponding to three times the S.D. of the signal for the blank, was 0.12 µg l^{-1}. When the purified ferricyanide was used, a limit of detection of 0.03 µg l^{-1} was obtained, for a sample volume of 1000 µl. However, the capacity of the cation-exchange column used for the purification was rapidly exceeded, and the blank values (and associated uncertainty) increased noticeably after the first calibration and detection limit determination.

Table 5
Concentration of lead in calcium supplements (µg g^{-1}) with 95% confidence intervals

	CaMgZn supplement	Oyster shell calcium supplement
Graphite furnace		
Method 1:	0.54 ± 0.05	0.68 ± 0.05
	0.51 ± 0.06	0.58 ± 0.05
Method 2:	0.46 ± 0.11	0.63 ± 0.06
	0.54 ± 0.09	0.69 ± 0.08
Method 3:	0.61 ± 0.06	0.71 ± 0.05
	0.57 ± 0.12	0.67 ± 0.06
Hydride generation		
	0.57 ± 0.11	0.66 ± 0.04
	0.56 ± 0.05	0.66 ± 0.04
Spike concentration	0.46	0.48
Sample + spike	0.97 ± 0.02	1.10 ± 0.02
% Recovery	89 ± 9	92 ± 9

The results of the analyses of the two materials by the four procedures are shown in Table 5. The 95% confidence intervals were calculated from the equations given in Ref. [26] and reflect the uncertainty due to the least squares calibration procedure. Visual inspection of the overlaps of the 95% confidence intervals shows: (a) that there was no significant difference between the results of the previously published ETAAS methods for the two sample materials; (b) the oyster shell tablet material contained a significantly higher concentration of lead than did the Ca/Mg/Zn material; and (c) the results for the FI-HG-ETAAS method were not significantly different from those of the ETAAS methods. The percent recoveries were $89 \pm 9\%$ for the Ca/Mg/Zn material and $92 \pm 9\%$ for the oyster shell material. The lead contents are in line with previously determined values for these materials [3,5,8,11].

It is concluded that lead in calcium supplements may be accurately determined by a FI-HG method in which the lead hydride, generated from a solution containing ferricyanide as oxidant, is trapped on the interior of a graphite furnace atomizer. The detection limit of 0.12 µg l^{-1} is adequate for the analyses of the tablets used in this study as this corresponds to 3 ng of lead in the sample mass (0.5 g) taken for analysis, i.e. 0.006 µg g^{-1}. The lowest concentration in commercially available supplements appears to be about 0.1 µg g^{-1} and thus the HG procedure, even with the higher detection limit, due to the lead contamination of the ferricyanide, has suitable performance characteristics. The high concentration of calcium (or of any other matrix component) did not produce a depressive effect in the FI method and it was possible to use standards without matrix matching. The FI-HG method, in which the matrix is not transferred to the interior of the graphite tube will be more robust in a routine analytical situation than one in which the dissolved sample is introduced directly into the furnace. As no significant differences were observed between the methods used, the lengthy heating of the sample in a muffle furnace could be omitted and a rapid and simple sample dissolution procedure used. Siitonen and

Thompson concluded [5] that similar results were obtained from a nitric acid microwave digestion and from a dry ash digestion procedure. As their microwave digestion procedure did not include the addition of hydrogen peroxide, it might be possible to omit this step also. However Wolf [3], who used a hot-plate, nitric and hydrochloric acid digestion, obtained low results for the lead in NIST SRM 1486 (bone meal) though pre- and post-digestion spike recoveries were 'excellent'. Better performance, in terms of detection limit, would be obtained if the concentration of lead in the ferricyanide could be decreased.

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