

Determination of lead in sediments and sewage sludge by on-line hydride-generation axial-view inductively-coupled plasma optical-emission spectrometry using slurry sampling

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Abstract Among the “traditional” hydride-forming elements, lead is probably the most difficult, and its determination in this form has rarely been reported in the literature. In this paper a simple and rapid method, axial-view inductively-coupled plasma optical-emission spectrometry using on-line hydride generation (HG–ICP–OES) from samples prepared as slurry, is proposed for determination of lead in environmental samples. The samples (20–50 mg, particle size $\leq 120 \mu\text{m}$) were treated with 1 mL aqua regia in a 40-kHz ultrasonic bath for 60 min. The slurry was diluted to a final volume of 50 mL with a 10% *m/v* solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The concentrations of NaBH_4 , tartaric acid, and $(\text{NH}_4)_2\text{S}_2\text{O}_8$, used for on-line plumbane generation were optimized by means of a complete factorial analysis applied to an aqueous standard solution and to the slurry of a sediment certified reference material (CRM). External calibration against aqueous standards in the concentration range 10–100 $\mu\text{g L}^{-1}$ was used for analysis of six CRM—three marine sediments, one river sediment, and two sewage sludges. Analysis of the filtered slurry showed that Pb was only partially extracted into the liquid phase. Several major concomitants tested did not affect the Pb

signal. The detection limit ($3s$, $n=10$) for 20 mg sample in a final volume of 50 mL was $5.0 \mu\text{g g}^{-1}$. Tin was the only other hydride-forming analyte that could be determined satisfactorily with Pb; for tin the detection limit was $1.0 \mu\text{g g}^{-1}$. The values obtained for Pb and Sn were not significantly different from the certified concentrations, according to the *t*-test at the 95% confidence level. Nine river sediments collected locally were also analyzed and the concentrations were in agreement with results obtained after total digestion.

Keywords Pb · ICP–OES · Slurry sampling · Hydride generation · Sludge and sediments

Introduction

The first paper on the application of hydride generation (HG) in atomic spectrometry was by Holak [1] in 1969; arsine was generated by adding zinc to the acidified test solution. Introduction of sodium tetrahydroborate as reducing agent in 1972 [2] increased to eight the number of elements that could be determined by use of this technique; lead is the last to be added to the list, in 1974 [3]. In contrast with the other hydride-forming elements, lead forms an instable compound, plumbane (PbH_4), which decomposes very quickly, resulting in poor hydride-generation efficiency. Lead therefore requires the presence of strong oxidizing agents and a complexing agent for reduction to PbH_4 [4–8]. This explains the relatively small number of publications about HG for this element. Despite the drastic conditions required, however, HG results in good detection limits for lead, and interference is avoided by separation of the analyte from the matrix when

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inductively-coupled plasma optical-emission spectrometry (ICP–OES) is used as the analytical technique [4–6, 9–12]. There is, however, no information in the literature about the determination of Pb by HG–ICP–OES using an axial-view instrument configuration.

One problem with analysis of volatile elements, for example Pb, is the sample-preparation step. High risks of sample contamination and analyte loss should be considered in the preparation of solid samples that require drastic conditions to be brought into solution, for example long preparation time and large amounts of chemicals; such work should be performed by an experienced analyst [13]. An alternative method, much faster and simpler, with lower risks, is slurry sampling, which has been used with success in several applications [13, 14]. Hydride generation combined with slurry sampling for atomic spectrometric techniques, for example atomic-absorption spectrometry (AAS), atomic-fluorescence spectrometry (AFS), ICP–OES, and ICP mass spectrometry (ICP–MS), has become a powerful analytical tool for determination of hydride-forming elements, especially in environmental and food samples [14–24].

Hydride generation, in comparison with conventional sample introduction in solution that uses pneumatic nebulization, in which only 1–3% of the sample is, in fact, analyzed, has the great advantage of analyte introduction efficiency close to 100%. In addition, in HG the vapor containing the analytes is separated from the matrix, usually eliminating spectral interferences completely, and non-spectral interferences in solution are limited to few exceptional cases. In this way, accuracy and low detection limits are obtained when HG is used. Speciation studies are also possible, because HG depends on the oxidation state of the analyte [25, 26].

Slurries are usually prepared in acid medium, to enable partial or total extraction of the analyte into the aqueous phase, where HG occurs after addition of a reducing agent. An advantage of slurry sample presentation, in comparison with the direct solid sampling, is that the concentration of the slurry can easily be varied in accordance with the analyte content of the sample [14, 27, 28]. Sample-introduction systems conventionally used for liquid samples, for example autosamplers, can also be used for slurries.

Few studies of HG of Pb from slurries have been reported in the literature, and these are restricted to use of AAS for detection. Madrid et al. [29–31] determined Pb in foodstuffs and biological samples and compared three oxidizing media for generation of plumbane, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ – HNO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ –lactic acid, and H_2O_2 – HNO_3 . The powdered samples were suspended in Triton X-100 and shaken with blown zirconia spheres until a slurry was formed. Of the three oxidizing media tested, use of $\text{K}_2\text{Cr}_2\text{O}_7$ –lactic

acid led to the best results for slurry samples of vegetables and fish and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ – HNO_3 led to good results for slurry samples of vegetables.

The objective of this work was to establish the optimum conditions for determination of Pb in sediments and sewage sludge by use of slurry-sampling HG–ICP–OES and an axial-view spectrometer. The possibility of determining other hydride-forming elements using the conditions optimized for Pb were investigated, taking advantage of the multielement capacity of the technique.

Experimental

Instrumentation

All measurements were performed with a Vista Pro (Varian, Mulgrave, Australia) simultaneous axial-view ICP–OES spectrometer coupled to a model VGA-76P on-line continuous chemical vapor-generation (CVG) system, also from Varian. The instrumental set-up and the operating conditions for the ICP were the same as described in previous publications [20–22], except that the sample-slurry tubing was 0.56 mm i.d. (Elkay No LK116-0533). The analytical line at 220.353 nm was chosen for determination of Pb. The experimental conditions for CVG are listed in Table 1. Argon of purity 99.996% from White Martins (São Paulo, Brazil) was used. The CVG system had a constant rotation, 50 rpm, combined with the same peristaltic pump rotation that controls the phase separator drain, to avoid pressure differences and, eventually, plasma extinction. An ultrasonic bath from Odontobrás (São Paulo, Brazil), model 1440 DA (40 kHz) was used to sonicate the slurries.

Reagents and materials

All chemicals were of analytical grade, unless otherwise specified. Water (resistivity 18.2 $\text{M}\Omega\text{ cm}$) was de-ionized by use of a Milli-Q system (Millipore, Bedford, MA, USA). The reagents used were: 65% (v/v) HNO_3 (Suprapur; Merck, Darmstadt, Germany; #1.00441.1000), 30% (v/v) HCl (Suprapur; Merck; #1.00318.0250), tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ (Mallinckrodt, Phillipsburg, NJ, USA; #2312),

Table 1 Conditions used for HG

Conditions	
Sample flow rate	3.0 mL min^{-1}
NaBH_4 and tartaric acid flow rates	2.5 mL min^{-1}
Argon flow rate	120 mL min^{-1}
NaBH_4 concentration	2.5% (m/v) (in 0.4% m/v NaOH)
Tartaric acid concentration	0.5% (m/v)

ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Mallinckrodt J.T. Baker, Phillipsburg, NJ, USA; #0762-01), 40% (v/v) HF (Merck #1.00338.1000), 70–72% (v/v) HClO_4 (Merck #1.00519.1000), Antifoam A (Sigma #5758), 0.45 μm cellulose filter (Millipore, Billerica, MA, USA; #HAWP04700) with a vacuum filtration system (Millipore; Sterifil 47 mm; #XX11.047.00). Standard solutions containing 1000 mg L^{-1} Pb(II) (Merck #1.19776.0500) and Sn (IV) (Merck #9929) were used. Solutions of NaBH_4 (Merck #1.06371.0100) of different concentrations (1.5%, 2.0%, and 2.5% *m/v*) in 0.4% (*m/v*) NaOH (Merck #1.06498.1000) were prepared by dissolution in water.

The certified reference materials (CRM) analyzed were: HISS-1 Marine Sediment and PACS-2 Marine Sediment (National Research Council Canada, NRCC, Ottawa, Ontario, Canada); CRM 146R, Sewage Sludge from Industrial Origin and CRM-144R, Sewage Sludge from Domestic Origin (European Community Bureau of Reference, BCR, Brussels, Belgium); RS-3 River Sediment from a round robin test [32] and SRM 2702 Marine Sediment (National Institute of Standards and Technology, NIST, Gaithersburg, MD, USA). Nine river sediments were collected at different points of the Iguaçú River bay (Curitiba, Paraná, Brazil).

Slurry preparation procedure

In accordance with previous experience [20–22], the certified materials were used in their original particle size ($\leq 120 \mu\text{m}$). The river sediment samples were dried at room temperature, ground in an agate mortar, and passed through a 149- μm sieve [33]. Each sample (20–50 mg) was weighed and placed in a 50-mL volumetric flask, and 1 mL of aqua regia was added. The mixture was placed in an ultrasonic bath for 60 min and the volume was made up with 10% (*m/v*) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution. The aqua regia concentration in the final slurry was therefore 2% (*v/v*). Before measurement one drop of antifoaming agent was added to the slurry and it was vigorously stirred manually for 30 s. Calibration was performed by use of aqueous standard solutions in the concentration range 10–100 $\mu\text{g L}^{-1}$ Pb(II), prepared in the same media as the slurries. A blank solution was run in parallel with the determinations and its Pb content taken into consideration.

Acid dissolution for comparison

For determination of total Pb in the locally collected river sediment, approximately 0.5 g sample was weighed, moistened with deionized water in a 50-mL Teflon beaker, mixed with 5 mL of concentrated HNO_3 , and the solution was evaporated to a small volume. Concentrated HNO_3 (2.5 mL), 2.5 mL 70–72% (v/v) HClO_4 , and 5 mL HF were

added and heated until perchlorate fumes were observed. After 30 min of fuming 5 mL 50% (v/v) HCl was added, and the mixture was boiled for 10 min and then cooled and diluted to 50 mL with de-ionized water [34]. The final solution was used for the determination of Pb by conventional nebulization ICP–OES.

Statistical analysis

The statistical program Statgraphics Plus 5.0 (Statgraphics, SC, USA) was used for optimization of the concentrations of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, tartaric acid, and NaBH_4 used for HG.

Results and discussion

Optimization

Three sets of conditions for HG were optimized by means of a complete factorial analysis [35] to obtain the best sensitivity for the Pb determination and the best repeatability in plumbane generation. The conditions examined were:

1. NaBH_4 (1.5, 2.0, and 2.5% *m/v*);
2. tartaric acid (0.5, 1.0, and 1.5% *m/v*); and
3. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (5.0, 7.5 and 10.0% (*m/v*) in de-ionized water, in 2% (v/v) HNO_3 , or in 2% (v/v) aqua regia)

using both an aqueous standard solution containing 50 $\mu\text{g L}^{-1}$ Pb(II) and a slurry of SRM 2702 (20 mg in 50 mL) containing approximately 53 $\mu\text{g L}^{-1}$ Pb. After establishing the matrix of the experimental design, the emission signal intensities in each run were obtained for the lowest, highest, and central points of the three factors studied. The standardized ($P=95\%$) bar plot for the main effects and combinations were obtained (not shown) so the relative importance of the effects could be compared. The minimum *t*-value at a 95% confidence level was 3.2 for the experiment. A result was regarded as significant when its value was $\geq \pm t$ [35, 36].

The sample slurry and the standard solution in water (no acid) containing $(\text{NH}_4)_2\text{S}_2\text{O}_8$ resulted in a vigorous and turbulent reaction with NaBH_4 , causing occasional extinction of the plasma. This set of conditions was therefore not considered further. The system was more stable when the sample slurry and the aqueous standard contained 2% (v/v) HNO_3 in addition to $(\text{NH}_4)_2\text{S}_2\text{O}_8$. No positive effect of reagent concentration was found for the standard solution. The effect of the NaBH_4 was positive and significant for the sample slurry, however. This possibility also was not considered in further investigations.

Similar behavior of the sample slurry and of the aqueous standard was found when aqua regia was used instead of nitric acid. The effect of aqua regia concentration was

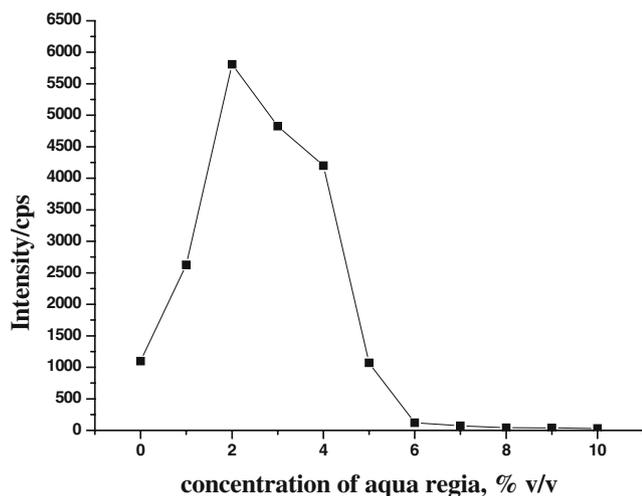


Fig. 1 Effect of aqua regia concentration on Pb signal intensity for an aqueous standard solution containing $50 \mu\text{g L}^{-1}$ Pb(II) in 10% (*m/v*) $(\text{NH}_4)_2\text{S}_2\text{O}_8$

checked separately by varying its concentration while the other reagent concentrations were kept constant. As shown in Fig. 1, the signal intensity was maximum for a concentration of 2%, decreasing substantially for higher and lower aqua regia concentrations. No explanation was found for this behavior. The $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentration had a positive and significant effect on the Pb signal for both slurry and aqueous standard, and the plasma was stable. NaBH_4 concentration had a positive, but not significant, effect. Although the tartaric acid concentration was not significant and had a negative effect for both the slurry and the aqueous standard, it was found that the Pb signal intensity was very low if tartaric acid was not present, showing the importance of this reagent, probably as a result of complexation of the metastable Pb(IV) [5–8]. With the objective of maximum sensitivity and plasma stability the medium selected was: 10% (*m/v*) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 2% (*v/v*) aqua regia and a low concentration (0.5% *m/v*) of tartaric acid. The NaBH_4 concentration adopted was 2.5% (*m/v*). The similar behavior of the standard and of the sample slurry in the presence of aqua regia indicates the possibility

Table 2 Figures of merit

	Pb	Sn
Correlation coefficient	0.999	0.999
Slope, ($\text{L } \mu\text{g}^{-1} \text{ s}^{-1}$)	76	79
LOD ($\mu\text{g g}^{-1}$) ^a	5.0	1.0

Calibration plots were obtained by use of aqueous standard solutions in 10% (*m/v*) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and 2% (*v/v*) aqua regia, for Pb(II) in the concentration range 10–100 $\mu\text{g L}^{-1}$ and for Sn(IV) in the concentration range 5–100 $\mu\text{g L}^{-1}$

^a LOD for 20 mg solid sample in a final slurry volume of 50 mL; 3s and $n=10$

Table 3 Concentrations ($\mu\text{g g}^{-1}$; $n=3$) of Pb and Sn in the CRM slurries and filtrates

Sample	Analyte	Certified	Filtrate	Slurry
SRM 2702	Pb	132.8±1.1	107.4±3.1	134.3±2.5
	Sn	31.6±2.4	30.5±0.7	29.6±1.7
HISS-1	Pb	3.13±0.40	2.8±0.4	3.4±0.3
	Sn	(0.11) ^a	0.13±0.02	0.13±0.02
PACS-2	Pb	183±8	135±6	180±5
	Sn	19.8±2.5	19.1±1.6	19.1±1.0
RS-3	Pb	129.0±1.7	107.6±2.5	130.9±2.7
	Sn	13.00±0.70	12.7±0.5	12.5±0.7
CRM 144R	Pb	106±4	77±4	97±5
	Sn	– ^b	11.8±0.5	11.5±0.5
CRM 146R	Pb	609±14	389±11	601±16
	Sn	– ^b	52±1	50±3
Pb	RSD range (%)		2–14	2–8
	Recovery range (%)		65–82	92–109
Sn	RSD range (%)		2–15	5–15
	Recovery range (%)		97–118	94–118

^a Information value only

^b Not certified

of external calibration by use of aqueous standard solutions in the same medium as the slurries.

Figures of merit

The analytical figures of merit are shown in Table 2. The detection limits for the samples were calculated as three times the standard deviation of results from ten measurements of the blank divided by the slope of the calibration plot, on the basis of 20 mg solid sample in a final volume of 50 mL. Because of to the strong oxidizing conditions of

Table 4 Concentrations ($\mu\text{g g}^{-1}$; $n=3$) of Pb and Sn, measured by use of slurry sampling and after total digestion, in river sediment samples collected in the Rio Iguaçú, Curitiba, Brazil

Sample	Slurry		Total digestion	
	Pb	Sn	Pb	Sn
Reservatório Iraí	29.9±3.2	3.6±0.3	28.3±0.9	<5.0 ^a
Rio Iraí (Pinhais a)	32.4±3.2	3.1±0.1	34.8±0.1	<5.0
Rio Iraí (Pinhais b)	30.0±3.4	2.8±0.3	28.8±0.7	<5.0
Rio Timbú	20.7±1.9	3.0±0.1	18.4±0.5	<5.0
Rio Iguaçú (Zoo)	53.3±1.2	7.5±0.1	50.9±0.6	7.7±0.6
Rio Iguaçú (Araucária)	29.5±0.8	4.2±0.2	28.6±0.2	<5.0
Rio Canguiri	22.6±0.9	3.3±0.1	21.5±0.4	<5.0
Rio Curralinho	27.8±0.8	4.9±0.1	26.8±0.3	5.2±0.1
Rio Cercado	18.9±2.0	3.1±0.2	19.8±0.2	<5.0
RSD range (%)	2–11	1–11	0.3–3	2–8

^a <5.0 indicates not detectable at a quantification limit of 5.0 $\mu\text{g g}^{-1}$ for conventional nebulization, and 0.5 g sample in a final volume of 50 mL

the medium, formation of the hydrides of arsenic and antimony and from the cold vapor of mercury was not efficient, resulting in poor detection limits, in comparison with values recently obtained in our laboratory [20–22]. For this reason, analysis of these analytes was not included in this work. The conditions optimized for Pb apparently favored formation of Sn(IV), however, resulting in highly efficient formation of SnH₄ and enabling determination of this together with Pb.

Interfering ions

The effect of several concomitant ions on generation of PbH₄ was studied. Aqueous standard solutions containing 50 µg L⁻¹ Pb(II) in 2% (v/v) aqua regia and 10.0% (m/v) (NH₄)₂S₂O₈ were analyzed in the presence of increasing concentrations of the ions. The ions investigated were Mn, Zn, and Cu up to 1.0 mg L⁻¹ (mg kg⁻¹ levels in the sediment, on the basis of 20 mg sample in 50 mL slurry, and total extraction of the ion into the aqueous phase), and K, Al, Fe, and Si up to 500 mg L⁻¹ (percentage (m/m) levels in the sediment, again on the basis of 20 mg sample in 50 mL slurry). In the concentration ranges investigated none of the ions had a significant effect on Pb signal intensity.

Analytical application

The optimized procedure was applied to the analysis of six certified environmental samples, using external calibration with aqueous standard solutions in the same medium as the slurry. To investigate the efficiency of extraction of the analyte into the aqueous phase the slurries were also filtered through 0.45-µm cellulose membrane filters, under vacuum. The slurries and the filtrates were analyzed using the same calibration plots; the analyte concentrations are shown in Table 3. The concentrations found for Pb and Sn in the slurries are in agreement with the certified values, according to the *t*-test at a confidence level of 95%, demonstrating the accuracy of the proposed method. Relative standard deviations (RSD) were below 15%, showing precision was adequate for slurry analysis. For tin, the concentrations measured in the slurry and in the filtrate are also in agreement, in accordance with the same criterion, indicating complete extraction of this analyte into the aqueous phase. For lead, however, recoveries in the filtrate were in the range of 65–82% only, indicating that part of the Pb is retained by the solid particles of the slurry, and only released during HG.

The procedure was applied to analysis of real river sediment samples, which were also totally digested and analyzed by ICP–OES, using conventional nebulization. The results in Table 4 show that the concentrations obtained

by the two procedures were in agreement, at a confidence level of 95% (paired *t*-test). As expected, the relative standard deviations were lower for the digested samples, especially for Pb, indicating better precision.

Conclusions

A simple and rapid method is proposed for determination of Pb in sediments and sewage sludges. Sample pretreatment is simplified by using slurries instead of digested samples, which would increase the risks of contamination and/or analyte loss. Calibration against aqueous standard solutions leads to accurate and precise results. Tin could be determined at the same time as lead. Detection limits in the sample are at µg g⁻¹ levels. Lead is partially retained by the solid particles of the slurry, being liberated only during HG.

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