

Determination of Trace Lead in Environmental Samples by Flow Injection and Hydride Generation Atomic Absorption Spectrometry

JUNFENG LIANG*[†], XIN ZHANG[‡], YUANQING ZHOU[‡] and QIUFEN HU[‡]

Kunming Institute of Botany, Chinese Academy of Sciences

Kunming-650204, P.R. China

Fax: (86)(871)8315280; E-mail: jfliang2000@163.com

A new method for the determination of lead is proposed using flow injection and hydride generation atomic absorption spectrometry (HG-AAS). For this studies, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is used as the oxidizing agent, 100 μL of sample and 100 μL of 3.0 % (m/v) NaBH_4 are simultaneously injected into two carrier streams, 0.5 % (m/v) tartaric acid and deionized water, respectively. A sampling rate of about 150 determinations per hour was achieved, requiring 15 mL of NaBH_4 and a waste generation of 250 mL. The detection limit of $0.3 \mu\text{g L}^{-1}$ for Pb was achieved and the relative standard deviation of 2.1 % for $10 \mu\text{g L}^{-1}$ Pb was obtained. The method was shown to be satisfactory for determination of traces of Pb in food, water and soil samples.

Key Words: Lead, Environmental samples, Flow-injection hydride generation, Atomic absorption spectrometry.

INTRODUCTION

Lead is an important element, both for its extensive use and high toxicity. The determination of traces of lead in a variety of environmental samples is of great importance^{1,2}. Several instruments, such as spectrofluorimetry, X-ray fluorescence spectrometry, neutron activation analysis, atomic absorption spectrometry, chemiluminescence and electrochemical analysis have widely been applied the determination of lead³⁻⁵. However, the determination of lead requires procedures that are sufficiently sensitive for detection at the $\mu\text{g L}^{-1}$ level. Traditionally, electrothermal atomic absorption spectrometry (ETAAS) has been applied in such cases, but, the direct determination of lead in complex matrices by ETAAS is usually difficult owing to matrix interference and separation procedures are often needed before the ETAAS determination^{6,7}.

[†]Research Institute of Tropical Forestry, Chinese Academy of Forestry, Guangzhou-510520, P.R. China.

[‡]Department of Chemistry, Yuxi Teacher's College, Yuxi-653100, P.R. China.

In this study, a flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS) system was employed for lead determination. The main characteristics of this flow injection system, such as high sampling rate, good accuracy, precision and sensitivity, are maintained. The method was applied to the determination of lead in food, water and soil samples and good results were obtained between the certified values and reference method.

EXPERIMENTAL

A microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China) was used for sample preparation.

For measurements, an atomic absorption spectrometer, SpectrAA-220 Varian (Victoria, Australia) was used. The determinations were carried out at 217 nm, bandpass of 1.0 nm and lamp current of 10 mA.

For atomization of lead, an electrothermic atomizer T-shaped quartz tube was used, which was cleaned weekly with acid⁸. One of tubes was the atomization chamber (170 × 8 mm i.d.) and other serving as the inlet of gases. The atomization cell was aligned on the optical axis of the spectrometer. The temperature was obtained with Ni-Cr resistance connected an Autc Model 2407 voltage regulator. For minimize the hot exchange with the environment, the atomizer was wrapped with ceramic cape.

In the flow system, oxidation of lead by ammonium persulphate in medium acid (0.5 % m/v tartaric acid) occurs into a reaction coil B1 (40 cm) and the reduction of lead by sodium tetrahydroborate occurs into a reaction coil B2 (20 cm) (Fig. 1). After of the second confluence point (P2), the reaction mixture reaches the gas-liquid separator⁹. At this point, the liquid phase was separated from the gaseous phase, which was a mixture of hydrogen and lead hydride. The liquid phase flows to a free-running drain while the gaseous phase (lead hydride + hydrogen) was purged by nitrogen (50 mL min⁻¹) into the atomization cell for determination by atomic absorption spectrometry.

The flow injection manifold is shown in Fig. 1. Polyethylene tubing (i.d. = 0.8 mm) was used for the loops, transmission line and coils. All solutions and the carrier were pumped using a Gilson Model Minipuls 3 peristaltic pump and Tygon pumping tubes. A flow injection system was operated in the merging zones configuration where sample and reagent were simultaneously injected into two carrier streams, tartaric acid and de-ionized water, respectively. The most attractive analytical characteristic of such methods is low reagent consumption. The reagent is consumed only in the presence of the sample and can otherwise be recovered continuously. A double proportional injector is used for this purpose¹⁰. The deionized water (resistivity 18.0 MΩ.cm), 0.5 % (m/v) tartaric acid

and 8.0 % (m/v) ammonium persulphate solutions were pumped at 1.4 mL min⁻¹. The utilization of the small reagent volumes (100 µL) minimizes the consumption of NaBH₄.

All reagents used were of analytical grade and deionized water was used for preparation solutions. A lead standard solution [1000 mg L⁻¹ Pb in 5 % (v/v) HNO₃] was obtained from the Chinese Standard Material Centre and the working solutions were prepared by diluted this solution with deionized water. A 3.0 % (m/v) NaBH₄ solution was prepared immediately before use by dissolving 3.0 g of the NaBH₄ in 0.05 mol L⁻¹ KOH. An 8.0% (m/v) (NH₄)₂S₂O₈ solution was prepared immediately before use by dissolving 8.0 g of the (NH₄)₂S₂O₈ in 100 mL of water. A 0.5 % (m/v) tartaric acid solution was prepared by dissolving 0.5 g of the tartaric acid in 100 mL of water.

Samples preparation

For the fresh (tap water from the Kunming and water from Panglong River, Kunming), the water samples were acidified with concentrated hydrochloric acid to obtain a pH near 1.0 to minimize adsorption of trace elements on the bottle walls and microorganisms proliferation.

For soil samples, A 100 mg of sample was weighed into a 25 mL of teflon high-pressure microwave acid-digestion bomb. To which, 2.5 mL of aqua regia was added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven. The system was operated at full power for 25 min. The digest was evaporated to near dryness. After cooling, the residue was dissolved with 10 mL of 5 % of nitric acid, then transferred into a 50 mL calibrated flask quantitatively and diluted to mark with 1 % of nitric acid.

For food samples, a 250 mg of samples were weighed accurately into the teflon high-pressure microwave acid-digestion bomb. 2 mL of concentrated nitric acid and 2 mL 30 % hydrogen peroxide were added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven. The system was operated at full power for 8.0 min. The digest was evaporated to near dryness. The residue was dissolved with 5 mL of 1 % of nitric acid, then transferred into a 10 mL calibrated flask quantitatively and diluted to mark with 10 mL of 1 % of nitric acid.

RESULTS AND DISCUSSION

The experimental conditions for determination of lead were established employing the manifold described in Fig. 1. The literature shows that there are difficulties with lead hydride formation due low yield and low stability of the volatile hydride¹¹. As mentioned, lead hydride generation requires the addition of an oxidizing agent. The increased efficiency of lead hydride generation in the presence of oxidizing agents has been attributed

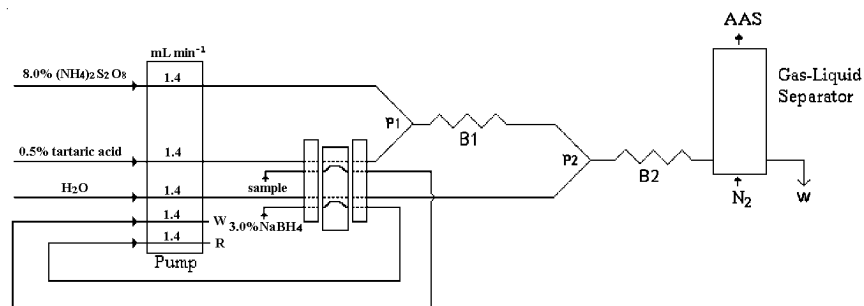


Fig. 1. Schematic diagram of the FI-HG-AAS system used. P1 and P2 are confluence points. B1 and B2 are reaction coils with lengths of 40 and 20 cm, respectively. W: Waste, R: Recycled solution, AAS: Atomic Absorption Spectrometric

to the formation of meta-stable Pb(IV) compounds before the formation of lead hydride in the reaction of lead with NaBH_4 ¹². In this work, ammonium persulphate was used for this purpose. The nature of acid-oxidant mixture [tartaric acid- $(\text{NH}_4)_2\text{S}_2\text{O}_8$] employed in this work is not reported in literature. The following hydride generation parameters were evaluated: the time necessary to the oxidation reaction (lead with ammonium persulphate) and reduction reaction (lead with NaBH_4), the oxidizing agent concentration, the NaBH_4 and tartaric acid concentrations, carrier flow rate, stripping/carrier gas flow rate, sample and reagent volumes and atomization temperature. The sample and NaBH_4 were injected in tartaric acid and water carried stream, respectively, using merging zones system. Every parameter was evaluated and for such purpose solutions of 0.1, 0.5 and 1.0 mg L^{-1} of Pb were prepared. The effect of varying the tartaric acid concentration on the signal analytical from Pb was evaluated for 0.25, 0.5, 1.0, 1.5, 2.0 and 3.0 % (m/v) tartaric acid. As can be seen in Fig. 2, the signals related to Pb increase up to a concentration of 0.5 % (m/v) tartaric acid. In addition, the response obtained from higher tartaric acid concentration was lower. Possibly, this is due to the formation of stable compounds of lead with tartaric acid. The 0.5 % (m/v) tartaric acid solution was chosen for further measurements.

The NaBH_4 concentration is an important parameter for lead hydride generation because this is formed in the presence of hydrogen generated by NaBH_4 in an acidic medium. Over there, H_2 acts as stripping gas. As H_2 amount depends on NaBH_4 and tartaric acid volumes, flow rates and concentrations, all these parameters should be evaluated. The Fig. 3 shows that the hydride generation from lead exhibits higher efficiency increasing NaBH_4 concentration. Therefore, a NaBH_4 higher than 1.0 % (m/v) was required to obtain complete lead hydride generation from lead. A 4.0 %

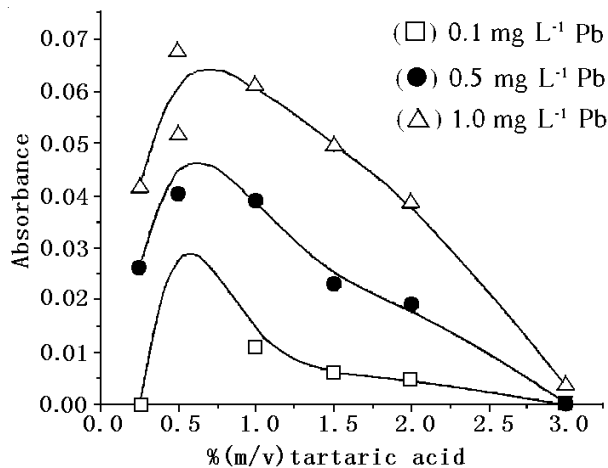


Fig. 2. Effect of the tartaric acid concentration on the responses for Pb solutions. The concentration of NaBH₄ and ammonium persulphate were 1.0 % (m/v) and 8.0 % (m/v), respectively

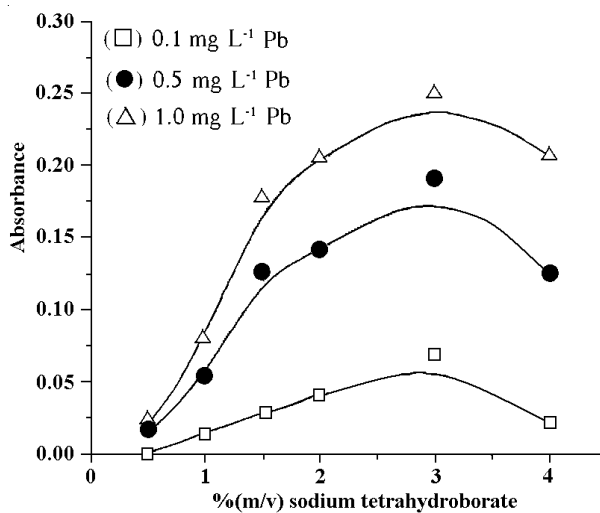


Fig. 3. Effect of NaBH₄ concentration on the lead hydride generation. The tartaric acid and ammonium persulphate concentrations were 0.5 % (m/v) and 8.0 % (m/v), respectively

(m/v) NaBH₄ concentration is not recommended because it shows a disturbance of the hydride generator due to high H₂ amounts. Thus, a NaBH₄ concentration of 3.0 % (m/v) was selected in order to obtain the best analytical performance. The flow injection system allows a lower amount of NaBH₄ to be used (100 μL), which represents considerable savings in the cost of analysis.

Fig. 4 shows results obtained using different $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentrations. The presence of oxidizing agents, as $(\text{NH}_4)_2\text{S}_2\text{O}_8$, increases the efficiency of lead hydride generation. When the oxidizing agent was increased, higher results were obtained. High blanks were obtained for higher oxidizing concentrations. The 8.0 % (m/v) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ concentration was chosen as being a selective medium and provide adequate lead hydride generation.

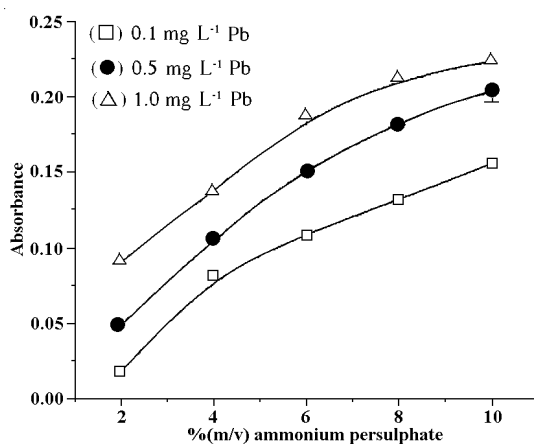


Fig. 4. Effect of the oxidizing concentration on the responses for Pb solutions. The concentration of NaBH_4 and tartaric acid were 3.0 % (m/v) and 0.5 % (m/v), respectively

The time necessary to oxidization reaction and lead hydride generation was evaluated using reaction coils of different lengths B1 (20, 30, 40 and 50 cm) and B2 (20, 30, 40 and 50 cm), respectively (Fig. 1). Results show that a reaction coil length of 40 cm is necessary to obtain oxidizing of Pb and a reaction coil length of 20 cm is necessary to obtain lead hydride generation. The analytical signal was not significantly affected by the length of B1 coil. However, for B2, it was markedly affected by the coil length. Then, for higher sensitivities the reaction coil lengths of 40 cm and 20 cm were preferred.

The influence of sample and reagent volumes on the efficiency of lead evolution was assessed over the range 50-150 μL . The sensitivity increased with increasing sample and reagent volumes. Higher volumes were not used in present method because, in this case, there is a large time for the analytical signal to return the base line and to maintain the compromise with the analytical frequency, sample and reagent volumes of 100 μL were used for further experiments.

In this flow injection system, the sample and NaBH_4 were injected in tartaric acid and water carried stream, respectively. The efficiency of the

lead hydride generation was studied for different flow rates of 0.5 % (m/v) tartaric acid and de-ionized water. Results indicate an increase in absorbance signals with an increase in flow rate up to 1.4 mL min^{-1} . For higher flow rates, the signal decreased. In this case, the sample and the reagent did not have sufficient time for mixture. Therefore, flow rates of 1.4 mL min^{-1} was used.

The carrier gas flow rate (N_2) was assessed over the range $25\text{-}100 \text{ mL min}^{-1}$. The N_2 always dilute the hydride, so, N_2 gas flow needs to be as low as possible. In lower flow rate N_2 , the separation gaseous phase and liquid phase was irregular and hydride was transport to the atomizer not effective for lower flow 50 mL min^{-1} . Hence, a 50 mL min^{-1} N_2 flow was selected as most convenient.

For each element forming hydride, there is an adequate temperature. The atomization temperature for lead was evaluated. It was observed that in the region below $800 \text{ }^\circ\text{C}$ only partial atomization occurred. The maximum sensitivity was achieved in $950 \text{ }^\circ\text{C}$.

Interference effects

The effects of representative potential interference that are known to interfere in the hydride process were tested. Sb(III), As(III), Se(IV), Mn(II), Fe(III), Cu(II), Ni(II) and Al(III) were evaluated in proposed method. To investigate the extent of their effects on the determination of lead, 0.1 mg L^{-1} of Pb(II) were spiked with increasing levels of these potential interferents. A serious signal depression was observed for Sb(III), As(III), Se(IV) and Mn(II) at a ten-fold excess (100 % signal depression). Interference was also caused by Al(III), Fe(III), Cu(II) and Ni(II) at a 10-fold higher level (90, 90, 70 and 40 % signal depression, respectively).

Madrid *et al.*¹³ observed that hydride forming elements (Se, As and Sb) and transition metals (Cu, Ni, Zn and Fe) caused serious interferences for lead hydride generation. However, it was possible to find a concentration range in which these elements did not affect the signal. According to Madrid *et al.*¹³ the magnitude of the effects were strongly dependent on the medium, oxidizing agent and atomization system used.

Analytical figures of merit

Under the best conditions for direct generation of lead hydride, the relative standard deviation of ten replicate determinations of $10 \text{ } \mu\text{g L}^{-1}$ lead was 2.1 %. The typical mathematical equation of the calibration curve obtained for lead standard solutions was $A = 0.0032 C_{\text{Pb}} (\text{ } \mu\text{g L}^{-1}) + 0.0148$, $r = 0.9993$. The linearity was observed for Pb(II) at a 0.5 mg L^{-1} .

The detection limit based on the $3\sigma/m$, where σ is the standard deviation of 10 measurements of a blank and m is the slope of the calibration graphs, was $0.3\ \mu\text{g L}^{-1}$ for Pb and the quantification limit ($10\sigma/m$) was $1.0\ \mu\text{g L}^{-1}$. The sensitivity achieved for proposed method is adequate for lead determination in environmental samples.

The literature shows that a detection limit of $0.5\ \mu\text{g L}^{-1}$ was obtained for generation of Pb hydride with *in situ* trapping in the graphite furnace^{14,15}. However, high blanks were found. The in-atomizer trapping procedure, which concentrate the lead in the atomizer prior to atomization, was reported by Tyson¹⁶. In this procedure, a greater sensitivity than that of direct introduction of the sample solution into the furnace, as a much larger volume of sample can be processed. The detection limit was $0.12\ \mu\text{g L}^{-1}$ for a 1000 μL injection volume. Li *et al.*⁷ also reported on the results of a procedure in which quantification was by ICP-MS. The detection limit of $0.007\ \mu\text{g L}^{-1}$ for Pb was achieved. Even being more attractive because of its low detection limits, the ICP-MS is a more expensive technique. Using GH-AAS technique, Madrid *et al.*¹¹ reported a detection limit of $1.5\ \mu\text{g L}^{-1}$ Pb and a sampling rate of about 180 determinations/h was achieved.

The proposed method was applied to the quantification of lead in food samples (Table-1), water and soil samples (Table-2). The accuracy of the method was evaluated by analyzing certified food reference material, GBW08426 and GBW08505. An ICP-MS method was used as reference method for water and soil samples. These results are in good agreement with the certified values and values of reference method.

TABLE-1
DETERMINATION OF LEAD IN CERTIFIED
STANDARD FOOD SAMPLES

Samples	Standard value ($\mu\text{g/g}$)	Proposed method ($\mu\text{g/g}$)	RSD % (n = 5)
Flour (GBW08426)	As(0.285), Ag(-), Ba(21.2), Bi(0.342), Ca(2900), Cd(0.218), Ce(1.25), Co(4.71), Cr(3.76), Cu(10.2), Fe(54), Hg(0.086), Mg(360), Mn(6.3), Mo(0.735), Ni(1.83), Pb(0.852), Sn(2.18)	0.836	2.0
Tea leaf (GBW08505)	As(0.191), Ag(-), Ba(15.7), Ca(2840), Cd(0.128), Co(2.25), Cr(0.8), Cu(16.2), Fe(373), Hg(0.142), Mg(2240), Mn(766), Ni(5.61), Pb(1.06), Sn(1.24), Se(0.0412), Zn(38.7),	1.120	2.2

TABLE-2
DETERMINATION OF LEAD IN THE WATER AND SOIL SAMPLES

Samples	Found ($\mu\text{g L}^{-1}$)	ICP-MS method ($\mu\text{g L}^{-1}$)	RSD % (n = 5)	Recovery (%) (n = 5)
Tap water	12.8	13.6	3.2	92-98
River water	43.1	41.5	2.9	94-105
Soil	16.4	15.6	2.4	90-97

Conclusions

The flow injection and hydride generation-atomic absorption spectrometry system described have to constitute an effective approach for the determination of lead by hydride generation technique. The proposed method provides adequate sensitivity and accuracy for the direct determination of lead in water samples without pre-concentration procedures. The coupling of flow injection system to lead hydride generation to provides advantages including the possibility of micro-sampling analysis, increased sample throughput (150 samples/h). NaBH_4 consumption is about 15 mL and waste generation in the order of 250 mL h^{-1} , thus making this method an environmentally friendly and sustainable procedure which reduces reagents consumption and waste generation. All these advantages making this method an attractive technique for routine determination of trace amounts of lead in environmental samples.

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