J. Braz. Chem. Soc., Vol. 16, No. 3B, 520-525, 2005.
Printed in Brazil - ©2005 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Determination of Trace Lead in Waters by Flow Injection Hydride Generation Atomic Absorption Spectrometry

Jane F. Neves Carrijo, Luciano C. Brasil and Nívia M. Melo Coelho*

Instituto de Química, Universidade Federal de Uberlândia. Av. João Naves de Ávila, 2160,
38408100 Uberlândia-MG, Brazil

Um sistema de injeção em fluxo para determinação de chumbo a concentrações de mg L^{-1} é proposto usando a Geração de Hidretos e Espectrometria de Absorção Atômica (HG-AAS). Para isto, $(NH_4)_2S_2O_8$ a 8,0% (m/v) é usado com agente oxidante e 100 μL de amostra e 100 µL de $NaBH_4$ a 3,0% (m/v) são injetados, simultaneamente, em duas correntes carregadoras de ácido tartárico a 0,5% (m/v) e água desionizada, respectivamente. A freqüência analítica de 150 determinações por hora foi encontrada e o consumo de $NaBH_4$ de 15 mL e o lixo gerado de 250 mL. O limite de detecção de 0,3 μg L^{-1} para Pb foi obtido e o desvio padrão relativo de 3,0% para 10 μg L^{-1} Pb. O método mostrou-se satisfatório para determinação de traço de Pb em material de referência certificado de águas de consumo e amostras de águas naturais.

A flow injection system for lead determination at concentration levels of mg L^{-1} is proposed using Hydride Generation Atomic Absorption Spectrometry (HG-AAS). To do this, 8.0% (m/v) $(NH_4)_2S_2O_8$ is employed as the oxidizing agent, and 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 de-ionized 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 of limit of 0.3 μg L^{-1} for Pb was achieved and the relative standard deviation of 3.0% for 10 μg L^{-1} Pb was obtained. The method was shown to be satisfactory for determination of traces of Pb in certified reference material of drinking waters and in natural water samples.

Keywords: lead, water, flow-injection hydride generation, atomic absorption spectrometry

Introduction

The lead is one of the elements that has received considerable attention, due to both its extensive use and high toxicity.[1] The determination of traces of lead in a variety of environmental samples is of great importance since lead is recognized as a cumulative poison to animals and human beings.[2]

The determination of lead requires procedures that are sufficiently sensitive for detection at the μg 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.[3] Inductively coupled plasma mass spectrometry (ICP-MS) is favored because of its low detection limits.[4] Even being more attractive, the ICP-MS is a more expensive technique. In spite of this, many researchers prefer AAS owing to its simpler and less expensive instrumentation.

Lead hydride generation and its application to spectrochemical analysis have been reviewed by Madrid and Cámara.[5] Hydride generation combined with atomic absorption spectrometric (HG-AAS) is a well developed technique can be used for the determination of volatile hydride-forming elements such as arsenic, selenium, antimony and others at trace levels.[6] The advantages of hydride generation atomic absorption spectrometry over other atomic absorption spectrometric techniques such as the flame and graphite furnace methods are increased atomization efficiency, higher selectivity because the analyte is removed from the matrix as a volatile compound and detection limits at the μg L^{-1} level or lower for the elements cited above. Considering these advantages, it is providing that the potential this technique should be to

---

* e-mail: nmmcoelho@ufu.br

applied for the lead and moreover, with this purpose it is possible to include this element in multi-element analysis schemes involving hydride generation.

Studies show that the efficiency of the lead hydride generation is critically dependent on the generation conditions and the use oxidizing agents is necessary in order to increase the efficiency of hydride generation.[7] This can be attributed to the difficulties with lead hydride formation, namely the low yield and low stability of the volatile hydride. Various reagents have been used for this purpose. $K_2Cr_2O_7$-malic acid, HNO_3-H_2O_2, HNO_3-$(NH_4)_2S_2O_8$ are some oxidizing agents commonly used.[8] Sensitivity and selectivity depend on the medium, the oxidizing agent and the atomization system used.

Generation of Pb hydride with *in situ* trapping in the graphite furnace was described by Aroza *et al.*[9] However, the problem with Pb hydride generation is the high reagent blank even using chemicals of the highest purity.[10, 11]

In this study, a flow injection hydride generation atomic absorption spectrometry (FI-HG-AAS) system was employed for lead determination. The merging zones approach to flow injection system utilizes the synchronized introduction of samples and reagents into unsegmented carrier streams. The main characteristics of the flow injection system, e. g. high sampling rate and good accuracy, precision and sensitivity, are maintained. The method was applied to the determination of lead in water samples. Good agreement was obtained between the certified values.

Experimental

Instrumentation

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. The signal from the spectrometer was displayed on printer HP-DeskJet 660C.

For atomization of lead, an electrothermic atomizer T-shaped quartz tube was used, which was cleaned weekly with acid following the procedure described by Coelho *et al.*[12] One of tubes was the atomization chamber (170 x 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 (Belo Horizonte, Brazil) voltage regulator. For minimize the hot exchange with the environment, the atomizer was wrapped with ceramic cape.

In the flow system, oxidization 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) (see Figure 1). After of the second confluence point (P2), the reaction mixture reaches the gas-liquid separator.[13] 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 FI manifold is shown in Figure 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 (Villiers Le Bel, France) 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 the very 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 purpose.[14] The de-ionized water (resistivity 18.0 MΩcm), 0.5% (m/v) tartaric acid and 8.0% (m/v) ammonium persulphate solutions were pumped at 1.4 mL

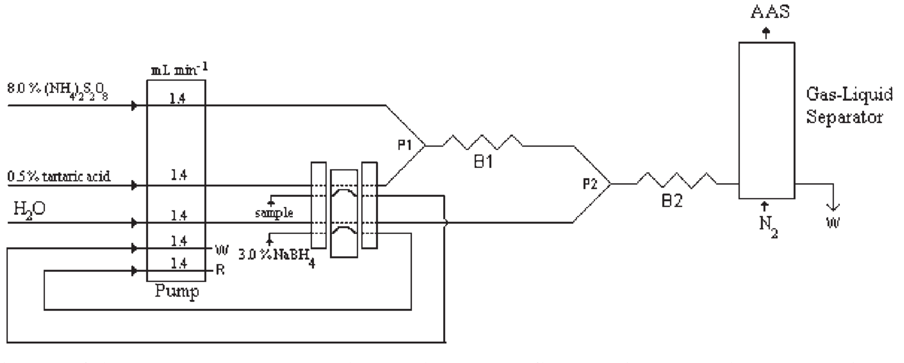

Figure 1. Schematic diagram of the FI-HG-AAS system used. P1 and P2 are confluence points. B1 and B2 are reaction coils with lengths of 40 cm and 20 cm, respectively. W: Waste, R: Recycled solution, AAS: Atomic Absorption Spectrometric.

min^{-1}. The utilization of the small reagent volumes (100 μL) minimizes the consumption of $NaBH_4$.

Chemicals

All reagents used were of analytical grade and de-ionized water was used for preparation solutions. A lead standard solution (Carlo Erba, Val de Reuil, France) with a Pb concentration of 1000 mg L^{-1} Pb in 5% (v/v) HNO_3 was diluted with de-ionized water to provide a working stock solution of 10.0 μg mL^{-1} Pb. Working solutions were prepared daily by dilution of the 10.0 μg mL^{-1} Pb solution. A 3.0% (m/v) $NaBH_4$ (Carlo Erba) solutions were prepared immediately before use by dissolving 3.0 g of the $NaBH_4$ in 0.05 mol L^{-1} KOH (Synth, São Paulo, Brazil). An 8.0% (m/v) $(NH_4)_2S_2O_8$ (Quimex, São Paulo, Brazil) solution was prepared immediately before use by dissolving 8.0 g of the $(NH_4)_2S_2O_8$ in 100 mL of water. A 0.5% (m/v) tartaric acid (Synth) solution was prepared by dissolving 0.5 g of the tartaric acid in 100 mL of water.

Samples

Water samples were collected from "Uberabinha River" (Uberlândia - MG, Brazil). Samples collected in polyethylene bottles were acidified with concentrated hydrochloric acid to obtain a pH near 1.0 to minimize adsorption of trace elements on the bottle walls and micro-organisms proliferation. Mineral water sample was obtained from the local market, in Brazil, and tap waters taken from Uberlândia and town near Uberlândia (Araguari, MG, Brazil). The certified reference material of drinking waters (APS1075, Lot#918109 and APS1071, Lot#918224) were obtained from Alpha Resources, Inc. (Stevensville, Michigan, USA). These standard solutions for certificate of analysis were prepared from high-purity metal, salts and oxides in 5.0% HNO_3.

Results and Discussion

Evaluation of lead hydride generation conditions

The experimental conditions for determination of lead were established employing the manifold described in Figure 1. The literature shows that there are difficulties with lead hydride formation due low yield and low stability of the volatile hydride.[7] 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 to the formation of meta-stable Pb (IV) compounds before the formation of lead hydride in the reaction of lead with $NaBH_4$.[5] In this paper, ammonium persulphate was used for this purpose. The nature of acid-oxidant mixture (tartaric acid - $(NH_4)_2S_2O_8$) employed in this work not yet be in detail 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 parameters were 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 to see in Figure 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 stable compounds of lead with tartaric acid. The 0.5% (m/v) tartaric acid solution was chosen for further measurements.

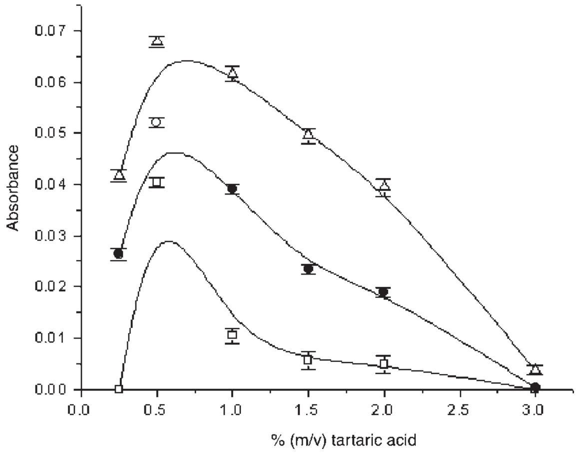

Figure 2. Effect of the tartaric acid concentration on the responses for Pb solutions. The concentration of $NaBH_4$ and ammonium persulphate were 1.0% (m/v) and 8.0% (m/v), respectively. (□) 0.1 mg L^{-1} Pb, (●) 0.5 mg L^{-1} Pb, (△) 1.0 mg L^{-1} Pb

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 Figure 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% (m/v) $NaBH_4$ concentration is not recommended because it shows a disturbance of the hydride generator due high H_2 amounts. Thus, a $NaBH_4$ 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 $NaBH_4$ to be used (100 μL), which represents considerable savings in the cost of analysis.

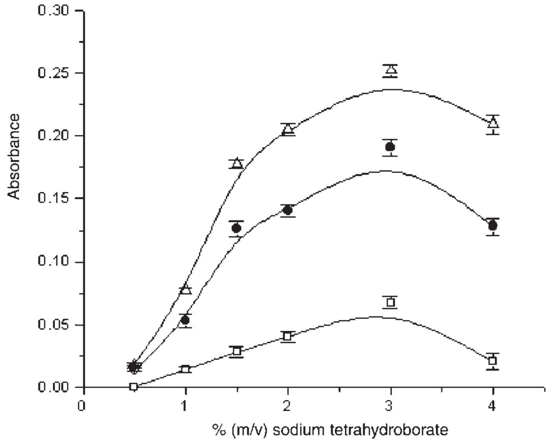

Figure 3. Effect of $NaBH_4$ concentration on the lead hydride generation. The tartaric acid and ammonium persuphate concentrations were 0.5% (m/v) and 8.0% (m/v), respectively. (□) 0.1 mg L^{-1} Pb, (●) 0.5 mg L^{-1} Pb, (△) 1.0 mg L^{-1} Pb

The Figure 4 shows results obtained using different $(NH_4)_2S_2O_8$ concentrations. The presence of oxidizing agents, as $(NH_4)_2S_2O_8$, 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) $(NH_4)_2S_2O_8$ concentration was chosen as being a selective medium and provide adequate lead hydride generation.

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 (see Figure 1). Results show that a reaction coil length of 40 cm is necessary to obtain oxidizing of Pb and a reaction coil length of than 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 this proposed 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.

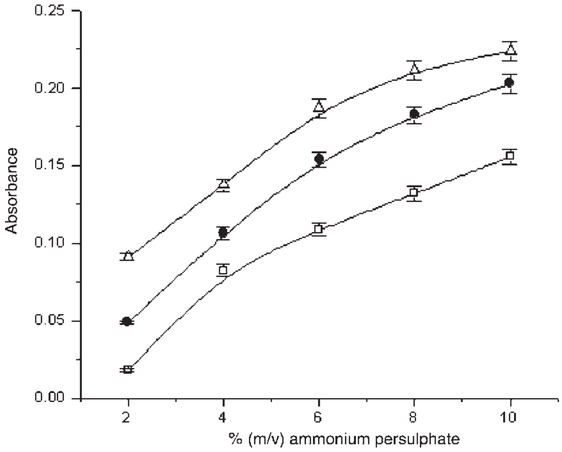

Figure 4. Effect of the oxidizing concentration on the responses for Pb solutions. The concentration of $NaBH_4$ and tartaric acid were 3.0% (m/v) and 0.5% (m/v), respectively. (□) 0.1 mg L^{-1} Pb, (●) 0.5 mg L^{-1} Pb, (△) 1.0 mg L^{-1} Pb

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. Further, flow rates of 1.4 mL min^{-1} was used.

The carrier gas flow rate (N_2) was assessed over the range 25-100 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 °C only partial atomization occurred. The maximum sensitivity was achieved in 950 °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.* [8] 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.*[8], 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 μg L^{-1} lead was 3.0%. The typical mathematical equation of the calibration curve obtained for lead standard solutions was A=0.0032 [Pb] + 0.0148, where A was the analytical signal (absorbance) and [Pb] expressed as μg L^{-1}. The correlation coefficient was 0.9983. The linearity was observed for Pb (II) at a 0.5 mg L^{-1}.

The detection limit based on the 3 σ/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 μg L^{-1} for Pb and the quantification limit (10 σ/m) was 1.0 μg L^{-1}. The sensitivity achieved for proposed method is adequate for lead determination in non-polluted water samples.

The literature shows that a detection limit of 0.5 μg L^{-1} was obtained for generation of Pb hydride with *in situ* trapping in the graphite furnace. [9, 10] However, high blanks were found. The in-atomizer trapping procedure, which concentrate the lead in the atomizer prior to atomization, was reported by Tyson *et al.* [11] In this procedure, has 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 μg L^{-1} for a 1000 μL injection volume. Li *et al.*[4] also reported on the results of a procedure in which quantification was by ICP-MS. The detection of limit of 0.007 μg 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.*[7] reported a detection limit of 1.5 μg L^{-1} Pb and a sampling rate of about 180 determinations per hour was achieved.

Sample analysis

The proposed method was applied to the quantification of lead in different water samples (Table 1). Results were ranged from 4.2 to 10.9 μg L^{-1} of Pb. The accuracy of the method was evaluated by analyzing drinking water reference material, APS 1075 and APS 1071, with a certified lead concentration of 40.0 ± 0.5 μg L^{-1} and 100.0 ± 1.0 μg L^{-1}, respectively. Results obtained were 39.8 ± 0.2 μg L^{-1} and 101.0 ± 0.2 μg L^{-1}, respectively. These results are in good agreement with the certified values. To validate the method for the analyses of water, two samples of mineral water were spiked with Pb (II) to give a final concentration of 40.0 and 80.0 μg L^{-1} of Pb. As can be seen in Table 2, recovery percentages from 95.0 and 97.0%, were obtained.

Table 1. Lead determination in water samples by proposed method

Samples	Lead concentration (μg L^{-1})
River	
I	10.9 ± 0.3
II	8.1 ± 0.2
III	8.9 ± 0.2
Tap water	
Araguari	7.2 ± 0.2
Uberlândia	4.2 ± 0.2
Mineral water	4.2 ± 0.2

I, II and III were river water samples collected in different points. Values are the average of five independent analysis ± the standard deviation.

Table 2. Experimental recovery on lead determination by FI-HG-AAS in mineral water samples spiked with 40.0 and 80.0 μg L^{-1} of Pb (II)

	Concentration (μg L^{-1})	Recovery (%)
Sample	N.D.	-
Sample + 40.0 μg L^{-1}	41.8	95.0
Sample + 80.0 μg L^{-1}	85.4	97.0

N.D.: not detectable.

Conclusions

The FI-HG-AAS system described has proven 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 per hour). $NaBH_4$ 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. Thus due all these advantages making this method an attractive technique for routine determination of trace amounts of lead in water samples.

Acknowledgements

The authors are grateful for the financial support given by the FAPEMIG Foundation (CEX2471/96 and CEX2253/97).

References

1. Lanphear, B. P.; Burgoon, D. A.; Rust, S. W.; Eberly, S.; Galke, W.; *Environm. Res.* **1998**, *76*, 120.
2. Harrison, R. M.; Laxen, D. D. H.; *Lead Pollution*, Chapman and Hall: London, 1981.
3. Yan, X. P.; Adams, F.; *J. Anal. At. Spectrom.* **1997**, *12*, 459.
4. Li, J.; Lu, F.; Umemura, T.; Tsunoda, K.; *Anal. Chim. Acta* **2000**, *419*, 65.
5. Madrid, Y.; Cámara, C.; *Analyst* **1994**, *119*, 1647.
6. Dédina, J.; Tsalev, D. L.; *Hydride Generation Atomic Absorption Spectrometry*, Wiley: Chichester, 1995.
7. Madrid, Y.; Chakraborti, D.; Cámara, C.; *Mikrochim. Acta* **1995**, *120*, 63.
8. Madrid, Y.; Bonilla, M.; Cámara, C.; *Analyst* **1990**, *115*, 563.
9. Aroza, I.; Bonilla, M.; Madrid, Y.; Cámara, C.; *J. Anal. At. Spectrom.* **1989**, *5*, 163.
10. Haug, H. O.; *Spectrochimica Acta* **1996**, *51B*, 1425.
11. Tyson, J.F.; Ellis, R.I.; Carnrick, G.; Fernandez, F.; *Talanta* **2000**, *52*, 403.
12. Coelho, N. M. M.; Silva, A. C.; Silva, C. M.; *Ciência & Engenharia* **2001**, *10*, 105.
13. Cadore, S.; Baccan, N.; *J. Anal. At. Spectrom.* **1997**, *12*, 637.
14. Bergamin-Filho, H.; Medeiros, J. X.; Reis, B. F.; Zagatto, E. A. G.; *Anal. Chim. Acta* **1978**, *101*, 9.

Received: October 25, 2002
Published on the web: February 28, 2005