

A sensitive flow injection system for lead determination in water and blood samples by HG-AFS

Beltrán, B.¹, Miranda, S.V.¹, Moreno, M.¹, Leal, L.O.¹

¹Environment Department, Advanced Material Research Center (CIMAV). Miguel de Cervantes 120, Complejo Industrial Chihuahua, Chihuahua, Chih. 31109, Mexico

Key words: Lead, Hydride generation, Atomic fluorescence, flow injection, water and biological samples

Abstract

Lead (Pb) is a heavy metal whose toxic properties are well documented. An excess of ingested lead poses a health risk affecting both the nervous system and biosynthesis of hemoglobin. A simple and sensitive flow-injection system coupled to hydride generation atomic fluorescence spectrometry (HG-AFS) was developed for ultra-trace lead determination. Plumbane (PbH₄) was generated utilizing two methods: in one of them was employed 5% (v/v) H₂O₂ as an oxidant with 1.5% (m/v) KBH₄ as a reducing agent and 1.5% (v/v) HCl solution. The second method involved 1.5% (m/v) K₃[Fe(CN)₆] as an oxidant/sensitizer, 1% (m/v) KBH₄ and 1.5% (v/v) HCl. Variables such as sample and reagent volumes, flow rates and reagent concentrations were tested. The best results were obtained with potassium ferricyanide K₃[Fe(CN)₆], with a detection limit of (0.03 µg L⁻¹) and a RSD of 1.1%. A study of interferences of the most common interfering ions was also performed. The proposed method was validated by means of certified reference materials (CRM), which are in good agreement with the certified values. Real samples such as tap water, mine water and human blood were also measured. This method offers some advantages over conventional laboratory techniques such as optimum sensitivity, higher sample throughput and the decrease of reagents and sample consumption.

Introduction

Heavy metals have special importance from ecotoxicological point of view due to their high toxicity and accumulation in various organisms. An excess of ingested lead is a real health hazard affecting both the nervous system and the biosynthesis of hemoglobin (Elçi et al., 2009). Thus the determination of lead and understanding its accumulation in biological organisms is increasingly important. Hydride Generation (HG) is one of the most popular analytical methods for the determination of trace levels of hydride-forming elements. The lead hydride is called plumbane (PbH₄) and is one of the most interesting and controversial cases (D'Ulivo et al., 2008). Little work has been done on lead hydride generation in comparison with other hydride forming elements: most likely due to the low yield and thermal instability of plumbane. Lead hydride generation process is considered very complex. The plumbane generation is more efficient for Pb(IV) than Pb(II) (D'Ulivo et al. (2008)) gave further evidence about the strong enhancement produced by the hexacyanoferrate (III), known as potassium ferricyanide (K₃Fe(CN)₆), in the generation efficiency of plumbane by formation of borano complex intermediates. The coupling of HG with AFS has provided a powerful tool for the determination of hydride-forming elements including lead (Chen et al., 2002). Atomic fluorescence spectrometry (AFS) has been employed because of its high sensitivity, wide linear range, ease of use and low cost (Leal et al., 2006). The aim of this study was the determination of lead in water and blood samples by FIA-HG-AFS technique, evaluating the efficiency of K₃[Fe(CN)₆] and H₂O₂ as oxidizing agents for plumbane generation and providing more information about this issue. Several variables such as sample and reagents volumes, flow rates and reagent concentrations were investigated in detail for both

methods, ferricyanide method (FeM) and peroxide method (PM). A study of interferences of the most common ions was also carried out. Certified reference materials (CRM) such as ground water (BCR-610) and mussel tissue (SRM-2976) were employed for the method validation.

Materials and methods

A non-dispersive atomic fluorescence spectrometer, AFS-640 (Raleygh Analytical Instrument Corp., Beijing, China) with a continuous flow-interval sampling vapor generation was employed as detector. The sample introduction system consists of a peristaltic pump with two channels, one of them for aspirating the reducing solution, whereas the other one for sample/carrier solution (HCl), a storage sample coil, a mixed module and two argon flows. Plumbane and co-generated hydrogen gas were transported by a carrier gas (argon) through the gas-liquid separator to the atomizer. The quartz tube atomizer is ignited to form the argon-hydrogen flame and make an effective atomization.

Series of Pb (II) standard solutions were prepared by gradually diluting 1000 mg L⁻¹ standard stock solutions (high-purity standards). 5% (v/v) H₂O₂ (J.T.Baker 30%) and 1.5% (m/v) [Fe(CN)₆] (J.T. Baker 99.7%) were used as additives. The 1.5% (m/v) reducing solution was prepared from KBH₄ (aldrich 98%) with KOH (J.T.Baker 87%). The carrier solution was made of 1.5% (v/v) HCl (37.6%, Baker intra-analyzed).

The tap water sample was analyzed without a pre-treatment whereas treated mine water was filtered. The blood sample was digested prior its analytical determination.

Results and discussion

In order to achieve the most efficient performance in terms of highest analytical sensitivity and lowest

deviation of signal (measure precision), some parameters were investigated for both methods, PM and FeM. The obtained results showed the best analytical performance with potassium ferricyanide (FeM method), achieving a detection limit of $0.03 \mu\text{g L}^{-1}$. It was selected for further experiments. A study of interferences of the most common interfering ions was also performed. Elements that form volatile hydrides produced the highest suppression of the signal. It is due their competition for the reducing agent, since they react faster than lead (Ramesh et al., 2010). Therefore, As, Sb, Hg and Se can suppress the signal by affecting the generation of plumbane in both methods. Low tolerance levels of some transition metals such as Cr, Fe, Ni, Co and Cu have been obtained. It can be due to the adsorption of the analyte hydride onto metal colloids that are formed by reduction (Leal et al., 2006). Generally we can say that FeM method suffers of severe interferences of foreign ions. Thus, a deeper study of the role of the masking agent is mandatory.

The proposed method was validated by the analysis of a groundwater reference material (BCR-610) and a solid reference material (mussel tissue, SRM-2976). As can be seen in Table 1, the obtained results are in good agreement with the certified values.

In order to evaluate the usefulness of the proposed technique in determining lead contents at the levels usually found in environmental and biological samples, two types of water and a blood sample were analyzed. Tables 2 and 3 show the analysis of tap water and treated mine water samples. The obtained recoveries are satisfactory, ranging from 94-107%. After a microwave digestion, the blood sample was analyzed (Table 4).

Table 1. Results of the analysis of certified reference materials.

Sample	Certified	Obtained
BCR-610 (mg kg^{-1})	7.78 ± 0.13	7.13 ± 0.05
SRM-2976 (mg kg^{-1} dry tissue)	1.19 ± 0.18	1.06 ± 0.22

Table 2. Lead concentration in tap water samples.

Added ($\mu\text{g L}^{-1}$)	Lead ($\mu\text{g L}^{-1}$)	Recovery (%)
0	0.16 ± 0.002	
2	2.07 ± 0.030	96
6	6.05 ± 0.002	98
10	9.77 ± 0.005	107
16	16.12 ± 0.120	100

Table 3. Lead concentration in treated mine water.

Added ($\mu\text{g L}^{-1}$)	Lead ($\mu\text{g L}^{-1}$)	Recovery (%)
0	20.23 ± 0.416	
20	39.05 ± 0.236	97
30	47.25 ± 0.422	94
40	56.73 ± 0.377	94

Table 4. Lead concentration in human blood sample.

Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
0	0.16 ± 0.040	
2	2.18 ± 0.038	101
4	4.04 ± 0.042	97
8	7.93 ± 0.058	97

Conclusions

The FI-HG-AFS system proposed for trace levels of lead determination evaluating two different methods has been developed. The use of potassium ferricyanide method showed better results. The proposed method offers some advantages such as optimum sensitivity and decreasing of reagents and sample consumption, which leads to a lower waste generation. In addition, the FI-HG-AFS system was shown to be suitable for the determination of lead in different sample matrices due to its high sensitivity. However, the study of interferences showed low tolerance to foreign ions. Thus, the use of a masking agent is mandatory. It was confirmed with the analysis of BCR 610, in which KI was added to reduce the interferences. The authors also recommended a detailed study of interferences, testing different masking agents. It will be develop in a second part of this investigation.

References

- Chen, S., Z. Zhang., H. Yu., W. Liu, and M. Su. 2002. Determination of trace level of lead by ICP-MS. *Anal. Chim. Acta.* 463,177-188.
- D'Ulivo, A., M. Onor., R. Spiniello, and E. Pitzalis. 2008. Mechanisms involved in chemical vapor generation by aqueous tetrahydroborate (III) in plumbane generation. *Spectrochim. Acta part B.* 63: 835-842.
- Elçi, L., Z. Arslan, and J.F. Tyson. 2009. Determination of lead in wine and rum samples by flow injection-hydride generation-atomic absorption spectrometry. *J. Haz. Mat.* 162:880-885.
- Leal, L.O., R. Forteza, and V. Cerdà. 2006. Speciation analysis of inorganic arsenic by a multisyringe flow injection system with hydride generation-atomic fluorescence spectrometric detection. *Talanta.* 69:500-508.
- Ramesh K., and P. Riyazuddin. 2010. Chemical interferences in hydride generation atomic spectrometry. *Trends Anal. Chem.* 29: 166-170.