Determination of lead in complex sample matrices by atomic fluorescence spectrometry: optimisation of online hydride generation

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Lead hydride or plumbane (PbH4) generation was optimised by exploiting a simple flow-injection method coupled to atomic fluorescence spectrometry (HG-AFS), and allowing ultra-trace lead determination. Plumbane was generated through two methods: (1) 5% (v/v) H2O2 was employed as oxidant with 1.5% (m/v) KBH4 as a reducing agent and 1.5% (v/v) HCl solution; (2) with 1.5% (m/v) K3[Fe(CN)6] as an oxidant/ sensitiser, 1% (m/v) KBH4 as a reducing agent and 1.5% (v/v) HCl. Variables such as reagent concentrations, flow rates and sample and reagent volumes were tested and critically compared. The best results were obtained with potassium ferricyanide K3[Fe(CN)6], achieving a detection limit of 0.03 µg Pb L−1 and a relative standard deviation (RSD) of 1.1%. The selected method was validated by analysis of certified reference materials such as SRM-2976 (mussel tissue) and BCR-610 (groundwater), with good agreement with the certified values. The developed methodology was successfully applied to different environmental sample matrices, such as rain water, tap water, ground water, spring water and drinking water, and biological samples, i.e., human blood, plasma and serum.

Keywords: lead hydride; oxidising agents; atomic fluorescence; water samples; blood analysis

1. Introduction

In recent years, interest in the determination of lead has been increased, particularly in biological, food and environmental sample matrices [1–4]. Lead has been extensively studied due to its high toxicity and bioaccumulation effect in organisms, since it is present in

the trophic chain even at very low concentrations [5]. Thus, in order to understand the metabolic disorders caused by Pb and its mechanisms of toxicology, lead determination has been carried out in some body fluids such as blood, serum and plasma [6].

As regards water systems, Pb pollution represents a serious influence in the quality of life for people, especially in urban areas. Although the concentration of lead in natural waters is extremely low (sub-ppb level) [7], it is important to monitor the level of lead in these environmental samples.

Hydride generation (HG) technique coupled with several spectrometric techniques is widely used for determination of elements that can form volatile hydrides such as Pb, at trace or ultratrace concentrations [8]. HG is carried out by the reaction of a derivatising reagent (tetrahydroborate(III), TBH) and the target analyte in acid medium [9]. This technique promotes the separation of the analyte from the matrix. However, some interference can occur in both, gas and liquid phases [10].

Nevertheless, there is a main drawback in lead determination by HG that should be taken into account. The efficiency of lead hydride production is low and has shown thermal instability, in comparison with other elements that form volatile hydrides [11]. Thus, lead HG depends greatly on experimental conditions and reagents used. That is, presence of additives such as oxidising agents, masking agents and/or chelating agents is required to improve lead hydride production [12].

The generation of lead hydride or plumbane (PbH_4) is one of the most interesting and controversial cases [9]. More efficient plumbane generation was reported for Pb(IV) than Pb(II)[13], while other authors found that the presence of an oxidant was mandatory to improve plumbane generation, independent of the lead oxidation state [14]. In the latter case, hydrogen peroxide was employed as the oxidising agent for the generation of lead hydride. Thus, they concluded that the oxidant can generate activated species, which in turn produce a catalytic effect in the formation of PbH_4. In the same way, potassium dichromate,

potassium permanga-nate and cesium sulphate(II) [15], ammonium peroxodisulphate [16] and potassium ferricyanide [9,17] have been employed as oxidising agents.

Potassium ferricyanide has been widely utilised in the generation of plumbane by formation of borano complex intermediates [18]. This reagent has proved to be effective in reducing the interferences and enhancing the formation of the Pb hydride [9,19]. Nevertheless, the role of oxidants in lead HG is still under investigation. Therefore, development and understanding of efficient plumbane generation is required for establishing optimal operation conditions of the analytical system [19].

Atomic fluorescence spectrometry (AFS) presents interesting analytical features such as low detection limits and a wide linear calibration range. AFS is compatible with online hydride/vapour generation systems; therefore, it is most suitable for measuring hydride/vapour-forming species [20]. The coupling of flow injection analysis (FIA) to HG-AFS has been applied for lead determination, providing good figures of merit [17,21].

Thus, the aim of this work was the optimisation and evaluation of two different protocols for online plumbane generation and their effects on lead analytical signal by HG-AFS, since until now a comparison between hydrogen peroxide and ferricyanide as oxidising reagents in plumbane generation is not reported. Furthermore, the positive effect of KI in the analytical signal of lead is described. Moreover, the selected methodology was validated by means of certified reference materials (SRM-2976 mussel tissue and BCR-610 groundwater) and applied to different complex sample matrices, such as rain water, tap water, ground water, spring water and drinking water, and biological samples, i.e., human blood, plasma and serum.

2. Experimental

2.1. Reagents

All chemicals used were of analytical reagent grade. All solutions were

prepared with Millipore purified water. Glassware was soaked in 10% (v/v) HNO3 and rinsed with Millipore water. Standard solutions of Pb were prepared by gradually diluting 1000 mg Pb L−1 standard stock obtained from CENAM (National Metrology Center, Mexico).

Nitric acid (99.99% w/w), hydrochloric acid (36–38% w/w), hydrogen peroxide (30% w/w), potassium hydroxide (87% w/w), potassium ferricyanide (99.5% w/w) and potassium iodide (99.6% w/w), were purchased from J.T. Baker (USA).

Two oxidising reagents were used for plumbane generation, hydrogen peroxide method (PM method) and potassium ferricyanide method (FeM method).

PM method: The reducing agent solution was prepared with 1.5% (m/v) of potassium borohydride (KBH4, Sigma Aldrich, USA) in 0.2% (m/v) KOH. A solution with 1.5% (v/v) of HCl and 5% (v/v) of H2O2 was utilised to prepare standards and samples.

FeM method: The reducing agent solution was prepared with 1% (m/v) of KBH4 and 1.5% (m/v) of potassium ferricyanide (K3Fe (CN) 6) in 0.2% (m/v) of KOH. Standard solutions and samples were prepared in 1.5% HCl solution. Besides, potassium iodide was added as a masking agent into the reducing solution at a concentration of 1.8% (m/v) for the analysis of certified reference material BCR-610 by FeM method.

A solution 1.5% (v/v) of HCl was employed as a carrier in both methods.

2.2. Procedure

Measurements were performed by means of an atomic fluorescence spectrometer AF-640 (Rayleigh Analytical Instrument Corp., Beijing, China). The

instrument was equipped with a gas–liquid separator (GLS), which allows the separation of PbH4 of the aqueous phase of the sample. The operating parameters of the AF-640 are summarised in Table 1. A super-cathode lamp (Rayleigh Analytical Instrument Corp., Beijing, China) was used as the radiation source (λ = 283 nm). Figure 1 depicts a schematic of HG-AFS system for Pb determination. First, the peristaltic pump drives the reducing solution and the carrier (1.5% HCl) or sample which goes inside a holding coil (HC, 281.5 cm length/1 mm i.d.). The peristaltic pump turns back on and the streams are dispensed towards a reaction coil (RC, 27 cm length/1 mm i.d.), where HG takes place. The liquid and gaseous phases are conducted to a GLS, where the liquid phase is discarded as waste. During this process, the volatile lead hydride (PbH4) and the hydrogen gas produced by the reaction are carried by argon gas with a flow rate of 400 mL min−1 into the atomiser. The temperature of the atomiser is controlled by the computer and divided into six modes: room temperature (no heating), 100°C, 200°C, 300°C, 400°C and 450°C. A single-wire auto-ignition device controlled by low voltage is mounted on the upper part of the atomiser. The high-intensity lamp emits its radiation onto the lead atoms in the ground state and the fluorescence signal, known as fluorescence intensity, which is quantised in a photomultiplier tube (detector). Data collection and processing as well as the control over the whole instrument were all carried out with the help of manufacturer software AF-640 1.3.

Table 1. Instrumental setting for HG-AF-640 instrument.

Parameter	PM	FeM
AFS		
Temperature of atomiser (°C)	100	Room temp.
Carrier argon flow (mL min^{-1})	300	400
Delay time (s)	6	4
Reading time (s)	24	22
FI system		
Load sample time (s)	10	8
Sample volume (mL)	1.6	1.3
Sample flow rate (mL min^{-1})	10	8
Chemical variables		
KBH4 % (m/v)	1.5	1
HCl % (v/v)	1.5	1.5
$K_3[Fe(CN)_6]$ % (m/v)	–	1.5
H_2O_2 % (v/v)	5	–

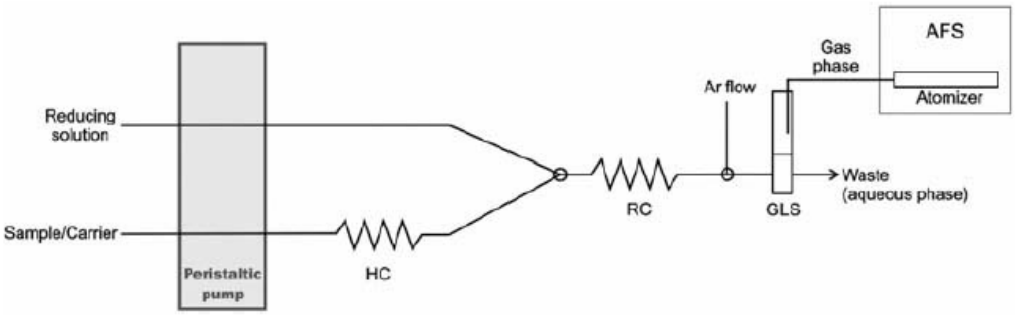

Figure 1. Scheme of HG-AFS system for lead determination. Holding coil, HC; reaction coil, RC; gas liquid separator, GLS; reducing solution (KBH_4 for PM and KBH_4–$K_3Fe(CN)_6$ in FeM); sample and carrier (1.5% HCl–5% H_2O_2 in PM and 1.5% HCl in FeM); carrier 1.5% HCl solution.

2.3. Sample pretreatment

In all cases, the HCl concentration was adjusted to 1.5% to ensure adequate and efficient generation of the plumbane.

Two certified reference materials, a groundwater sample (BCR 610, Community Bureau of Reference BCR, European Commission) and a lyophilised mussel tissue (SRM 2976, National Institute of Standards and Technology, USA), were employed for validation of the developed methodology. For this purpose, 0.5 g

of SRM-2976 was weighed into a microwave Teflon vessel, to which 1.2 mL of nitric acid and 3.5 mL of water were added. After digestion, the sample was diluted to 50 mL with 1.5% HCl solution.

The BCR-610 was acidified to a concentration of 1.5% HCl solution. However, the addition of 1.8% (m/v) KI as a masking agent into the reducing solution (KBH4)was mandatory in order to avoid interferences of foreign ions [10]. In addition, rain water, tap water, ground water, spring water and drinking water samples were analysed. First, the water samples were filtered in order to remove particles or dust. Then, they were acidified until a 1.5% concentration of HCl.

In order to ensure accuracy in a complex matrix such as blood, the sample pretreatment is the most critical step. Thus, blood samples were separated in fractions and Pb was analysed in entire blood, plasma and serum. First, 1 g of sample was weighed and placed in a Teflon (PTFE) vessel, and then 10 mL of concentrated HNO3 solution was added. The blank must contain the same amount of reagent (10 mL of HNO3). The blood, serum and plasma samples were digested in a microwave digester MARSx (CEM Corporation, USA). After that, each sample was filtered, heated to dryness and dissolved in a solution of 1.5% HCl to 100 mL. The microwave digestion procedure was carried out in agreement with the method and programme setup, both proposed by the microwave digester manufacturer.

3. Results and discussion

3.1. Optimisation of experimental conditions

In order to achieve the most efficient performance in terms of highest analytical signal and best precision, some parameters were investigated for both

methods, PM and FeM. The optimisation of the variables was carried out by the univariate method.

The AFS parameters, including carrier argon flow, delay and reading times, were optimised and are summarised in Table 1. Values of lamp current, auxiliary cathode current and atomiser height were those recommended by the AF-640 user manual.

The atomiser temperature affects the complete atomisation of Pb from plumbane [5]. Room temperature (no heating), 100°C, 200°C and 300°C were tested in order to optimise the atomisation temperature. The FeM method was carried out at room temperature, while PM method required an additional temperature of 100°C in the atomisation process.

The influence of sample volume on the efficiency of plumbane generation was assessed for both, PM and FeM, methods within the range 0.3–2.4 mL. As can be expected, Pb analytical signal increased linearly with increasing sample volume up to 2.1 mL and 1.6 mL for the PM and FeM methods, respectively (Figure 2), as a result of more plumbane generated. If the sample volume increases, the residence time also increases (maintaining a constant flow rate), which also favours plumbane generation. However, taking into account that higher sample volumes reduce sample frequency and increase reagent consumption, an optimal sample volume was chosen in order to reach a compromise between higher analytical signal and sample throughput. Thus, a required and adequate volume of 1.6 mL (10 s load time) was chosen for PM method, whereas 1.3 mL (8 s load time) was selected for FeM method. In addition, the chosen values had lower standard deviation between their

measurements.

The peak signal height was strongly dependent on the sample flow rate. Then, seeking a compromise among the frequency, sensitivity and precision of the measurements, optimal sample flow rate was found to be varying within the ranges 8–13 mL min−1 for PM method and 6–16 mL min−1 for FeM method. In both methods, the analytical signal of lead increased with increasing flow rate until 10 mL min−1, and gradually decreased with higher flow rates. It can be due to an incomplete plumbane generation reaction, since higher flow rates shorten residence times. Thus, a flow rate of 10 mL min−1 was selected in both methods (Figure 3).

The residence times in RC were calculated for both methods taking into account the optimised sample volume (1.6 mL and 1.3 mL for PM and FeM, respectively) and the optimised sample flow rate 10 mL min−1. The values obtained were 9.6 s for PM method and 8 s for FeM method.

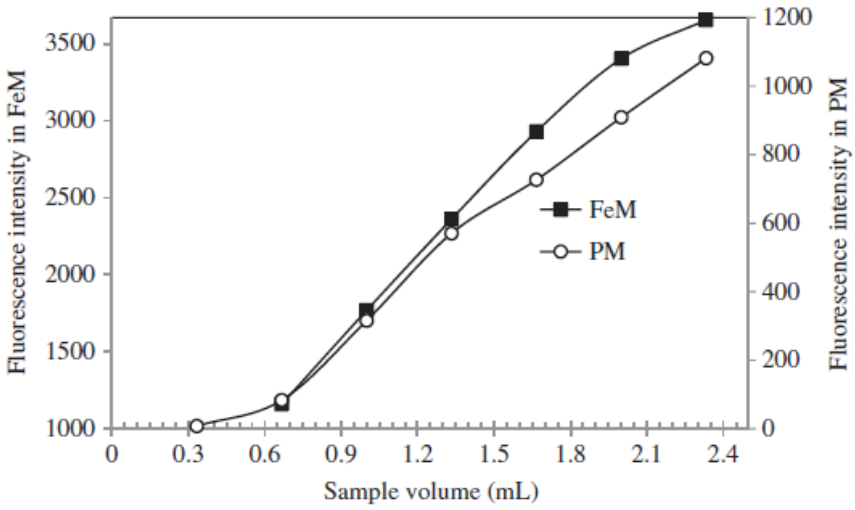

Figure 2. Optimisation of sample volume for PM and FeM methods. Conditions of PM: 20 µg L^{-1} Pb solution, 1.5% (m/v) KBH_4, 1.5% (v/v) HCl, 5% (v/v) H_2O_2. Conditions of FeM: 10 µg L^{-1} Pb solution, 1% (m/v) KBH_4, 1.5% (v/v) HCl, 1.5% (m/v) $K_3Fe(CN)_6$. Sample flow rate of 10 mL min^{-1} for both methods.

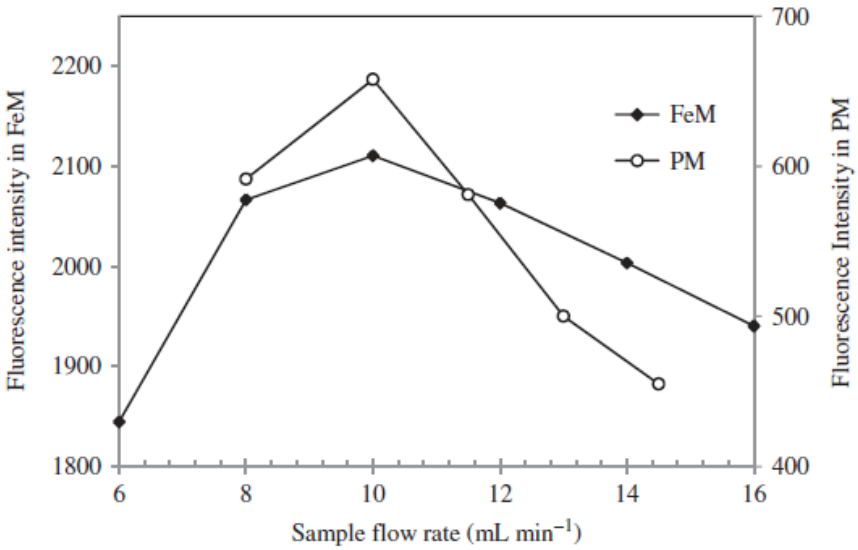

Figure 3. Sample flow rate optimisation for PM and FeM methods. Conditions of PM: 20 µg L^{-1} Pb solution, 1.5% (v/v) HCl, 5%(v/v) H_2O_2, 1.6 mL sample volume. Conditions of FeM: 10 µg L^{-1} Pb solution, 1% (m/v) KBH_4, 1.5% (v/v) HCl, 1.5% (m/v) $K_3Fe(CN)_6$, 1.3 mL sample volume.

3.2. Chemical variables

The KBH4 solution was used as both, reducing agent and hydrogen supplier, which was necessary to support the argon–hydrogen flame. Low concentrations of KBH4 could not effectively reduce the analyte to hydride and sustain the argon–hydrogen flame, while higher concentrations (>2.5% m/v) increase the signal. However, there is an excessive foaming and aerosol formation, which tended to cause trouble for phase separation. In addition, reagent consumption is also increased. Some works have reported that in the first stage of gas–liquid separation, the foam might be entrapped in the gas phase and introduced into the atomiser [22]. Therefore, an optimisation of the KBH4 concentrations was made. Then, 1.5% and 1% (m/v) of TBH were chosen for the PM and FeM methods, respectively (Figure 4).

In the case of PM method, increasing H2O2 concentration causes increase in fluorescence intensity, but the precision of the measurements decreases. Thus, a

solution of 5% (v/v) hydrogen peroxide was chosen as the optimal value (Figure 5). In the case of FeM method, 1.5% (m/v) potassium ferricyanide was selected as the optimal value, giving the highest analytical signal and the smaller standard deviation (Figure 6).

It was observed a considerable increase in the analytical signal of 10 µg L−1 lead with the use of ferricyanide, since it was increased six-fold in comparison with that obtained with hydrogen peroxide in the determination of the same concentration. It has been reported that the reaction of TBH with hexacyanoferrate(III) forms ‘special’ hydroboron intermediates which react efficiently with Pb(II), giving strong enhancement of plumbane generation efficiency [9].

In order to maintain the stability of the whole system during the HG process and to optimise the performance of the overall system, it is recommended to employ a single HCl concentration for carrier solution, samples and standards, which would be favourable to maintain the highest sensitivity [23]. In this work, the optimal concentration of HCl was tested in the range of 1–2.5% (v/v), which was in agreement with previous works [21,23]. Thus, 1.5% (v/v) HCl was chosen for both, PM and FeM, methods because higher acid concentrations caused a decrease in the Pb analytical signal (Figure 7).

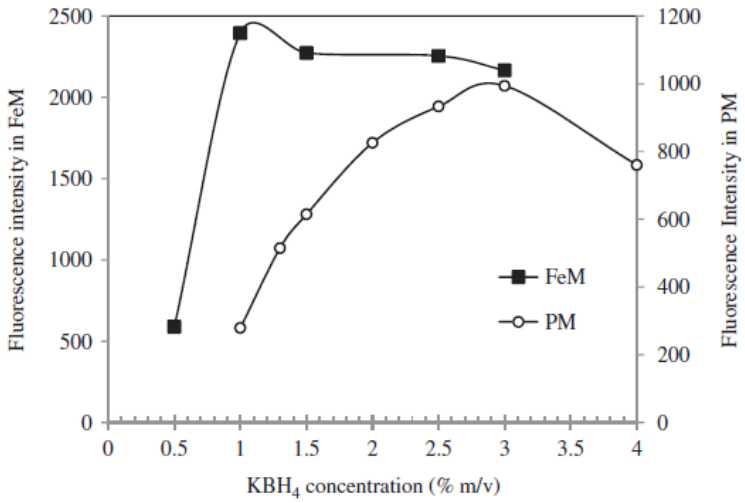

Figure 4. Effect of KBH_4 concentration on the Pb analytical signal. Conditions of PM: 20 µg L^{-1} Pb solution, 1.5% (v/v) HCl, 5% (v/v) H_2O_2, 1.6 mL sample volume. Conditions of FeM: 10 µg L^{-1} Pb solution, 1.5% (v/v) HCl, 1.5% (m/v) $K_3Fe(CN)_6$, 1.3 mL sample volume.

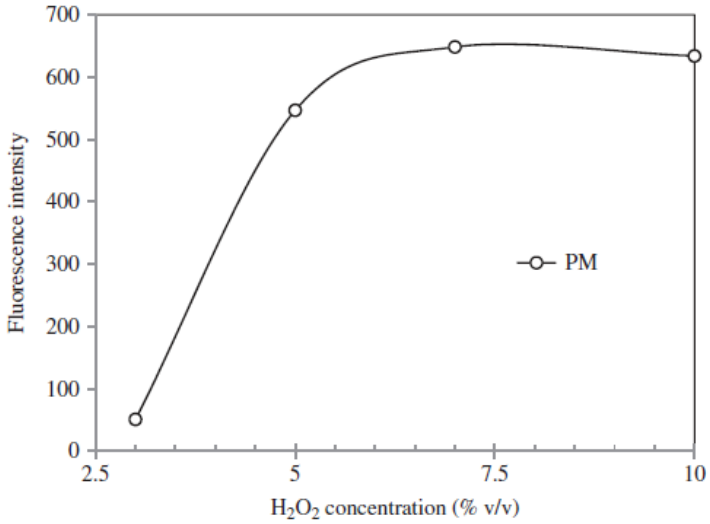

Figure 5. Optimisation of oxidising agent. Conditions for PM: 20 µg L^{-1} Pb solution, 1.5% (v/v) HCl, 1.5% KBH_4 (m/v), 1.6 mL sample volume.

3.3. Analytical parameters

The analytical figures of merit were evaluated under the optimal experimental conditions and summarised in Table 2. For both PM and FeM methods, calibration curves were constructed. Linear range, detection and quantification limits,

correlation coefficient and relative standard deviation (RSD) were also obtained. RSD was evaluated from 15 successive injections using a Pb standard of 3μgL−1 for PM and 1.2 μg L−1 for FeM. The detection limit (LOD) was calculated as three times the standard deviation of 10 successive blank signal measurements divided by the slope of the calibration curve (3σ/s), while the quantification limit (LOQ) was calculated as 10σ/s [1].

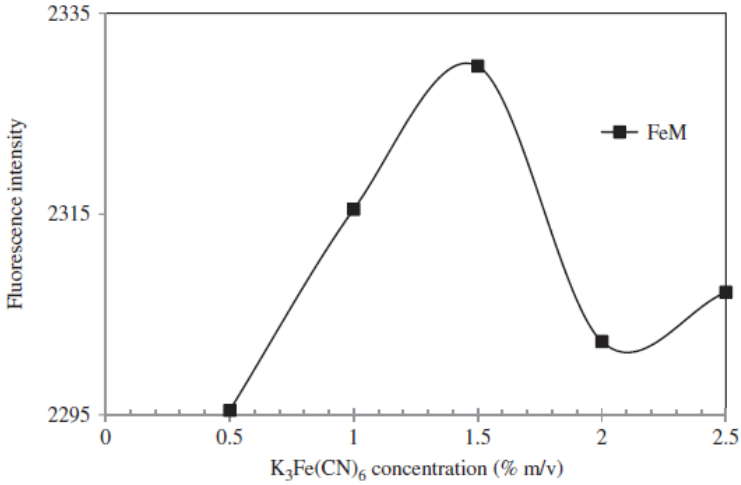

Figure 6. Optimisation of oxidising agent. Conditions for FeM: 10 μg L^{-1} Pb solution, 1.5% (v/v) HCl, 1% (m/v) KBH_4, 1.3 mL sample volume.

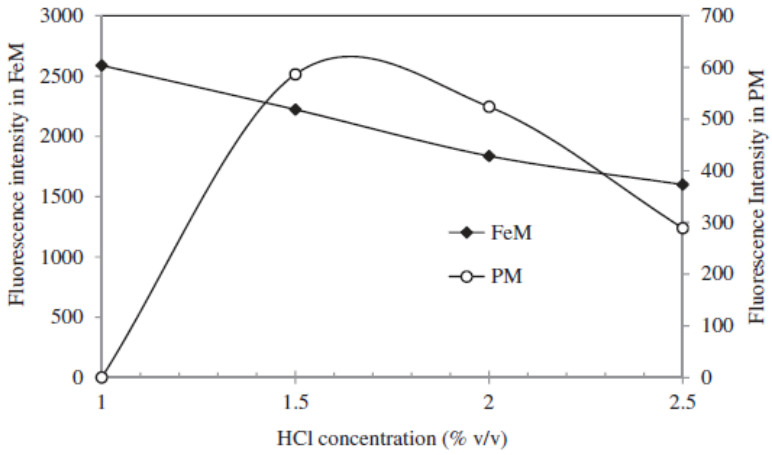

Figure 7. Influence of HCl concentrations on analytical signal of lead. Conditions for PM: 20 μg L^{-1} Pb solution, 1.5% (m/v) KBH_4, 5% (v/v) H_2O_2, 1.6 mL sample volume. Conditions for FeM: 10 μg L^{-1} Pb solution, 1% (m/v) KBH_4, 1.5% (v/v) HCl, 1.5% (m/v) $K_3Fe(CN)_6$, 1.3 mL sample volume.

Table 2. Analytical parameters in plumbane generation.

Analytical parameter	PM	FeM
Detection limit (μg L^{-1}) (n = 10)	0.42	0.03
Quantification limit (μg L^{-1}) (n = 10)	1.4	0.1
Linear range (μg L^{-1})	1.4–80	0.1–80
Determination coefficient (r^2)	0.9994	0.9986
RSD (%) (n = 15)	7.1	1.1
Injection frequency (h^{-1})	53	70

3.4. Selection of the methodology

The selection of the most appropriate method was conducted taking into account: (1) the optimisation of AFS parameters and chemical variables; and (2) analytical parameters.

As mentioned above, potassium ferricyanide enhances the analytical signal of lead, providing higher sensitivity for FeM method.

Low value of RSD obtained for the FeM method indicates a better precision than the PM methodology, i.e., FeM gave a RSD of 1.1% (n = 15), more than six-fold lower than PM (7.1% RSD, n = 15). In addition, detection limits of 0.03 and 0.42 μgPbL−1 were achieved for the FeM and PM methods, respectively, showing a lower LOD for FeM method. Consumption of sample and reducing agent of FeM method was lower than that of the PM method. Even more, a higher injection frequency was accomplished by means of FeM and it was carried out at room temperature, while PM method required an additional temperature of 100°C in the atomisation process. Thus, FeM method provides better figures of merit, which convert it into a powerful tool in the analytical measures of low Pb concentrations either in environmental or biological samples. In addition, FeM decreases the

sample and reagent consumption and, as a consequence, there is reduction in waste generation.

3.5. Accuracy evaluation

The accuracy of the FeM method was evaluated by analysing two certified reference materials: groundwater (BCR-610) and mussel tissue (SRM-2976). The obtained results (7.13 ± 0.05 and 1.1 ± 0.2 mg Pb kg−1 for BCR-610 and SRM-2976, respectively) are in good agreement with the certified values (7.78 ± 0.13 and 1.19 ± 0.18 mg Pb kg−1 for BCR-610 and SRM-2976, respectively). T-tests were conducted in order to compare the experimental data with the certified concentrations, and no significant differences were found at a confidence level of 95% for n =3.

Nevertheless, the analysis of BCR-610 was affected by the presence of interfering ions. The content of the certified groundwater includes both transition metals (Al, Cu, Ni) and other hydride-forming elements such as As and Cd. In order to solve this drawback, potassium iodide was tested as a masking agent and added to the reducing solution, since it has been reported that the mode of KI addition has an influence on its effect as masking agent. Thus, masking effect is observed when KI was added to THB, but not when it is added to sample [24]. KI masks interferences of Cu on the analytical determination of Sb due to the formation of CuI precipitate [25]. In our experiment, no precipitate was observed. However, the use of KI improved the analytical signal of lead, leading to good recoveries of Pb in BCR-610. Recent studies on the mechanism of HG [26,27] suggest that the role of additive-analyte could be the formation of suitable analyte precursors, which are

more reactive towards THB than the analyte. This hypothesis could explain the action of KI in the analysis of BCR-610.

3.6. Application of FI-HG-AFS technique for lead determination in biological and environmental samples

It is possible to evaluate the impact of lead poisoning in aquatic systems, since the methodology proposed can be applied to lead monitoring in waters at ultratrace concentration levels. In addition, the method offers excellent analytical features. Then, Pb determinations were carried out in rain water, tap water, ground water, spring water and drinking water samples.

On the other hand, the analysis of lead in biological samples is an important tool for the monitoring of occupational and environmental health; for this reason and in order to demonstrate other applications of the developed method, human blood, plasma and serum samples were also analysed. Spiking/recovery assays were performed at different concentration levels of lead for the evaluation of matrix interferences of real samples. External calibration method was used for the FI-HG-AFS measurements to determine the amount of Pb in environmental and biological samples. Table 3 shows the spike levels and the results obtained in the analysis of these samples. In all cases, lead recoveries were between 94% and 110%. Thus, the method has been proven to be reliable for lead determination at trace levels, with excellent accuracy.

4. Comparison between FeM using FI-HG-AFS and other methods

As can be seen in Table 4, the LOD and the linear range of the FeM method were better than other methods exploiting HG-AAS [1,28] and HG-AFS[19].

However, LOD similar or

Table 3. Determination of lead in complex matrix samples by FeM method and HG-AFS.

Sample	Added ($\mu g\ L^{-1}$)	*Found ($\mu g\ L^{-1}$)	Recovery (%)
Tap water	0	0.5 ± 0.05	–
	0.5	1.04 ± 0.05	108
	2	2.50 ± 0.05	100
Rain water	0	0.16 ± 0.05	–
	0.5	0.67 ± 0.07	102
	2	2.10 ± 0.05	97
Ground water	0	0.16 ± 0.07	
	0.5	0.64 ± 0.06	96
	2	2.04 ± 0.06	94
Spring water	0	<LOQ	
	0.5	0.50 ± 0.05	100
	2	2.10 ± 0.07	105
Drinking water	0	<LOQ	
	0.5	0.50 ± 0.007	100
	1	0.97 ± 0.04	97
Human blood	0	<LOQ	–
	2	2.05 ± 0.009	102
	4	3.87 ± 0.02	97
	6	6.10 ± 0.02	102
	8	7.90 ± 0.03	99
	10	9.99 ± 0.02	100
Human serum	0	0.117 ± 0.002	–
	2	2.036 ± 0.002	96
	4	4.078 ± 0.002	99
	6	5.959 ± 0.016	97
	8	7.740 ± 0.016	95
	10	10.24 ± 0.04	101
Human plasma	0	<LOQ	–
	2	2.2 ± 0.2	110
	4	4.08 ± 0.19	102
	6	6.01 ± 0.2	100
	8	7.75 ± 0.07	97
	10	10.25 ± 0.08	102

Note: *The results are expressed as the mean of three replicates ± SD.

Table 4. Comparison between the FeM method and other methods in Pb determination by HG.

*Detection technique	Detection limit ($\mu g\ L^{-1}$)	RSD (%)	Injection frequency (h^{-1})	Sample volume (mL)	Reference
FI-HG-AAS	0.3	3	–	1	[1]
FI-HG-AAS	0.4	3.8	70	0.75	[28]
FI-HG-AFS	0.3	4.1	–	–	[23]
SPE-HG-AFS	0.016	3.4	30	11.7	[21]
SPE-HG-AFS	0.003	3.8	15	10.7	[17]
FI-HG-AFS	0.03	1.1	70	1.3	Present work

Note: *FI-HG-AAS, flow injection-HG-atomic absorption spectrometry; FI-HG-AFS, flow injection-HG-AFS; SPE-HG-AFS, solid phase extraction coupled with HG-AFS.

Lower by several orders of magnitude than those of the FeM method were found [17,21]. Moreover, these methods required high sample volumes (11.7 and 10.5 mL), since they use preconcentration procedures, reducing at the same time the injection frequency. Thus, if sample volume is a great concern, especially in the analysis of biological samples, one of the advantages of the FeM method is the low consumption of sample (1.3 mL). The linear range of FeM method was 0.1–80 µg L−1, which allows the analysis of samples in a wide range of concentrations with a high sensitivity. In addition, other analytical parameters, such as RSD (1.1%) and injection throughput of 70 h−1, were improved with the FeM method.

5. Conclusions

The methodology based on the use of potassium ferricyanide as an oxidant reagent in a FI-HG-AFS system was proved to be suitable for Pb trace level determination in a variety of environmental and biological samples. It makes of this method an attractive technique for routine determination of trace amounts of lead, with further advantages such as simplicity and lower running costs. In addition, the method offers a low detection limit, avoiding pre-concentration procedures, a wide linear range and good repeatability. On the other hand, it should be highlighted that in the determination of lead by HG it is mandatory to use additives such as oxidising and masking agents to improve the efficiency of the reactions by means of activated species intermediates to avoid chemical interferences. The addition of KI to the reducing solution was suitable for avoiding chemical interferences in BCR-610 analysis. The applicability of the technique was tested in the analysis of environmental samples such as natural waters (rain water, tap water, ground water,

spring water and drinking water) and biological matrices (blood, serum and human plasma, SRM-2976) with satisfactory results.

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