

Research Article

Trace Lead Measurement and Online Removal of Matrix Interference in Geosamples by Ion-Exchange Coupled with Flow Injection and Hydride Generation Atomic Fluorescence Spectrometry

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A flow injection method has been developed for the direct determination of free available Pb(II). The method is based on the chemical sorption of Pb(II), from pH7 solutions, on a column packed of chelating resin. The retained complex was afterwards eluted with hydrochloric acid followed by hydride generation with reduction by tetrahydroborate. The preconcentration system proposed in this paper allows the elimination of great part of the saline content in the sample. A thorough scrutiny was made for chemical variables and FI parameters. With a sampling volume of 10.5 mL, quantitative retention of Pb (II) was obtained, along with an enrichment factor of 40 and a sampling frequency of 15 h⁻¹. The detection limit, defined as 3 times the blank standard deviation (3 σ), was 0.0031 ngml⁻¹. The precision was characterized by an RSD value of 3.78% (at the 4 ng·ml⁻¹ level, $n = 11$). The developed method has been applied to the determination of trace Pb in three standard reference materials. Accuracy was assessed through comparing the results with the accepted values.

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1. Introduction

There is an ongoing need to determine lead because of its extensive distribution and high toxicity; lead is among the most toxic heavy metals for human health. The main methods for lead measurement include GFAAS [1], ICP-MS [2], and HG-AFS [3]. ICP-MS and HG-AFS have lower detection limits than GFAAS. The HG-AFS method, however, uses much simpler and cheaper equipment and therefore is more practical in laboratory use. However, despite the sensitivity and selectivity of atomic fluorescence spectrometric (AFS), there is a great necessity for the preconcentration of trace lead prior to its determination, basically due to its low concentrations or the matrix interferences in aqueous samples. To improve the sensitivity and selectivity, preconcentration procedures such as liquid-liquid extraction, precipitation coprecipitation, ion-exchange, and solid phase extraction (SPE) are generally used before the

detection. Ion-exchange technique and SPE have increasingly become popular because of its several major advantages: high enrichment/collection factors, better removal of interferent ions, high performance and rate of reaction process, and the possibility of the combination with several detections methods. Ion-exchange/SPE coupled with flow injection (FI) on-line microcolumn separation and preconcentration techniques has been proved to be a good idea. This combination not only provides an improvement in the detection limits, but also reduces the interference from matrix. The method has so far been proposed for the determination of trace lead in diverse samples. The following examples have been reported for these several years.

Lead in drinking water was preconcentrated as 2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol complexes on a minicolumn packed with Amberlite XAD-16 prior to its determination by ICP-AES using pneumatic nebulization [4]. A flow injection method using a minicolumn loaded

with 8-hydroxyquinoline immobilized on controlled pore glass was also described for the determination of trace lead along with copper, cadmium, zinc, nickel, and iron by ion chromatography [5]. On-line preconcentration and simultaneous determination of heavy metal ions in different water samples by ICP-AES were carried out using retention of diethyldithiocarbamate chelates on an octadecyl silica minicolumn [6]. A cationic resin (Chelex 100) for preconcentration and elimination of interferences was also used for the spectrophotometric determination of lead in water samples [7]. Methylthiosalicylated silica gel and chitosan were used for preconcentration of lead for ICP-AES determination [8] and spectrophotometric detection of lead-dithizone complex in aqueous medium [9], respectively. Lead in seawater was complexed with 8-hydroxyquinoline-5-sulfonic acid (8-HQS) and then collected on a mini-column filled with florisil [10]. Total lead and lead isotope ratios in natural waters were determined using sorption of lead complexes with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one on the inner walls of PTFE knotted reactor in advance of the on-line ICP-TOFMS detection [11]. Lead in wine and water was preconcentrated on a mini-column filled with polyurethane form modified with 2-(2-benzothiazolylazo)-p-cresol [12] or Pb-Spec resin [13] for the FAAS determination of lead. For the determination of lead in environmental samples, the on-line formed lead-pyrrolidinedithio carbamate complex was sorbed on the polyurethane form, subsequently eluted by 2-methyl-4-pentanone, and determined by FAAS [14]. Chelating resin, MuromacA-1 [15], and a new packing material, acrylic acid grafted PTFE fibers [16], were used for on-line of lead in urine and environmental and biological samples, respectively. Mai Kuramochi have reported the flow injection determination of lead in iron and steel [17], river water [18], glazed ceramic, and sea water [18, 19] using Pb-Spec resin for on-line preconcentration of lead and atomic spectroscopic detection. A nanometer-sized alumina packed microcolumn was used for on-line preconcentration of V, Cr, Mn, Co, Ni, Cu, Zn, Cd, and Pb in environmental samples [20]. Dimitrova-Koleva et al. [21] have developed for the separation and preconcentration of traces of Ag, Cd, Co, Ni, Pb, U, and Y from natural water samples with subsequent detection by ICP TOF MS. a PCTFE beads for on-line preconcentration of chromium (VI) and lead in water samples [22]. The detection techniques of the aforementioned reports are mostly ICP-AES and AAS; to the best of our knowledge, few research works on the use of ion-exchange coupled with flow injection and HG-AFS for the determination of trace lead.

The aim of this work was to develop a sensitive and selective FI-HG-AFS method for the determination of trace lead and to investigate the potential of this "more refined" on-line separation method for the determination. The matrix of samples is removed on-line by an FI system and a microcolumn filled with D401. The extent of interferent effect can be minimized by increasing the concentration of the analyte while keeping the interferent at a minimum. The analyte collected on the column was eluted with HCl and used to facilitate hydride generation. For the sake of improving the performance of the procedure, special

TABLE 1: Operating parameters of the AFS.

PMT-voltage	320 mv
Main lamp current	80 mA
Lamp ancillary electrode current	30 mA
Argon carrier gas flow rate	600 mlmin ⁻¹
Atomization temperature	Low (200°C)
Observation height	7 mm

attention is given to the design of FI manifolds. The detection limit of this procedure is comparable or even superior to those obtained with detection by HG-ICPMS [10, 23, 24] or HG-ETAAS [25], while a significant improvement was achieved as compared with the published FI-HG-AFS procedures [26]. The proposed method, which is convenient, low cost, and sensitive, was successfully applied to the analysis of environmental samples, and its accuracy was tested by the analysis of certified reference materials.

2. Experimental

2.1. Apparatus. An AF-610 atomic fluorescence spectrometer with a commercial gas liquid separator (Beijing Raileigh Analytic Instrument Corporation) was used, and the operating parameters of the AFS instrument are summarized in Table 1. A lead hollow cathode lamp was used as the radiation source. The hydride and hydrogen generated were separated from liquid in the first-stage gas-liquid separator (GLS1) and swept by an argon flow through the second-stage gas-liquid separator (GLS2) and finally into the atomizer, where the hydride was atomized by an argon-hydrogen flame.

The flow injection analytical system applied was a JTY-1B FI multifunction solution autohandling system (Faculty of Material Science and Chemical Engineering, China University of Geosciences). Figure 1 shows the manifold for on-line ion-exchange used in this study. The manifold program for this FI system is showed in Table 2. All the tubes used were 1 mm i.d. PTFE tubing.

2.2. Reagents. All chemicals were of analytical reagent, and deionized water was used throughout. Working standard solutions of lead were prepared by appropriate stepwise dilution of a 1000 mg l⁻¹ stock standard solution to the required $\mu\text{g l}^{-1}$ levels just before use. A 10 g l⁻¹ sodium tetraborate solution containing 20 g l⁻¹ potassium ferricyanide (K₃Fe(CN)₆) was prepared by dissolving the NaBH₄ and K₃Fe(CN)₆ reagent in 2 g l⁻¹ sodium hydroxide solution just before use; 3% HCl (v/v) solution was used as eluent.

5% NaOH (m/v) solution and 10% (m/v) sulfocarbamide solution were also used in this work.

The ion-exchange resin minicolumns were built up by packing the D401 Chelating resin (about 0.08 g, 60 mesh) into a 3.0 cm × 2.0 mm i.d Teflon tube. Plug of glass wools was placed at both ends of the column to avoid resin loss during system operation.

2.3. Sample Pretreatment. Three certified reference materials, GSD-8, GBW-07114, and GSD-6 (National Center

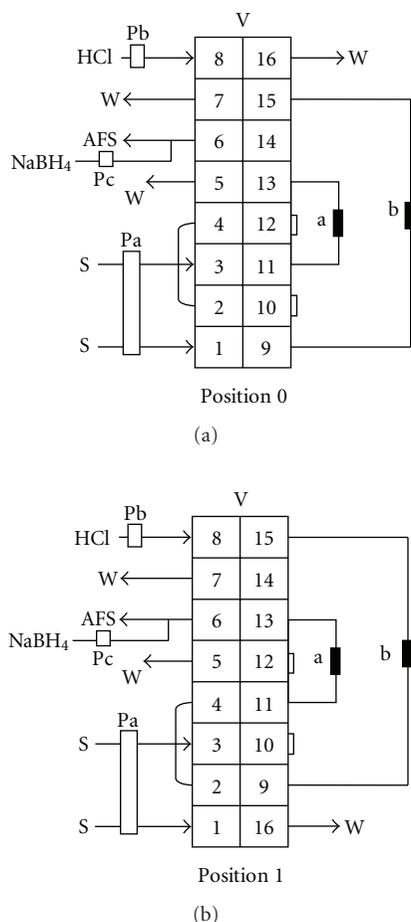


FIGURE 1: Diagram of the flow system used to pre-concentration and determination of lead by ion-exchange coupled with HG-AFS, (a) the sample load process and (b) the elution process. Pa, Pb and Pc, peristaltic pumps; V, 8 channel rotary injection valve; S, sample; a and b, microcolumns; T, T-tube; W, waste.

for Standard Materials, Beijing, China), were used for the validation of the developed methodology.

0.5000 g of the sample was precisely weighed into a 30 ml PTFE crucible was wetted by 5 mL of hydrofluoric acid, and followed by 7 mL of concentrated hydrofluoric acid and 2 mL of perchloric acid, heating up for 10~20 minutes at low temperature on a sand bath till dense white fumes appeared. After cooling, 3 ml of nitric acid was added. It was again heated to the appearance of the dense white fumes. After cooling, 4 ml of 50% HCl (v/v) was added to the crucible to dissolve the residue; the final digests of the solid samples were adjusted to pH = 7 with 5% NaOH (m/v) solution and diluted to the mark with water in a 100 ml volumetric flask.

A calibration graph was plotted for standards of each sample. Standards and analytical blanks were treated in the same way as the samples.

2.4. Operating Procedure. The diagram of the FI manifold and its operational sequence are represented in Figure 1 and Table 2, respectively. In step 1, the sample was pumped

through the microcolumn. The sampling volume is controlled by the sampling time. In the next step, the column was washed with deionized water to remove any salt residues coming from the matrix. In step 3, the analyte adsorbed in the column was eluted with HCl (3% v/v) solution and led into the gas-liquid separator. After the determination, the columns were washed with deionized water to return it to the condition in preparation for loading the next sample.

The flow system used was operated in the time-based mode and deionized water served as the carrier stream.

3. Results and Discussion

In order to achieve the most of efficient performance in terms of highest analytical sensitivity and lowest deviation of signals (measurement precision), some experimental parameters were investigated. After an initial assessment to select approximate values for each parameter, optimization of the variables was carried out by the univariate method.

3.1. Development of the Flow Injection Ion-Exchange Manifold. The flow system in our work is optimized to achieve a better enrichment efficiency and detection limit. In previous reports, the FI ion-exchange manifold was designed to pre-concentration of metal ions using a single column, which is tedious and time-consuming, causing the enrichment factor and sampling frequency hard to improve. To solve the problem, the double column system is used in this paper: the sample was pumped through columns a, and b simultaneously (Figure 1), in the stage of elution; eluent was pumped through columns a, and b in series. The comparison experiments showed that signal peak of the double column system is twice of the single column system's.

Before elution step, air is used to push out the waste water of the loop, which is the improvement of the manifold in our work. With this amelioration, the sensitivity and reproducibility are improved effectively. Table 3 showed the fluorescence intensity of 10 ngml⁻¹ lead solution obtained with different two eluting process by HG-AFS determination in the same condition.

3.2. The AFS Parameters. The AFS parameters, including lamp current, atomizer height, negative high voltage of the photomultiplier, carrier argon flow, were investigated in the term of sensitivity and reproducibility. The optimized parameters were summarized in Table 1.

3.3. The Choice of the Resin and the Medium of Hydride Generation. In this paper, D401 chelating resin is used as the ion-exchanger of lead; experiments show that the 60 mesh resin has the optimal enrichment efficiency. HCl solution was chosen for eluting lead and the medium of hydride generation.

With NaBH₄ as reducing reagent, its concentration affects significantly the hydride generation. The results showed that an enhancement of the signal was observed with the increase of NaBH₄ concentration up to 1.5% (w/v), while an even higher concentration led to a deterioration of the

TABLE 2: The operating program of the FI ion-exchange system.

Step	Times (s)		Pump rate (mlmin ⁻¹)		Valve position	Description
	Pa	Pb	Pa	Pb		
0	180	180	3.5	0	0	Pa is active, sample load and lead are preconcentration in columns a, and b
1	1	1	0	0	0	Pa stops; sample loops dip into water
2	10	10	3.5	0	0	Water pushes the remain sample of the loop to pass through the columns
3	5	5	0	2	1	Pb is active; remain water of the loop is pushed out by air
4	1	1	0	0	1	Pa stops; sample loops dip into the eluent
5	20	20	0	2	1	Pa drives eluent to pass through b and a in series
6	20	20	0	7	1	Pb and Pc are active; sample is reacted with NaBH ₄ and pushed to AFS for determination.
7	2	2	4	0	0	Tube is washed by water

TABLE 3: Comparison of different eluting process (4 ngml⁻¹ Pb).

Type	Fluorescence intensity	RSD (% <i>n</i> = 10)
With the step of air pushing out water	765	3.5
Without the step of air pushing out water	586	8.8

sensitivity. Considering the sensitivity and saving reagents, a concentration of 1% (w/v) was therefore employed.

3.4. Optimization of the Chemical Variables.

3.4.1. The Effect of Sample Acidity on the Retention of Lead.

A 4 ngml⁻¹ lead standard solution was used to optimize the acidity of the sample. The sample acidity was adjusted with hydrochloric acid within the range of 0~8% (0, 0.2%, 0.4%, 0.8% 2%, 4%, 8%, v/v). The results are shown in Figure 2. Figure 2 indicates that the maximum retention of lead occurs in neutral media, and the fluorescence intensity is declined markedly between 0~0.8% HCl. However, the retention is not changed markedly between 0.8~8% HCl. The explanation is that the chelating agent becomes a chelating form in alkaline medium, while it is preferentially H⁺ when the pH is low. In our subsequent experiments, pH7 was selected.

3.4.2. Eluting Acid Concentration and Speed. The lead chelate adsorbed on the column could be eluted by hydrochloric acid of different concentrations and at different eluting speeds. The results (Figure 3) has shown that the signal increased as the HCl concentration increased to 4%, then a small decrease was obtained in the range 4~14%. The decrease of the signal at concentrations higher than 4% may be due to the dilution of the analyte by the excessive generation

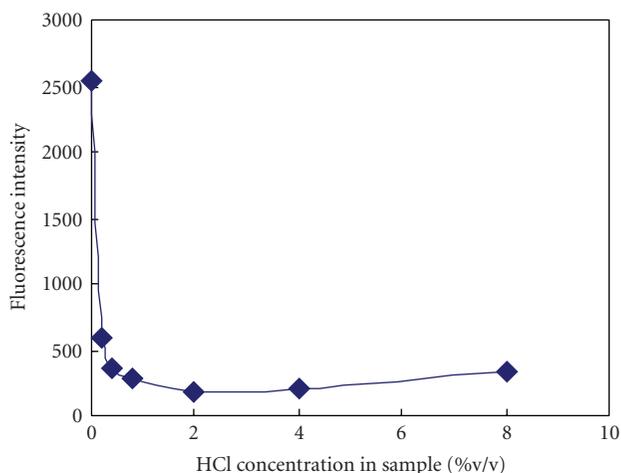


FIGURE 2: Effects of sample acid concentration on chelating reaction between Pb and speed (4 ngml⁻¹ Pb solution; 180 seconds sample load time; injection speed 3.5 mlmin⁻¹; 10 seconds washing time).

of hydrogen, which is byproduct of the hydride generation reaction. Although the maximum of the signal has occurred at the HCl concentration of 4%, the generation of hydride of lead derived a better efficiency in the range 1%~3% (HCl, v/v), and taking into account the acidity of eluting and the acidity of hydride generation, 3% HCl was selected throughout.

The effect of the eluting is similarly examined within the range 2~7 mlmin⁻¹, the results (Figure 4) indicated that the determination signal reached a maximum at a 1 mlmin⁻¹, and the sensitivity was dropped with the increase of the eluting speed to 3 mlmin⁻¹, while afterwards the curve was leveled off and only a small change was obtained within the range of 3~5 mlmin⁻¹. At higher eluting speed, a significant decrease of the signal was observed. Although a lower speed is preferential for the effective eluting, it took a longer time and sacrificed the sampling frequency. As mentioned above that flow resistance was frequently encountered by employing

TABLE 4: Performance data for the on-line ion-exchange pre-concentration HG-AFS system.

Calibration graph, 0–10 $\mu\text{g}\cdot\text{l}^{-1}$	
Regression equation (fluorescence intensity versus concentration ($\mu\text{g}\cdot\text{l}^{-1}$))	$Y = 102.33x + 13.52$
Correlation coefficient	0.9991
Sampling frequency	15 h^{-1}
Enrichment factor	40
Detection limit (3σ)	$0.0031 \text{ ng}\cdot\text{ml}^{-1}$
Relative standard deviation ($4 \text{ ng}\cdot\text{ml}^{-1}$ of Pb, $n = 11$)	3.78%
Sampling consumption	10.5 mL

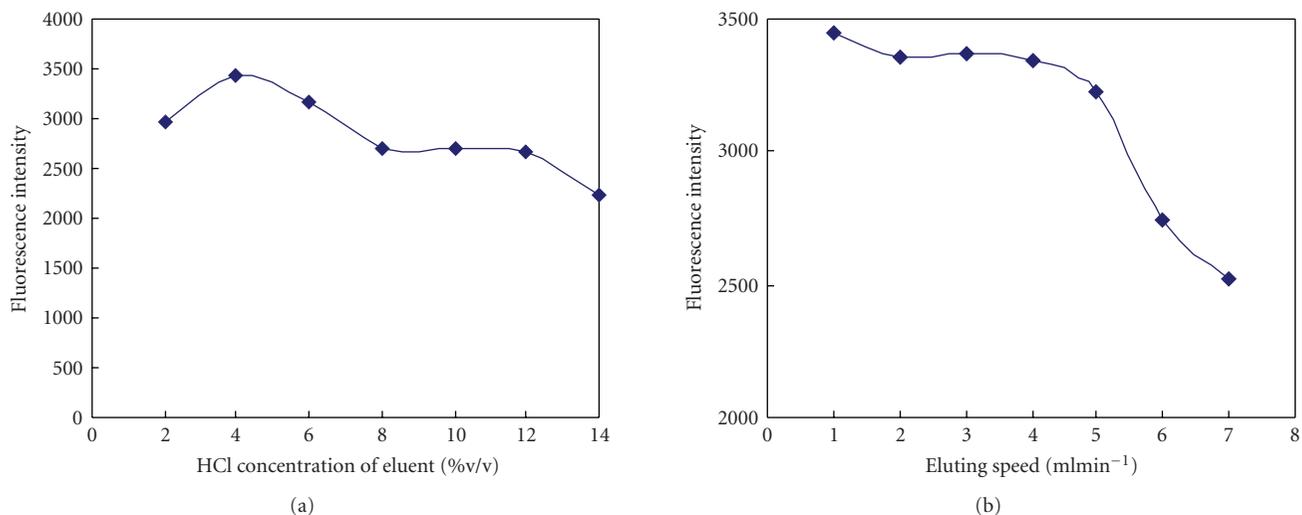


FIGURE 3: (a) Effects of eluent acid concentrations and eluting speed (4 ngml^{-1} Pb solution; 180 seconds sample load time; injection speed 3.5 mlmin^{-1} ; 10 seconds washing time). (a) Different concentrations of HCl versus signal of pb. (b) eluting speed versus signal of pb, eluting with 3% HCl.

TABLE 5: Analysis of reference material ($\omega(\mu\text{g}\cdot\text{g}^{-1})$, $n = 10$).

Sample	Recommended value	Founded values	RSD (%)
GSD-8	20.0	18.2	4.8
GBW-07114	4.4	4.1	5.2
GSD-6	27.0	25.6	4.6

higher flow rates. As a compromise, a eluting speed of 3 mlmin^{-1} was employed for further experiments. The speed of NaBH_4 solutions during hydride generation was also optimized, by adopting an identical speed for the two streams.

3.4.3. Sampling Time and Speed. The sample load time and injection speed were optimized for achieving adequate enriching times of lead in the column. The results has shown that, with sample load time increasing, the signal almost increased linearly at a constant injection speed. Although the enrichment factor for lead in the column could be improved for a longer sample load time, the analytical time is also prolonged, and the consumption of reagents increases at the same time. For these reasons, the sample load time was set at 180 seconds. For a 180 seconds sample loading time,

the results of a sample injection speed test are shown in Figure 4. At first, the signal increased with injection speed, but the increment of signal decreased when the injection speed increased more rapidly ($> 3 \dots 5 \text{ mlmin}^{-1}$). This result was explained that with injection speed increasing, the lead chelate could not be taken in the column because of the shortened time of adsorption between the chelate and sorbent in the column. Thus, an injection speed of 3.5 mlmin^{-1} was selected.

3.5. Interferences. The potential interfering effects of some foreign species, which are frequently encountered in geosamples, were tested with the present procedure. At a Pb concentration of 10 ng/ml , Fe ($5 \mu\text{g/ml}$); Cr, Ca, Zr, V ($500 \mu\text{g/ml}$); Al (5 mg/ml); As^{3+} , Se^{2+} ($50 \mu\text{g/ml}$); Cu, Ni ($100 \mu\text{g/ml}$) did not interfere with the determination (no tests for more higher concentration levels). For general geosamples, the contents of the above metal ions in sample digests or after appropriate dilution will not exceed the tolerant concentration levels. If the contents of Fe and Cu exceed the tolerant concentration levels, they can be masked by 10% (m/v) sulfocarbamide solution. So in most cases, the present procedure can be directly employed, and no further treatment of masking reagents are needed.

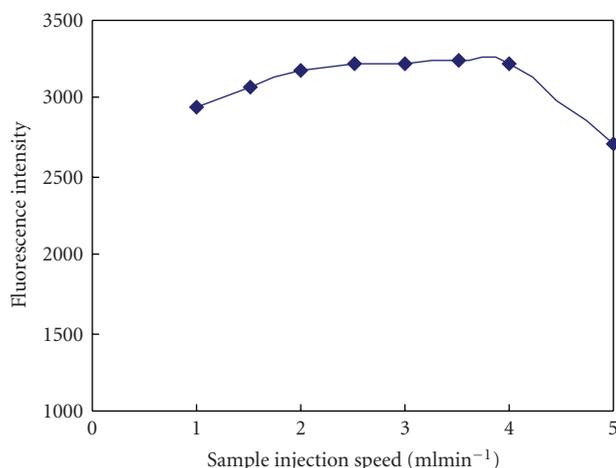


FIGURE 4: Sample injection speed (4 ngml⁻¹ Pb solution; pH 7; washing with water for 10 seconds; 180 seconds sample load time; eluting with 3% HCl).

3.6. Performance and Validation of the Procedure. Under the optimal conditions, the performance data obtained for the flow injection on-line ion-exchange preconcentration system for Pb with hydride generation atomic fluorescence spectrometry were summarized in Table 4. With a sample loading volume of 10.5 ml and a retention time of 180 seconds, an enrichment factor of 40 and a sampling frequency of 15 h⁻¹ was obtained. The detection limit (3σ) was (0.0031 ng·ml⁻¹) and the relative standard deviation (RSD) was 3.78% ($n = 11$) at the 4 ng·ml⁻¹ level.

At a similar precision level, a comparison of the detection limit of the present procedure with the reported one [26] (8 ng l⁻¹) based on hydride generation protocol with detection by AFS has shown that the detection limit of the present protocol (3.1 ng l⁻¹) is superior to the published procedures. Namely, the method of this paper was much improved with respect to the HG-AFS-based procedures. The procedure was validated using certified reference materials, that is, GSD-8, GBW-07114, and GSD-6. The obtained results were summarized in Table 5 with an agreement between the obtained results and the certified values.

4. Conclusions

A method of on-line FI separation system coupled with HG-AFS for the determination of sup-trace lead in geosamples has been developed. Parameters of the operation system including pH value of chelating reaction, sample loading time and injection speed, eluting acid concentration and eluting speed, and instrumental parameters of HG-AFS were optimized and selected. The detection limit of this method estimated as 3x standard deviation of the procedural blank was 3.1 ng l⁻¹. Three standard reference materials were used to assess the accuracy of the method. The Pb concentration measured was in good agreement with the certified value; this method can be used to determine the sup-trace lead in high-salt samples.

Acknowledgments

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