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Determination of lead by electrothermal atomic absorption spectrometry using ionic liquid single drop microextraction

Saeid Nazari

Department of Chemistry, Faculty of Science, Sabzevar Tarbiat Moallem University, Sabzevar, (IRAN)

E-mail: nazari@sttu.ac.ir; nazari@chemist.com

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ABSTRACT

A simple and efficient method for rapid extraction and determination of the trace levels of lead was developed by single drop microextraction combined with electrothermal atomic absorption spectrometry detection. 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) was used as both extractant and chemical modifier and ionic liquid, 1-butyl-4-methylpyridinium trifluoromethylsulfonate [BMPy][TfO] as the extraction solvent. Lead was complexed with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) and extracted into a 4 μ L ionic liquid drop. The extracted complex was directly injected into the graphite furnace. Several factors that influence the microextraction efficiency, such as type and volume of organic solvent, pH, concentration of chelating agent, extraction time, stirring rate and effect of salt were investigated and the optimized microextraction conditions were established. Under the optimum conditions, the enrichment factor and recovery were 465 and 93%, respectively. The calibration graph was linear in the range of 0.02- 1 μ g L⁻¹ with correlation coefficient of 0.9987 under the optimum conditions of the recommended procedure. The detection limit based on the 3S_p criterion was 0.008 μ g L⁻¹ and relative standard deviation for (RSD) for ten replicate measurement of 0.1 μ g L⁻¹ and 0.3 μ g L⁻¹ lead was 4.2 and 3.5% respectively. The characteristic concentration was 0.007 μ g L⁻¹ equivalent to a characteristic mass of 28 pg. The results for determination of lead in reference materials local tap water, river and well water demonstrated the accuracy, recovery and applicability of the presented method.

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KEYWORDS

Ionic liquid;
Single drop microextraction;
Preconcentration;
Electrothermal atomic
absorption spectrometry;
Lead.

INTRODUCTION

Lead is used in building construction, lead-acid batteries, bullets and shot, weights, and is part of solder, pewter, fusible alloys and radiation shields. Lead poisoning (also known as plumbism, colica pictonium, saturnism, Devon colic, or painter's colic) is a medical

condition caused by increased levels of the heavy metal lead in the body. Lead interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing potentially per-

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manent learning and behavior disorders. Symptoms include abdominal pain, headache, anemia, irritability, and in severe cases seizures, coma, and death. Routes of exposure to lead include contaminated air, water, soil, food, and consumer products. Occupational exposure is a common cause of lead poisoning in adults. One of the largest threats to children is lead paint that exists in many homes, especially older ones; thus children in older housing with chipping paint are at greater risk. Prevention of lead exposure can range from individual efforts (e.g. removing lead-containing items such as piping or blinds from the home) to nationwide policies (e.g. laws that ban lead in products or reduce allowable levels in water or soil).

Humans have been mining and using this heavy metal for thousands of years, poisoning themselves in the process. Although lead poisoning is one of the oldest known work and environmental hazards, the modern understanding of the small amount of lead necessary to cause harm did not come about until the latter half of the 20th century. No safe threshold for lead exposure has been discovered—that is, there is no known amount of lead that is too small to cause the body harm.

Therefore it is important to monitor the levels of lead in environments. Several analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS)^[1], ICP-atomic spectrometry^[2,3], electrothermal atomic absorption spectrometry^[4] and flame atomic absorption spectrometry (FAAS)^[5] have been widely used for the determination of trace metal in different samples.

Although the development of modern analytical instruments allows great enhancement in aspects of analysis, in many cases the available analytical instrumentation does not have enough sensitivity for the analysis of natural samples. Sample preparation is still a bottleneck for overall throughput because the steps involved often employ large volumes of hazardous organic solvents, are time consuming and/or expensive. Besides, there might also be the problem of contamination and sample loss. As a consequence, different preconcentration techniques used for separation and preconcentration of trace lead such as liquid-liquid extraction^[6], cloud point extraction^[7,8], solid phase extraction^[9-13] and electrochemical deposition^[14], etc.

The solvent microextraction technique effectively

overcomes these difficulties by reducing the amount of organic solvent and by allowing sample extraction and preconcentration to be done in a single step. The technique is faster and simpler than conventional methods. It is also inexpensive, sensitive and effective for the removal of interfering matrix. Solvent microextraction is a form of solvent extraction with phase ratio values higher than 100^[15-19]. This technique uses simple equipment which is found in most analytical laboratories and also has been used for sample preparation of organic components and has coupled with chromatography methods. We developed this technique in our laboratory and reported for the first time on the coupling of liquid phase microextraction (LPME) with spectrometry to determine inorganic compounds. Using this technique, arsenic in variety of samples was determined^[15].

Recently, room temperature ionic liquids (RTILs) have aroused increasing interest for their promising role as alternative media in synthesis, separation and electrochemistry, etc^[20,21] as a result of their unique chemical and physical properties. RTILs can dissolve a wide spectrum of organic, organometallic, and inorganic compounds. Also, they have no detectable vapor pressure and are relatively thermal stable. So, there is no loss of solvent through evaporation with ionic RTILs^[22]. This will avoid environmental and safety problems due to volatilization, as is the case in traditional organic solvents. Therefore, they are proposed as novel solvent systems to replace traditional solvents that are generally toxic, flammable, and volatile. RTILs are regarded to have the potential to be alternative reaction media for “Green Chemistry”^[23]. Ionic liquid based liquid phase microextraction (IL-LPME) has also been applied to extract different organic compounds, and shows some advantages over conventional extraction techniques, such as fast, easy to operate and avoiding highly toxic chlorinated solvent^[24-26]. However, there were few reports on the application of IL-LPME for the preconcentration of metal ions^[27,28].

In this work, a typical ionic liquid of 1-butyl-4-methylpyridinium trifluoromethylsulfonate, [BMPy][TfO] was adopted as extraction solvent for single drop microextraction of Pb. 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) was employed as the extractant to extract metal ions from aqueous solution into [BMPy][TfO] and also as the chemical modifier

for the subsequent graphite furnace atomic absorption spectrometry determination. The developed method was applied to the determination of trace Pb in environmental samples.

EXPERIMENTAL

Instrumentation

A Shimadzu model AA-6300G atomic absorption spectrometer (Kyoto, Japan) with GFA-EX7i graphite furnace atomizer and D2 lamp for background correction was used. A lead hollow cathode lamp (Hamamatsu photonics, Kyoto, Japan) was used as the radiation source adjusted at the operating current at the wavelength of 283.3 nm with 0.7 nm spectral bandpass. All measurements were performed using peak height and gas stop mode. The measurement conditions are given in TABLE 1. All pH measurements were made by a Metrohm digital pH meter (model: 691, Herisua, Switzerland) with a combined glass electrode.

TABLE 1 : Applied conditions for determination of lead using SDME-GFAAS

Optimum analytical conditions				
Lamp current	10 mA			
Wavelength	283.3 nm			
Spectral bandwidth	0.7 nm			
Signal processing	peak height			
Purge gas	Ar			
Back ground correction	D ₂			
GFA heating programme				
Stage	Furnace temperature (°C)	Mode	Time (s)	Ar flow rate (L min ⁻¹)
Drying	120	ramp	15	1.5
Ashing	400	step	15	1.5
Atomization	1800	step	3	gas stop
Clean up	2500	step	2	1.5

A 10 µl Hamilton 7105 syringe (Hamilton, Reno, NV, USA) was used to suspend the drop of the acceptor phase and to inject it into the graphite furnace atomizer. Samples were stirred in 5 ml flat-bottom vial containing Teflon-line septa using an electronic magnetic stirrer (VWR Scientific, West Chester, PA, USA).

Reagents

All reagents used were at least of analytical grade.

Water was deionized to a resistivity of 18MΩcm in a Milli-Q system (Millipore, Bedford, MA, USA). A lead stock solution (1000 mg L⁻¹ Pb) was prepared dissolving high-purity Pb(NO₃)₂ (SPEX, Eddison, NJ, USA). Working solutions were prepared daily in 1% (v/v) HNO₃ by proper dilution of the stock solution. The chelating agent, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) was supplied from Merck. 1-butyl-4-methylpyridinium trifluoromethylsulfonate [BMPy][TfO] was purchased from Merck (Darmstadt, Germany) and used as obtained.

The chelating agent, 1 × 10⁻³ mol L⁻¹ solutions of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) were prepared by dissolving appropriate amount of PMBP (analytical grade, Merck) in methanol (Merck).

Sample preparation

Tap, river and well water samples were collected in acid-leached polyethylene bottles. Sabzevar tap water sample was collected from our Laboratory (Sabzevar Tarbiat Moallem University, Sabzevar). The river water samples were collected from Atrak in Khorasan Province. The well water sample was collected from Sabzevar Tarbiat Moallem University in Sabzevar. The only pretreatment was acidification to pH 2 with nitric acid, which was performed immediately after collection, in order to prevent adsorption of the metal ions on the flask walls. They were stored in a dark place at 4 °C and analyzed within 24 h of collection without previous treatment or filtration. After sampling, they were filtered through acid cleaned 0.22 µm pore size membrane filters (Millipore Corporation, Bedford, MA, USA) and stored in polypropylene bottles at 4 °C. Standard reference materials NIST 1640 (National Institute of Standard and Technology NIST, USA), JB-1, JB-1a and JB-2 as powder obtained from geological survey of Japan (GSJ) were used for validation of the method. The powder was dissolved in 15 ml of a mixture of 500 ml HF, 165 ml H₂SO₄ and 40 ml HNO₃ at 150 °C in a teflon beaker overnight.

Extraction procedure

Two ml of lead solution was adjusted at pH=5 and transferred to a 5 ml vial with a PTFE septum and a 6 mm magnetic bar. Then 100 µL 1 × 10⁻⁴ mol L⁻¹ PMBP solution was added. The vial was placed on a magnetic stirrer with a stirring rate of 600 rpm. A 4 µl of

Full Paper

[BMPy][TfO] was taken by the Hamilton syringe whose needle was used to pierce the vial septum. The syringe was clamped in such a way that the tip of the needle was located at a fixed position in the sample solution. The syringe plunger was depressed to expose the drop and the stirring commenced.

The Pb-PMBP complex was extracted from aqueous solution into the [BMPy][TfO] single drop. After the extraction, the microdrop was retracted and directly injected into the graphite furnace tube for subsequent determinations.

RESULTS AND DISCUSSION

Influence of type of modifiers

Several modifiers containing Pd, Ru, Rh, Ir, V, Mo, W, Ni, Mg, Ascorbic acid, separately or in their combinations, were tested. Mg modifier was used by injecting 0.2% Mg and sample solution with equal volumes. [(W.Pd)(c)+Pd(i)] modifiers were used for coating containing 40 μg of each of W and Pd from 0.1% of their solutions at temperatures of 2300°C and 2100°C respectively and injecting 10 μl of 0.1% (w/v) Pd on top of 10 μl sample solution (without extraction). [Pd(c)+Pd(i)] modifier was used as coating of 60 μg Pd onto the graphite tube at 1800°C and injecting of 10 μl solution of 0.1% (w/v) Pd on top of 10 μl of sample solution. [W.Pd.Mg](c) modifier was used as coating of 40 μg of each of W, Pd and Mg solution at the appropriate temperatures. Added of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) to lead solution in direct injection without preconcentration step has increased the signal. PMBP showed the best results in contrast to [(W.Pd)(c)+Pd(i)], [Pd(c)+Pd(i)] and [W.Pd.Mg](c) for direct determination of lead. PMBP was employed as the extractant to extract metal ions from aqueous solution into microdrop and also as the chemical modifier for the subsequent graphite furnace atomic absorption spectrometry determination.

Influence of the sample pH

It is important to evaluate the effect of pH on the extraction efficiency of lead. The effect of pH on the complex formation and extraction of lead from water samples was studied within the range of 2.0 -10.0. Figure 1 shows the influence of pH on the extraction of

Pb- complex with [BMPy][TfO] as extraction solvent. As can be seen in Figure 1, the extraction system provided highest efficiency at pH of 4.0. In order to obtain much larger enrichment factor and satisfactory precision, pH 4.0 was chosen for the subsequent analysis.

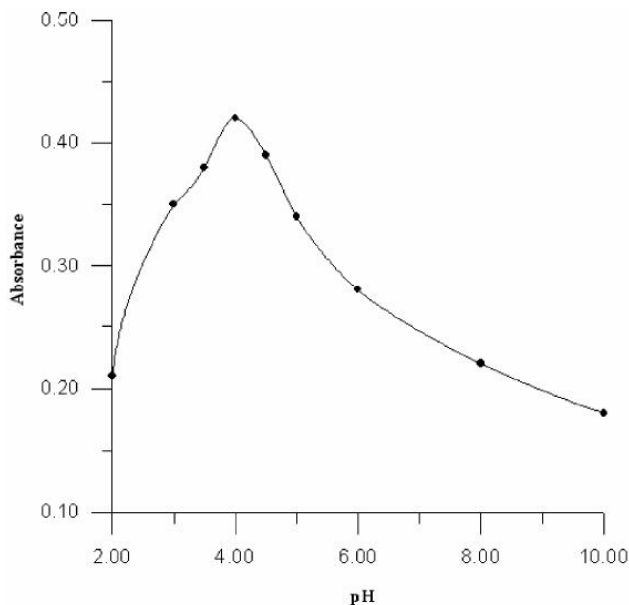


Figure 1 : Influence of pH on the absorbance of lead obtained from SDME.

Influence of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP)

The influence of the concentration of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone in the aqueous solution on the lead complex formation was investigated for 0.1 $\mu\text{g L}^{-1}$ solution of lead extracted for 8 minutes and the results are shown in Figure 2. The absorbance signal increased with increasing concentrations from 0.1 to 4×10^{-4} mol L^{-1} , as a result of the high extraction efficiency of the Pb-complex to [BMPy][TfO] microdrop. For concentrations above 4×10^{-4} mol L^{-1} , the absorbance remained unchanged, as excess did not improve extraction efficiency or mass transfer. Thus, 4×10^{-4} mol L^{-1} was employed as the optimum concentration of PMBP.

Influence of droplet volume

One of the important factors in SDME, which has great influence on the extraction efficiency, is the volume of the microdrop. The influence of drop size was investigated in the range of 1-4 μl . The signal enhanced with increases the microdrop volume. When drop size

exceeded 4 μL , it became too unstable to be suspended at the needle tip. For this reason, 4 μL drop volume was used for further studies.

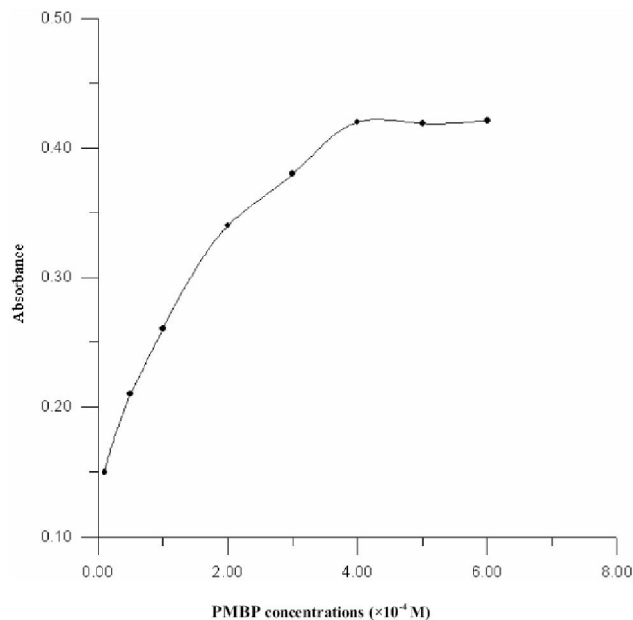


Figure 2 : Influence of concentration of PMBP on the absorbance of lead obtained from SDME.

Influence of stirring rate

Magnetic stirring was used to facilitate the mass transfer process and thus improve the extraction efficiency. According to film theory, convective–diffusive mass transfer at high stirring rate diminishes the thickness of static solution layer around drop, leading to a better mass transfer between the sample solution and the extracting microdrop. The stirring rate was optimized for extraction process. Figure 3 illustrates the effects of stirring rate on the enrichment factor increased with increasing of the stirring rate up to 600 rpm, because, in high stirring rate, a relatively large vortex is formed in the lower region of the organic solvent, but instability of droplet limited the phenomenon, thus 600 rpm was chosen for further experiment.

Influence of extraction time

Mass transfer is a time-dependent process and the maximum absorbance signal is attained when the system is at equilibrium. Therefore, the extraction time plays a very essential role in the whole process. The dependence of extraction efficiency upon extraction time was studied within a range of 2–12 minute in the constant experimental conditions. All measurements were car-

ried out with $0.1 \mu\text{g L}^{-1}$ lead. Figure 4 shows the absorbance of lead versus extraction time. The results showed an increase of the lead absorbance up to 8 minute and leveling off at higher extraction time. Therefore, 8 minutes was used as the optimum extraction time.

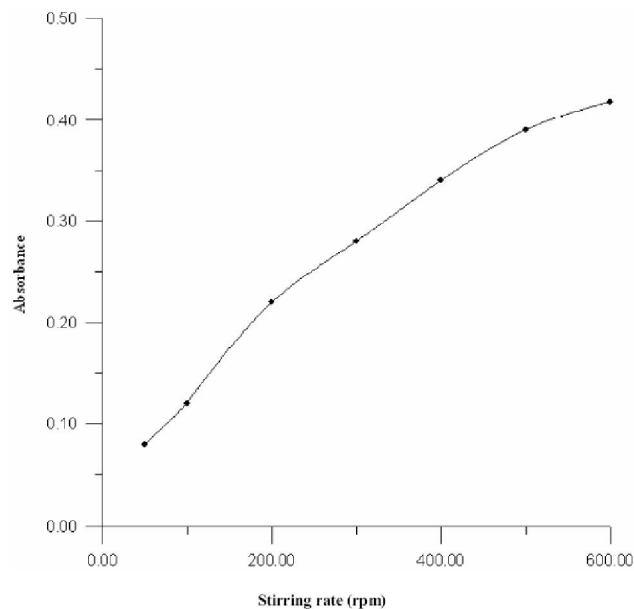


Figure 3 : Influence of stirring rate on the absorbance of lead obtained from SDME.

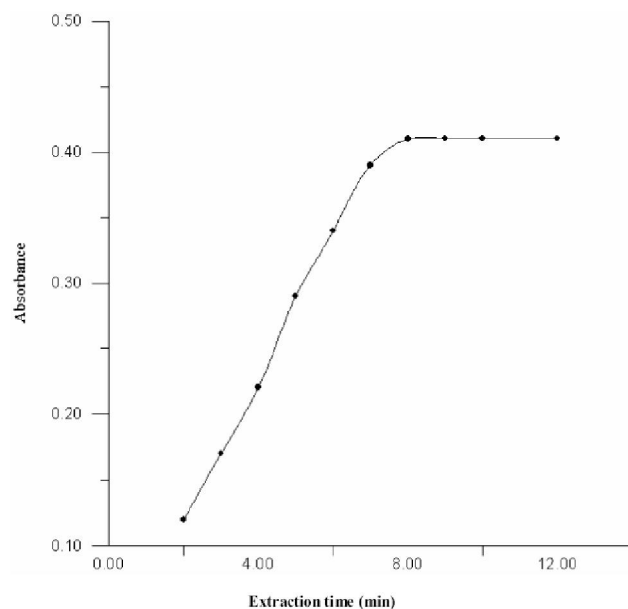


Figure 4 : Influence of extraction time on the absorbance of lead obtained from SDME.

Influence of ionic strength of solution

Addition of salt to the solution may have several effects on extraction. More commonly, the presence of salt increases the ionic strength of the solution and affects

Full Paper

the solubility of analyte. Extraction is usually enhanced with increasing salt concentration and increased polarity of the compound (salting-out effect). The influence of ionic strength was evaluated at 0-5% (w/v) NaCl levels while other parameters were kept constant. Salt addition has no significantly effect on extraction recovery. Therefore, all the extraction experiments were carried out without adding salt.

Influence of foreign ions

Preconcentration procedures for trace elements in the high salt content samples can be strongly affected by the matrix constituents of the sample. The influence

TABLE 2 : Effect of interferences on the recovery of 0.1 $\mu\text{g L}^{-1}$ Pb(II) in water sample using SDME-GFAAS

Interferent	Concentration ($\mu\text{g L}^{-1}$)	Interferent/Pb(II) ratio	Recovery (%)
Na ⁺	1,000	10,000	99.5
Li ⁺	100	1,000	100.5
K ⁺	100	1,000	101.2
Ca ²⁺	100	1,000	100.3
Mg ²⁺	100	1,000	99.8
Ba ²⁺	100	1,000	101.0
Bi ³⁺	100	1,000	99.3
Mn ²⁺	100	1,000	98.3
Co ²⁺	100	1,000	101.5
Al ³⁺	100	1,000	98.8
Fe ²⁺	100	1,000	99.5
Fe ³⁺	100	1,000	99.8
Ni ²⁺	100	1,000	99.6
Sn ⁴⁺	100	1,000	98.9
Zn ²⁺	100	1,000	100.4
Cr ³⁺	100	1,000	99.1
Ag ⁺	30	300	99.2
Cd ²⁺	30	300	98.8
Cu ²⁺	30	300	98.9
Si ⁴⁺	30	300	99.7
Hg ²⁺	10	100	98.8
Cl ⁻	1,000	10,000	99.5
Br ⁻	1,000	10,000	98.4
NO ₃ ⁻	100	1,000	100.5
CH ₃ COO ⁻	100	1,000	99.8
SCN ⁻	100	1,000	99.7
SO ₄ ²⁻	100	1,000	100.2
CO ₃ ²⁻	100	1,000	99.3
PO ₄ ³⁻	100	1,000	99.7
S ₂ O ₈ ²⁻	100	1,000	99.7
SeO ₃ ²⁻	100	1,000	99.4

of the common co-existing ions in natural water samples on the lead recovery was investigated. For this purpose, according to the recommended procedure, 2 ml of solution that contains 0.1 $\mu\text{g L}^{-1}$ of lead and various amounts from interfering ions, were preconcentrated and determined. A given species was considered to interfere if it resulted in a $\pm 5\%$ variation of the GFAAS signal. The results are summarized in TABLE 2, proving that the lead recoveries were almost quantitative in the presence of an excessive amount of the possible interfering cations and anions.

Analytical figure of merits

Under the optimum conditions described above, the analytical performance characteristics of the proposed method are listed in TABLE 3.

TABLE 3 : Analytical characteristics of SDME-GFAAS for determination of lead.

Parameter	Analytical feature
Linear range ($\mu\text{g L}^{-1}$)	0.02- 1
Correlation coefficient (r^2)	0.9987
Limit of detection ($\mu\text{g L}^{-1}$)(3σ , $n=10$)	0.008
Repeatability (RSD %) ($n=10$, 0.1 $\mu\text{g L}^{-1}$)	4.2
Repeatability (RSD %) ($n=10$, 0.3 $\mu\text{g L}^{-1}$)	3.5
Enrichment factor (EF) ^a	465
Sample Volume (ml)	2
Sample introduction Volume (μl)	4
Sample preparation time (min)	8
Recovery (%)	93

^a Enrichment factor is the slope ratio of calibration graph after and before extraction.

Calibration curve was calculated based on 2 ml of aqueous solution of lead treated at the optimized conditions. A linear calibration graph was obtained over the range of 0.02 to 1 $\mu\text{g L}^{-1}$ lead after preconcentration with a calibration curve slope of 0.33 $\text{L } \mu\text{g}^{-1}$ and correlation coefficient of 0.9987. The detection limit was calculated as three times the standard deviation of the peak absorbance for injection of 4 μl of ten extractions of the blank, using the single drop microextraction procedure. The detection limit was calculated to be 0.008 $\mu\text{g L}^{-1}$ with absolute value of 32 fg for 4 μl injection into the graphite furnace. The relative standard deviation for (RSD) for ten replicate measurement of 0.1 $\mu\text{g L}^{-1}$ and 0.3 $\mu\text{g L}^{-1}$ lead was 4.2 and 3.5% respectively. The

characteristic concentration was $0.007 \mu\text{g L}^{-1}$ equivalent to a characteristic mass of 28 pg. The enrichment factor (EF) was obtained from the slope ratio of calibration graph after and before extraction, which was about 465. The extraction recovery (R%) was 93% which was calculated by equation (1).

$$R\% = (V_{\text{drop}} / V_{\text{solution}}) \times EF \times 100 \quad (1)$$

Application

In order to establish the validity of the proposed procedure, the method has been applied to the determination of lead in standard reference materials NIST 1640 (National Institute of Standard and Technology NIST, USA), JB-1, JB-1a and JB-2 as powder obtained from geological survey of Japan (GSJ). The powder was dissolved in 15 ml of a mixture of 500 ml HF, 165 ml H₂SO₄ and 40 ml HNO₃ at 150 °C in a teflon beaker overnight. To show the applicability of the method, local tap water, river and well water were analysed for its lead content. The results obtained are presented in TABLE 4.

TABLE 4 : Results (mean \pm standard deviation based on eight replicate analysis) of determination of lead in reference materials and water samples.

Sample	Lead added ($\mu\text{g L}^{-1}$)	Lead found ($\mu\text{g L}^{-1}$)	Recovery %
River water	0	0.45 ± 0.02	-
	0.2	0.64 ± 0.04	98.4
	0.4	0.84 ± 0.07	99.1
Well water	0	0.31 ± 0.03	-
	0.2	0.49 ± 0.05	97
	0.4	0.72 ± 0.08	101
Tap water	0	0.11 ± 0.02	-
	0.2	0.31 ± 0.04	101
	0.4	0.52 ± 0.06	102
Reference Material	Certified value	Measured value	Recovery %
JB-1 ^a	$10.0 (\mu\text{g g}^{-1})$	$9.82 \pm 0.37 (\mu\text{g g}^{-1})$	98.2
JB-1a ^a	$6.76 (\mu\text{g g}^{-1})$	$6.69 \pm 0.32 (\mu\text{g g}^{-1})$	99.0
JB-2 ^a	$5.36 (\mu\text{g g}^{-1})$	$5.23 \pm 0.41 (\mu\text{g g}^{-1})$	97.5
NIST 1640 ^b	$27.89 \pm 0.14 (\mu\text{g L}^{-1})$	$28.56 \pm 1.4 (\mu\text{g L}^{-1})$	102.4

^aObtained from geological survey of Japan, GSJ; ^bFrom National Institute of Standard and Technology NIST (USA).

CONCLUSIONS

In this work, an efficient method for extraction

and preconcentration of Pb has been developed based on SDME technique using RTIL 1- butyl- 4-methylpyridinium trifluoromethylsulfonate prior to GF-AAS determination. The results show a very promising technique for the determination of lead in variety of samples at $\mu\text{g L}^{-1}$ levels without the needs for any sophisticated device. Apart from extremely high sensitivity and relatively free from interferences, the procedure is very simple, fast, inexpensive, environment-friendly and benefits a very low detection limit. The results show that lead could be determined with very high sensitivity and relatively good reproducibility in aqueous sample such as tap, river and well water as well as solid samples e.g. soils.

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