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Abstract: An automated sequential-injection online preconcentration system was developed for the determination of lead by inductively coupled plasma–atomic emission spectrometry (ICP–AES). The preconcentration of lead was performed with a minicolumn containing a lead-selective resin, Analig Pb-01, which was installed between a selection and a switching valve. In an acidic condition (pH 1), lead could

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be adsorbed on the resin. The concentrated lead was afterward eluted with 25 μL of 0.06 M nitrilotriacetic acid (NTA) solution (pH 9) and was subsequently transported into the nebulizer of ICP-AES for quantification. The selectivity of the resin toward lead was examined using a solution containing a mixture of 61 elements. When a sample volume of 5 mL was used, the quantitative collection of lead ($\geq 97\%$) was achieved, along with an enrichment factor of 19, a sampling frequency of 12 samples hr^{-1} , a detection limit of 70 pg mL^{-1} , and a lowest quantification limit of 100 pg mL^{-1} . The linear dynamic range was 0.1 to 5 ng mL^{-1} , and the relative standard deviation ($n = 9$) was 0.5% at a 5 ng mL^{-1} Pb level. The detection limit of 30 pg mL^{-1} and lowest quantification limit of 50 pg mL^{-1} could be achieved when 10 mL of sample volume was used. The accuracy of the proposed method was validated by determining lead in the standard reference material of river water (SLRS-4), and its applicability to the determination of lead in environmental river water samples was demonstrated.

Keywords: Determination of lead, ICP-AES, online preconcentration, Pb-selective resin, sequential injection

INTRODUCTION

Lead is widespread in the environment, and its presence is not only of natural source but also from its industrial use. A large amount of lead is used for storage batteries, cable sheath, solders, paint, plumbing materials, and radiation shielding.^[1] One of the most serious environmental problems associated with lead comes from its use in leaded gasoline (tetraethyl lead), which comprises 80–90% of all the existing environmental lead contamination. The uptake of lead into the biological chain is hazardous to health due to its high toxicity even at trace level. Long-term overexposure can cause numerous health problems, such as anemia and other blood disorders, damage to nervous system and brain, kidney disease, and reproductive impairment in men and women.^[2,3] Therefore, the monitoring of lead in the environment is absolutely required.

In general, the concentration of lead in natural waters is extremely low (sub parts per billion level) so that any preconcentration steps must be included in an analytical method to ensure the detection sensitivity of a conventional instrumental detection method employed for its determination.^[4] The preconcentration procedures, which employ solid-phase extraction (SPE), provide dual advantages: an increase in analyte concentrations to measurable levels and the removal of potentially interfering matrices.

Various flow injection analysis (FIA) methods have been reported so far for the determination of trace amounts of lead in various environmental samples. Most of the methods employed SPE as an online preconcentration step, prior to appropriate detection methods, such as atomic absorption spectrometry (AAS),^[5–7] electrothermal atomic absorption spectrometry ETAAS,^[8,9] flame atomic absorption spectrometry (FAAS),^[10–15] inductively coupled plasma–

mass spectrometry (ICP-MS),^[4] and inductively coupled plasma–atomic emission spectrometry (ICP-AES).^[16–18] Recently, Wan et al.^[19] reported a significant improvement in capability for the detection of lead with hydride generation–atomic fluorescence spectrometry (HG-AFS) by coupling a flow injection online preconcentration and separation procedure for trace lead using an imino-diacetate chelating resin packed in a minicolumn. Lead, which was collected on the column, was eluted with HCl, followed by hydride formation before AFS measurement. Although the limit of detection achieved was 4 pg mL^{-1} , the applicability of this method for the determination of lead was at the sub $\mu\text{g mL}^{-1}$ to several tens $\mu\text{g mL}^{-1}$ level. In addition, although the sensitivity of this method is superior to other online separation and preconcentration protocols coupled with ETAAS and ICP-MS detection, the hydride (PbH_4) formed is unstable at room temperature, and the formation has slow kinetics and relatively poor generation efficiency.

A sequential injection analysis (SIA) comes next to the evolution process of continuous-flow analysis concept. SIA is very useful for tedious and time-consuming pretreatment of samples prior to measurement because it is more robust and versatile and is characterized by the use of discrete volumes and variable-flow conditions throughout the analytical cycle.^[20] However, only a few papers have been reported so far for the determination of lead using the pretreatment of samples based on SIA. Sequential injection/ICP-MS in combination with online solvent extraction for the determination of lead was reported by Wang and Hansen.^[21] Although the method is very sensitive (LOD: 11 pg mL^{-1}), the use of organic solvent, methyl isobutyl keton (MIBK), could not be avoided. Sequential injection/anodic stripping voltammetry^[22,23] allows simultaneous determination of lead, copper, cadmium, and zinc. Because the detection limit for lead is at several tens ng mL^{-1} level, it is not suitable for natural water samples. An interesting method with a sequential injection system for trapping of lead on the beads in the lab-on-valve (LOV) operated in parallel with ETAAS provides good sensitivity for lead detection (LOD: 0.3 ng mL^{-1}).^[24] However, the renewable step for the bead loaded with dithizone-impregnated Sephadex G-25 beads is necessary for every operation cycle. Recently, Aracama et al.^[25] reported a SIA method for the determination of lead in water samples using time-based colorimetric detection. The concentration of lead was assessed from its catalytic effect on the reaction of resazurine reduction by sulfide in an alkaline medium. The method, however, is strongly interfered with by Cu(II) , Co(II) , Ni(II) , and other transition metals. Therefore, the addition of sample pretreatment, which is often tedious, was required: in the method, potassium iodide is added to the samples in acidic medium to form lead-iodo-complexes followed by retaining the complex on the anionic exchange resin to allow the separation and the preconcentration of lead.

In this work, the automated SIA system coupled with ICP-AES detection for the determination of lead (II) was developed. A macrocycle immobilized silica gel sorbent (Analig Pb-01), which is selective for the adsorption of

lead,^[26] was packed in minicolumn and installed into the SIA system to allow the online preconcentration, as well as the separation of lead (II) from commonly existing matrices in the water samples. Experimental variables considered to be important factors in improving sensitivity, such as an eluent concentration, a sample and an eluent flow rate, pH of sample, ICP-AES parameters, were carefully optimized. Peak height was used as an analytical signal for the preparation of a calibration graph. The selectivity of the resin toward lead was also examined using a mixture containing 61 elements. The proposed method provides high selectivity, as well as high sensitivity and excellent collection efficiency of lead in environmental river water samples. In addition, the sensitivity achieved by the current method is superior to other flow-based analytical methods in association with ICP-AES detection.^[16–18,27] Further, the sensitivity can be improved by using a larger volume of samples or a more sensitive detection system like ICP-MS.

MATERIALS AND METHODS

Instrumentation

An ICP-AES system (Vista Pro, Seiko Instruments, Chiba, Japan) was used for the measurement of lead. The operating conditions of ICP-AES are summarized in Table 1. The ICP-AES was coupled with a laboratory-assembled sequential injection system, which consists of a syringe pump (SP; Hamilton, Reno, Nevada, USA) with volumes of 2.5 mL, a six-port selection valve (SL; Hamilton, Reno, Nevada, USA), and a six-way switching valve (SV; Hamilton, Reno, Nevada, USA). The pump and the valves were controlled by a computer. The program was written using

Table 1. Operating conditions of ICP-AES

Spectrometer	Vista Pro
Plasma conditions	
RF power	40 MHz, 1.2 kW
Plasma gas flow rate (L min ⁻¹)	Ar 15.0
Auxiliary gas flow rate (L min ⁻¹)	Ar 1.50
Nebulizer gas flow rate (L min ⁻¹)	Ar 0.75
Spray chamber	Glass cyclonic spray chamber
Nebulizer	K-style concentric glass nebulizer
Torch	One-piece low-flow extended torch in the axial view mode
Data acquisition	
Measurement mode	Time scan mode
Emission line	220.353 nm

ICP-AES, inductively coupled plasma–atomic emission spectrometry.

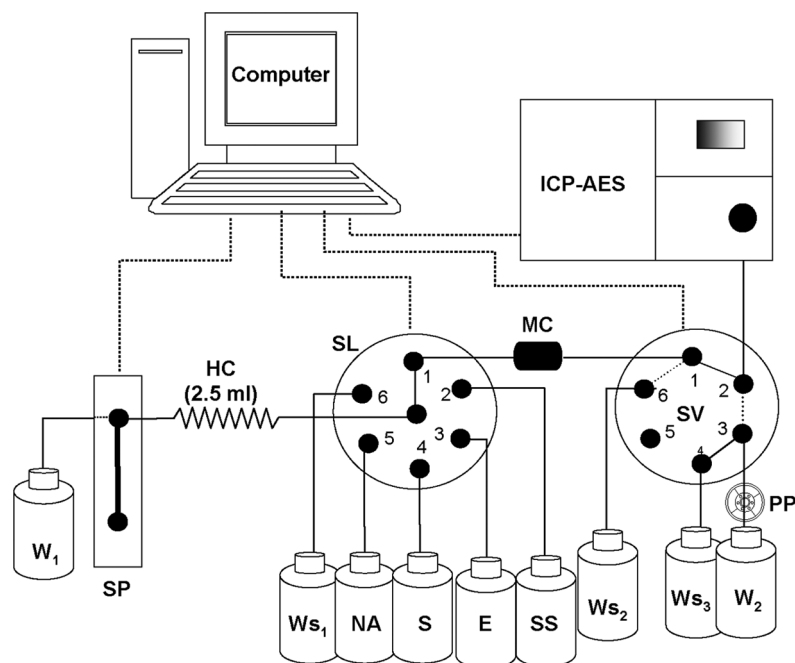


Figure 1. Sequential injection online preconcentration manifold for the determination of lead (at inject position) SP: syringe pump, SL: selection valve, SV: switching valve, MC: mini-column (40 mm $\times$ 2 mm i.d.) containing Analig Pb-01 resin, HC: holding coil, PP: peristaltic pump, S: sample, SS: standard solutions of Pb^{2+} , E: eluent (0.06 M NTA pH 9), NA: 0.1 M nitric acid, W: ultrapure water, Ws: waste.

LabVIEW software, which was accompanied by some advantages for data collection, analysis, storage, and controlling instruments.

The sequential injection manifold used in this work is shown in Fig. 1. The PTFE tubing (0.8 mm i.d.) was used for assembling all flow lines involving a holding coil.

Reagents and Materials

Standard solutions of lead were prepared by diluting a 1000 mg L^{-1} stock solution for AAS (Wako Pure Chemicals, Osaka, Japan) with 0.1 mol L^{-1} HNO_3 (ultrapure reagent grade: Kanto Chemicals, Tokyo, Japan). An 0.06 M nitrilotriacetic acid (NTA) (Dojindo Laboratories, Kumamoto, Japan) solution was prepared by dissolving 1.15 g NTA in 100 mL of 0.5 M ammonium acetate buffer (pH 9). Acetic acid (minimum 96%) and ammonia water (29%) used for the preparation of ammonium acetate buffer were of an electronic industrial reagent grade (Kanto Chemicals, Tokyo, Japan). Ultrapure water (18.3 $\text{M}\Omega\text{ cm}^{-1}$ resistivity) prepared by an Elix 3/

Milli-Q Element system (Nihon Millipore, Tokyo, Japan) was used throughout. All other reagents used for this experiment were of the highest grade now commercially available in Japan.

The lead-selective resin, Analig Pb-01 (size, 60–100 mesh; capacity, 0.20 mmol g⁻¹), was purchased from GL Sciences Inc. (Tokyo, Japan). The resin is a proprietary polymeric organic material that has sequestering ligand agents that are said to be highly selective for lead in acidic media containing relatively high concentrations of other competing ions. The sorption ability of the resin is based on molecular recognition and macrocyclic chemistry. The minicolumn was prepared by packing the resin into the PTFE tubing (4 cm × 2 mm i.d.) equipped with the plugs of quartz wool at both ends of the tubing to keep the resin in the column. The sample solutions were filtered through the membrane filter of nitrocellulose ester (0.45 μm, Advantec, Ehime, Japan) and adjusted to pH 1 with nitric acid before introduced to the sequential injection system.

Operating Procedures

The whole procedure runs through four steps, during which the carrier (ultrapure water) is pumped continuously into the ICP-AES by a peristaltic pump fixed in the instrument.

Step 1: Column Conditioning

In this step, SV is in load position, and SP is set up to aspirate 1000 μL (at flow rate of 100 μL s⁻¹) of 0.1 M HNO₃ via the port 5 of SL, which is then dispensed through the port 1 at flow rate of 100 μL s⁻¹ for conditioning the column.

Step 2: Separation and Preconcentration

SV is in load position, and SP is set to aspirate 2500 μL of the samples into the holding coil via the port 4 of SL (at flow rate of 100 μL s⁻¹), followed by flowing it into the column via the port 1 (at flow rate of 40 μL s⁻¹) for the preconcentration of lead and the separation of matrices. This step was repeated two times to introduce total sample volume of 5 mL, and it was repeated four times when 10 mL of sample volume was required.

Step 3: Washing

After the sample is loaded to the column, 500 μL of ultrapure water (W₁) is aspirated into the syringe (at flow rate of 200 μL s⁻¹), and immediately afterward dispensed to wash the column via the port 1 of SL (at flow rate of 50 μL s⁻¹), while SV is still in load position.

Step 4: Elution and Transportation of the Eluate to ICP-AES

In this step, the syringe pump is set to aspirate 25 μL of 0.06 M NTA (pH 9) into the holding coil via the port 3 of SL in 1 s, followed by aspirating ultrapure water (W_1) into syringe (at flow rate of $200 \mu\text{L s}^{-1}$) to fill the syringe up to 2500 μL . Then, SL is switched to the port 1, while SV is switched to the inject position, as shown in Fig. 1. Afterwards, the solution in the holding coil, which consists of 25 μL of 0.06 M NTA (in the front side) and 2475 μL ultrapure water (in the back side), is dispensed to elute collected lead in the column (at flow rate of $40 \mu\text{L s}^{-1}$) followed by its detection with ICP-AES.

RESULTS AND DISCUSSION

Optimization of the Sequential Injection Online Preconcentration System

Factors affecting the collection/preconcentration of lead on the column, such as sample pH and sample loading rate, were studied. The acidity of sample was varied from pH 1 to pH 9 by adjusting the lead solution (which is also containing other 60 elements) with 0.1, 0.01, and 0.001 M HNO_3 for pH 1 to 3, while other pHs were adjusted using 0.02 M ammonium acetate buffer pH 4 to pH 9. The highest peak intensity was obtained at pH from 1 to 3, whereas the peak intensity decreased at $\text{pH} \geq 4$. Although the resin, Analig Pb-01, is claimed to be a lead-selective resin, it seems to be affected by other competing ions coexisting in the solutions, which can reduce the adsorption efficiency of lead on the resin. Therefore, pH 1 of the sample was selected for further experiments by considering two reasons: first, at pH 1, the resin is very selective for lead over other metal ions, which is explained in a later section; and second, any precipitation during sample preparation can be avoided because the solubility product of lead as $\text{Pb}(\text{OH})_2$ and PbS , as well as in other metal ions, is very small. The sample loading rate was varied at the flow rate from 10 to $70 \mu\text{L s}^{-1}$. It was found that the flow rate from 10 to $40 \mu\text{L s}^{-1}$ did not give any significant effect on the peak height of Pb^{2+} , whereas the peak height decreased when the sample flow rate is $\geq 50 \mu\text{L s}^{-1}$, because the sorption equilibrium for lead on the resin could not be achieved. Accordingly, the sample loading flow rate of $40 \mu\text{L s}^{-1}$ was selected.

Factors affecting the elution of lead were also examined. An NTA solution was used as an eluent due to its strong complex formation with lead, which results in complete desorption of lead adsorbed on the column. The rate of the complex formation between NTA and lead seems to be fast because the eluent flow rate of $40 \mu\text{L s}^{-1}$ only with 25 μL of 0.06 M NTA (pH 9) enabled complete elution of lead from the column. Mono- and di-protonated forms of NTA have significantly slower rate than NTA itself. Therefore,

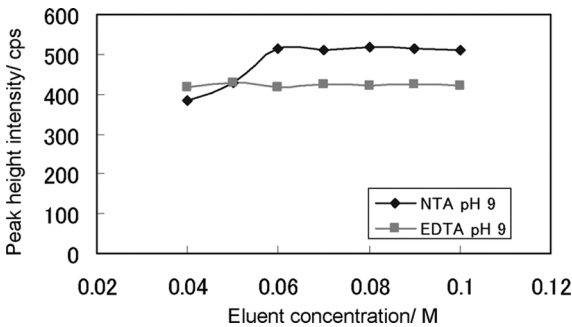


Figure 2. Effect of eluent type and concentration on the peak height intensity sample: 5 ng mL⁻¹ Pb²⁺ (5 mL), other conditions are the same as in Table 1 and Table 2.

pH 9 of NTA solution was adopted during this experiment. Effective elution of lead collected on the column with NTA, as well as EDTA, at various concentrations (pH 9) was also studied. The results in Fig. 2 show that there is no significant increase in peak height intensity when EDTA at the concentration range 0.04–0.1 M was used as an eluent, which means that the lead collected on the column was completely eluted at all concentration ranges examined. In contrast, the peak height intensity increased when the concentration of NTA increased above 0.04 M and was identical in the range 0.06–0.1 M. Such results showed that a higher concentration of NTA resulted in more complete elution of lead, and NTA seems to be a better eluent than EDTA, although the stability constant of Pb(II)-EDTA is larger than Pb(II)-NTA. The optimized SIA parameters are summarized in Table 2.

Selectivity of the Resin at pH 1

The selectivity of Analig Pb-01 resin was examined using an off-line column method. The solution containing 61 elements in 0.1 M HNO₃, each concentration of which was 5 ng mL⁻¹, was passed through the column. After the

Table 2. Optimized conditions for sequential injection online preconcentration system

Parameter	Range examined	Selected
pH of sample	pH 1–9	pH 1
Sample loading rate	10–70 μL s ⁻¹	40 μL s ⁻¹
Eluent type	NTA, EDTA (pH 9)	NTA (pH 9)
Eluent flow rate (NTA)	10–70 μL s ⁻¹	40 μL s ⁻¹
Eluent concentration (NTA)	0.04–0.1 M	0.06 M
Eluent volume (NTA)	10–2000 μL	25 μL

Table 3. Recoveries of Pb²⁺ and other elements at pH 1 (selectivity of Analig Pb-01 resin)

Element	Found (ng mL ⁻¹) ^a	Recovery (%)	Element	Found (ng mL ⁻¹) ^a	Recovery (%)
Pb	4.89 ± 0.02	97.7	Gd	0.52 ± 0.00	10.5
Ag	4.43 ± 0.42	88.5	Ce	0.52 ± 0.02	10.4
Sc	1.88 ± 0.12	37.7	Pd	0.51 ± 0.05	10.3
Mg	1.85 ± 0.19	37.0	Ga	0.51 ± 0.06	10.2
Al	1.77 ± 0.01	35.4	In	0.51 ± 0.06	10.2
Hf	1.34 ± 0.03	26.8	Er	0.51 ± 0.01	10.2
Nb	1.33 ± 0.04	26.6	Dy	0.51 ± 0.03	10.1
Tl	1.23 ± 0.04	24.7	Th	0.50 ± 0.06	10.0
Zn	1.22 ± 0.06	24.3	Be	0.50 ± 0.01	10.0
Zr	1.22 ± 0.07	24.3	Nd	0.50 ± 0.02	10.0
Ba	1.15 ± 0.02	23.0	Te	0.49 ± 0.01	9.7
Fe	1.04 ± 0.08	20.9	Pt	0.49 ± 0.05	9.7
Sc	1.04 ± 0.03	20.8	La	0.48 ± 0.04	9.6
Sr	0.91 ± 0.05	18.2	Co	0.47 ± 0.06	9.4
Hg	0.86 ± 0.07	17.3	U	0.46 ± 0.05	9.3
K	0.80 ± 0.09	15.9	Rh	0.46 ± 0.05	9.2
Cr	0.69 ± 0.05	13.7	Li	0.45 ± 0.03	9.1
Mn	0.68 ± 0.04	13.7	Ta	0.44 ± 0.04	8.9
Bi	0.65 ± 0.06	13.0	Sb	0.42 ± 0.01	8.5
Mo	0.64 ± 0.02	12.70	V	0.42 ± 0.02	8.3
Yb	0.56 ± 0.01	11.2	Rb	0.41 ± 0.05	8.3
W	0.55 ± 0.01	11.1	Na	0.41 ± 0.09	8.3
Tm	0.55 ± 0.02	11.0	Ge	0.41 ± 0.01	8.2
Ho	0.54 ± 0.02	10.8	Se	0.39 ± 0.02	7.7
Tb	0.54 ± 0.01	10.7	Cu	0.36 ± 0.02	7.2
Lu	0.53 ± 0.00	10.7	Cs	0.36 ± 0.05	7.1
Pr	0.53 ± 0.01	10.6	As	0.35 ± 0.02	7.0
Sm	0.53 ± 0.03	10.6	Ni	0.35 ± 0.01	6.9
Y	0.53 ± 0.00	10.5	B	0.31 ± 0.03	6.2
Eu	0.53 ± 0.00	10.5	Ca	0.12 ± 0.03	2.5
Cd	0.52 ± 0.06	10.5			

Mean values with ± standard deviations for five measurements.

^aSample: 5 ng mL⁻¹ of each element.

elution with 0.06 M NTA (pH 9), the eluates were measured by ICP-AES for Ca, Na, Mg, K, and Fe, whereas other elements were measured by ICP-MS. As shown in Table 3, only lead could be recovered almost completely (97.7%). Silver was recovered about 88.5%, whereas the recovery of other elements was less than 40%. Accordingly, it can be said that the resin has excellent selectivity and strongest affinity toward lead, compared with other elements at pH 1. Another investigation was performed using online system. In this

case, the synthetic sample solutions (pH 1) containing 5 ng mL⁻¹ Pb²⁺, 0.5 mol L⁻¹ NaCl, 0.05 mol L⁻¹ MgSO₄, 0.05 mol L⁻¹ Ca(HCO₃)₂ and 0.02 mol L⁻¹ KNO₃ were introduced to the system according to the procedures shown in “Materials and Methods.” As a result, the peak height intensity of 5 ng mL⁻¹ Pb²⁺ did not show any significant difference between the solutions with and without coexisting metals, which means that the proposed method can be applied to the separation and preconcentration of lead from high matrix background, such as seawater samples.

Peak Profile and Analytical Parameters

The peak profiles of 0.2–5 ng mL⁻¹ Pb²⁺ (sample volume used: 5 mL) were obtained under the optimum conditions shown in Table 2. Interesting results were obtained when different nebulizer gas flow rates were used, as shown in Fig. 3. When the nebulizer gas flow rate of 0.75 L min⁻¹ was used, high

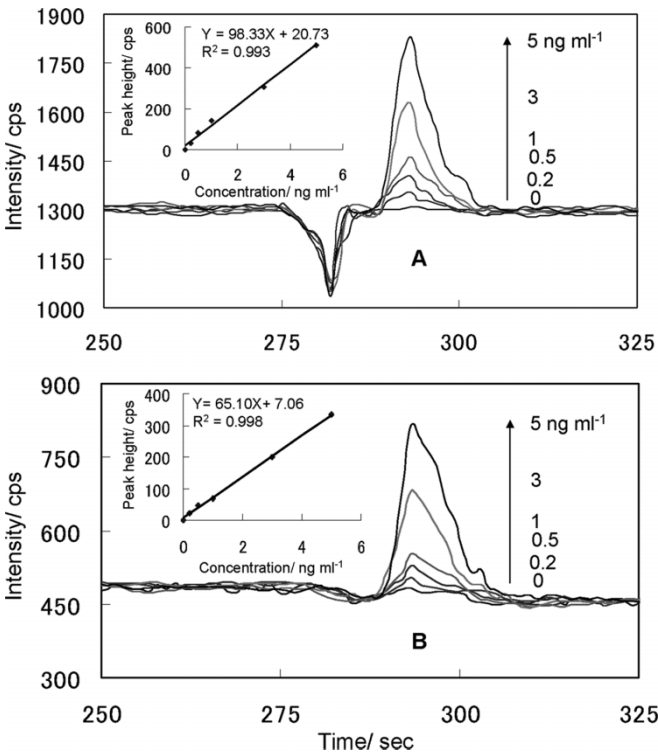


Figure 3. Peak profiles and calibration graphs of lead A: nebulizer gas flow rate at 0.75 L min⁻¹, B: nebulizer gas flow rate at 0.9 L min⁻¹, volume of sample: 5 mL, other conditions are the same as in Table 1 and Table 2.

baseline and large negative peak were observed. However, it did not affect the peak signal of lead. The negative peak is caused by a solution gap when the switching valve is changed from the load to the inject position. On the other hand, the low baseline and the small negative peak appeared when the nebulizer gas flow rate of 0.90 L min⁻¹ was used, though the baseline noise was similar to that of lower gas flow rate. However, the peak height intensity (defined as the peak top signal subtracted by the baseline signal) at the nebulizer gas flow rate of 0.75 L min⁻¹ is higher than that of 0.90 L min⁻¹. From these results, it seems that a lower nebulizer gas flow rate can result in higher sensitivity. However when 0.60 L min⁻¹ of the nebulizer gas flow rate was used, the plasma of ICP-AES is not so stable. Probably, it is caused by the formation of relatively large droplets in aerosol. Accordingly, 0.75 L min⁻¹ nebulizer gas flow rate was used for the best condition as compromise to sensitivity, as well as plasma stability.

When 5 mL of sample volume was used, the linear equation of calibration graph was $Y = 65.1X + 7.06$ with a correlation coefficient of 0.998 for nebulizer gas flow rate of 0.9 L min⁻¹. The limit of detection (LOD) defined as three times the signal-to-noise ratio was 0.11 ng mL⁻¹. Enrichment factor, which is calculated by comparing peak height intensity of 5 ng mL⁻¹ Pb²⁺ (sample volume: 5 mL) with and without preconcentration column, was 12. When the nebulizer gas flow rate of 0.75 L min⁻¹ was used, the linear equation was $Y = 98.3X + 20.73$ with correlation coefficient, LOD, and enrichment factor of 0.993, 0.07 ng mL⁻¹ (≈70 pg mL⁻¹), and 19, respectively. The linear dynamic range of the proposed method was 0.1 to 5 ng mL⁻¹.

Analysis of River Water Samples

In order to evaluate the accuracy of the proposed method, a certified reference material for river water, SLRS-4 (National Research Council Canada), was examined. The feasibility of the current system was also demonstrated to

Table 4. Analytical results for the determination of lead in river water samples

Sample	Found (ng mL ⁻¹)		
	Proposed method	ICP-MS	Certified
SLRS-4 ^{a,c}	0.091 ± 0.008		0.086 ± 0.007
River water A ^{b,d}	1.42 ± 0.06	1.31 ± 0.03	
River water B ^{b,c}	0.084 ± 0.009	0.074 ± 0.002	
River water C ^{b,c}	0.055 ± 0.006	0.050 ± 0.002	

^aStandard reference material of river water (National Research Council Canada).

^bThe samples were taken on March 1, 2006.

^cSample volume: 10 mL.

^dSample volume: 5 mL.

the determination of lead in several river water samples. The results are summarized in Table 4. It is found that there is no significant difference in lead concentration between the results obtained by the proposed method and the certified value. Similarly, the analyses of lead in river water samples were found to compare well between the proposed method and the ICP-MS method. Some results for lead concentrations in river waters, as well as SLRS-4 reference material, are close to the LOD of the proposed method, in which the sample volume used is 5 mL. Therefore, to improve the detectable level for lead, 10 mL of sample volume was used for river water B, river water C, and SLRS-4, whereas for river water A, 5 mL of sample volume was adequate. By using 10 mL of sample volume, the limit of detection of the proposed method could be reduced to about 0.03 ng mL^{-1} ($\approx 30 \text{ pg mL}^{-1}$) with the lowest quantification limit of 50 pg mL^{-1} and linear dynamic range of 0.05 to 5 ng mL^{-1} , although a longer analysis time was required (8 min/sample).

CONCLUSIONS

The proposed method, sequential injection online preconcentration coupled with ICP-AES detection, enables the accomplishment of the determination of lead in river water samples with satisfactory results. The use of lead-selective resin, Analig Pb-01, as an online preconcentration packing for the column treatment installed to an automated system allowed highly selective and sensitive detection of lead in environmental river water samples. The relatively rapid separation and preconcentration of lead from high background matrix, such as seawater samples, will be possible by using this method.

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