Automated online preconcentration system for the determination of trace amounts of lead using Pb-selective resin and inductively coupled plasma-atomic emission spectrometry

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Automated On-line Preconcentration System for the Determination of Trace Amounts of Lead Using Pb-Selective Resin and Inductively Coupled Plasma-Atomic Emission Spectrometry

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Abstract

An automated sequential-injection on-line 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 mini-column 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 be adsorbed on the resin. The concentrated lead was afterward eluted with 25 μl of 0.06M 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 (≥ 97%) was achieved, along with an enrichment factor of 19, a sampling frequency of 12 samples h^{-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.

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Introduction

Lead is widely spread in the environment, and its existence is not only of natural source but also of its industrial use. A large amounts of lead is used for storage batteries, cable sheath, solders, paint, plumbing materials and radiating shielding.[1] One of the most serious environmental problems of lead comes from the use of leaded-gasoline, tetraethyl lead, which reaches to 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, reproductive impairments 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 ppb level) so that any preconcentration steps must be included in an analytical method to assure 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 on-line 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, Wang et. al[19] reported a significant improvement for the detection capability of lead for hydride generation-atomic fluorescence spectrometry (HG-AFS), by coupling a flow injection on-line preconcentration

and separation procedure for trace lead using an imino-diacetate chelating resin packed in a mini-column. 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}, however, the applicability of this method for the determination of lead was in sub μg ml^{-1} to several ten μg ml^{-1} level. In addition, although the sensitivity of this method is superior to other on-line separation and preconcentration protocols coupled with ETAAS and ICP-MS detection, however, the hydride (PbH$_4$) formed is unstable at room temperature, and the formation is slow kinetics, and relatively poor generation efficiency.

A sequential injection analysis (SIA) comes next to the evolution process of continous-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 paper 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 on-line 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. Since the detection limit for lead is several ten 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 from

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-iodocomplexes 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

mini-column and installed into the SIA system to allows the on-line 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 present method is superior to other flow-based analytical methods in corporation with ICP-AES detection.[16-18, 27] Further, the sensitivity can be improved by using a larger volume of samples or more sensitive detection system like ICP-MS.

Experimental

Instrumentations

An ICP-AES system (Vista Pro, Seiko Instruments, Japan) was used for the measurement of lead. The operating conditions of ICP-AES were summarized in Table 1. The ICP-AES was coupled with a laboratory-assembled sequential injection system, which consists of a syringe pump (SP: Hamilton, USA) with volumes of 2.5 ml, a 6-port selection valve (SL: Hamilton, USA), and a 6-way switching valve (SV: Hamilton, USA). The pump and the valves were controlled by a computer. The program was written using LabVIEW software, which accompanied by some advantages for data collection, analyse, storage and controlling

instruments.

The sequential injection manifold used in this work was 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, Japan) with 0.1 mol l^{-1} HNO_3 (ultrapure reagent grade: Kanto Chemicals, Japan). A 0.06M nitrilotriacetic acid (NTA) (Dojindo Laboratories, Japan) was prepared by dissolving 1.15 g NTA in 100 ml of 0.5M 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, Japan). Ultrapure water (18.3 $M\Omega$ 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., Japan. The resin is a proprietary polymeric organic material which 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 mini-column was prepared by packing the resin into the PTFE tubing (4 cm x 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, Japan) and adjusted to pH 1 with nitric acid before introduced to the sequential injection system.

Operating procedures

The whole procedure runs through 4 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 0.1M HNO$_3$ 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 2 times to introduce total sample volume of 5 ml, and it was repeated 4 times when 10 ml of sample volume required.

Step 3: Washing. After the sample is loaded to the column, 500 μl of ultrapure water (W$_1$) is

aspirated into the syringe (at flow rate of 200 μl s^{-1}), and immediately afterwards 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 μl 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 consist 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 μl s^{-1}) followed by its detection with ICP-AES.

Results and discussion

Optimization of the sequential injection (SI) on-line 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 from1 to 3, whereas the

peak intensity decreased at pH $\geq$ 4. Although the resin, Analig Pb-01, is claimed as 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 later section, and second, any precipitation during sample preparation can be avoided since the solubility product of lead as $Pb(OH)_2$ 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 μl s^{-1}. It was found that the flow rate from 10 to 40 μl 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 $\geq$ 50μl s^{-1}, because the sorption equilibrium for lead on the resin could not be achieved. Accordingly, the sample loading flow rate of 40μl 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 is seems to be fast because the eluent flow rate of 40 μl s^{-1} only with 25 μl of 0.06M NTA (pH 9) enabled complete elution of lead from the column. Mono- and di-protonated form of NTA are significantly slower rate than NTA itself. Therefore, pH 9 of NTA solution was adopted during this experiment. Effective elution of lead collected on the column with NTA, as well

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as EDTA, at various concentrations (pH 9) was also studied. The results in Fig. 2 shows that there is no significant increase in peak height intensity when EDTA at the concentration range of 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 contrary, the peak height intensity increased when the concentration of NTA increased above 0.04 M, and was identical in the range of 0.06-0.1M. 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 were 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 0.1M HNO_3, each concentration of which was 5 ng ml^{-1}, was passed through the column. After the elution with 0.06M 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 to other elements at pH 1. Another investigation was performed using

on-line system. In this case, the synthetic sample solutions (pH 1) containing 5 ng ml^{-1} Pb^{2+}, 0.5 mol l^{-1} NaCl, 0.05 mol l^{-1} MgSO$_4$, 0.05 Ca(HCO$_3$)$_2$, and 0.02 KNO$_3$ were introduced to the system according the procedures shown in experimental section. As a result, the peak height intensity of 5 ng ml^{-1} Pb^{2+} did not show any significant different 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} Pb^{2+} (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 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 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 of the signal to noise ratio was 0.11 ng ml^{-1}. Enrichment factor, which is calculated by compared peak height intensity of 5 ng ml^{-1}Pb^{2+} (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 a correlation coefficient, LOD, and the enrichment factor were 0.993, 0.07 ng ml^{-1} ($\approx$ 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 present system was also demonstrated to 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 in a good comparability between the proposed method and 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 sample volume used is 5 ml. Therefore, to improve the detectable level for lead, 10 ml of sample volume were 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 volumes, the limit detection of the proposed method could be reduced to about 0.03 ng ml^{-1} ($\approx$ 30 pg ml^{-1}) with the lowest quantification limit of 50 pg ml^{-1} and linear dynamic range of 0.05 – 5 ng ml^{-1}, although the longer analysis time was required (8 min/sample).

Conclusion

The proposed method, sequential injection on-line preconcentration coupled with ICP-AES detection, enables the accomplishment of the determination of lead in river water samples with satisfied results. The use of lead-selective resin, Analig Pb-01, as an on-line 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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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 acquision	
Measurement mode	Time scan mode
Emission line	220.353 nm

Table 2 Optimized conditions for sequential injection (SI) on-line 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 Pb^{2+} and other elements at pH 1 (selectivity of Analig Pb-01 resin)

Element	Found (ng ml^{-1})[*]	Recovery (%)	Element	Found (ng ml^{-1})[*]	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			

[*] Sample: 5 ng ml^{-1} of each element.

Mean values with ± standard deviations for 5 measurements.

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[1,3]	0.091 ± 0.008		0.086 ± 0.007
River water A[2,4]	1.42 ±0.06	1.31±0.03	
River water B[2,3]	0.084 ±0.009	0.074 ±0.002	
River water C[2,3]	0.055 ±0.006	0.050 ±0.002	

[1] Standard reference material of river water (National Research Council Canada)

[2] The samples were taken on March 1, 2006

[3] Sample volume: 10 ml
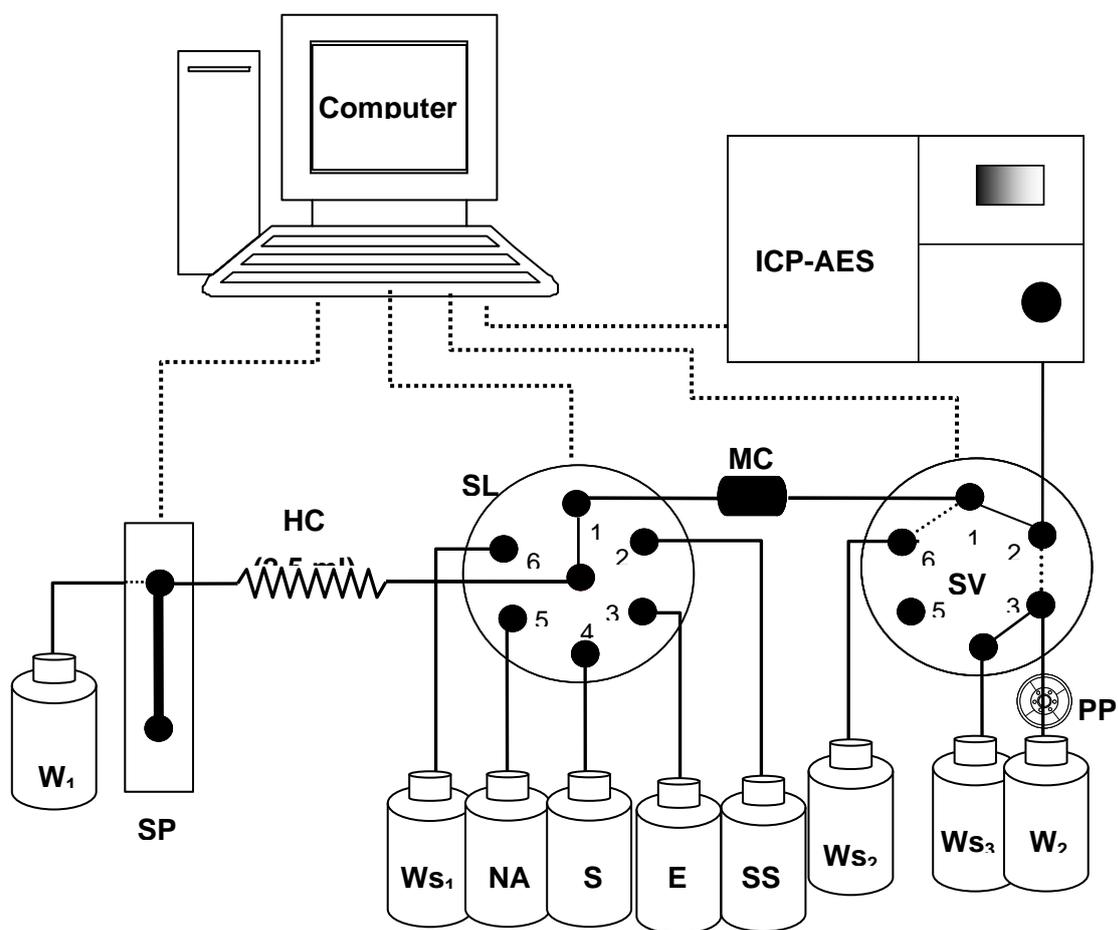
[4] Sample volume: 5 ml

Figure

Fig. 1 Sequential injection on-line preconcentration manifold for the determination of lead (at inject position)

SP: syringe pump, SL: selection valve, SV: switching valve, MC: mini-column (40 mm x 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 (0.06M NTA pH 9), NA: 0.1M nitric acid, W: ultrapure water, Ws: waste
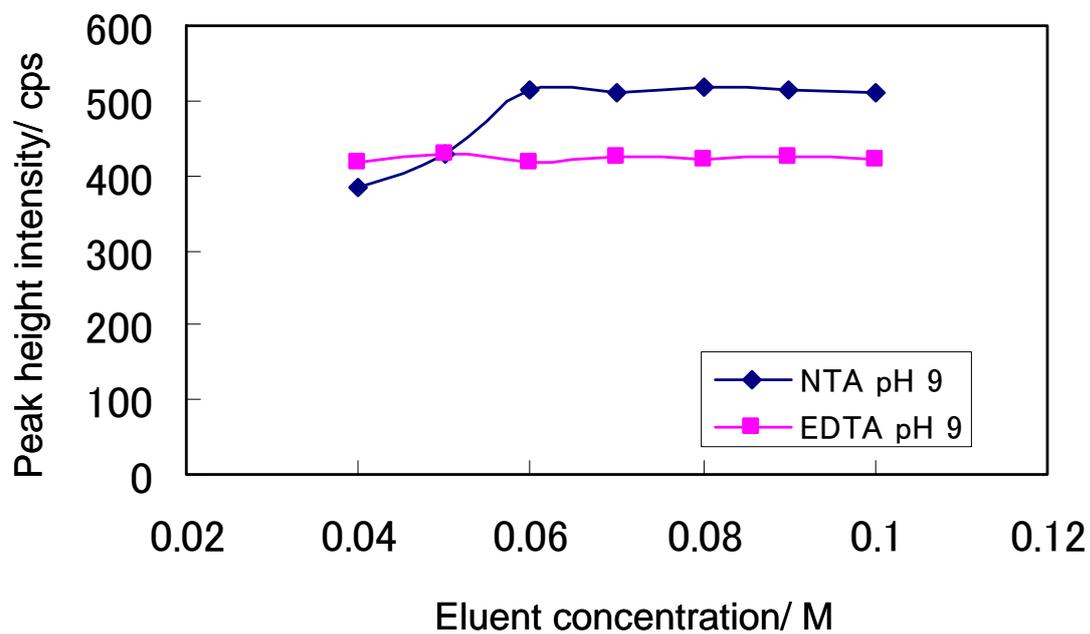
Fig. 2 Effect of eluent type and concentration on the peak height intensity

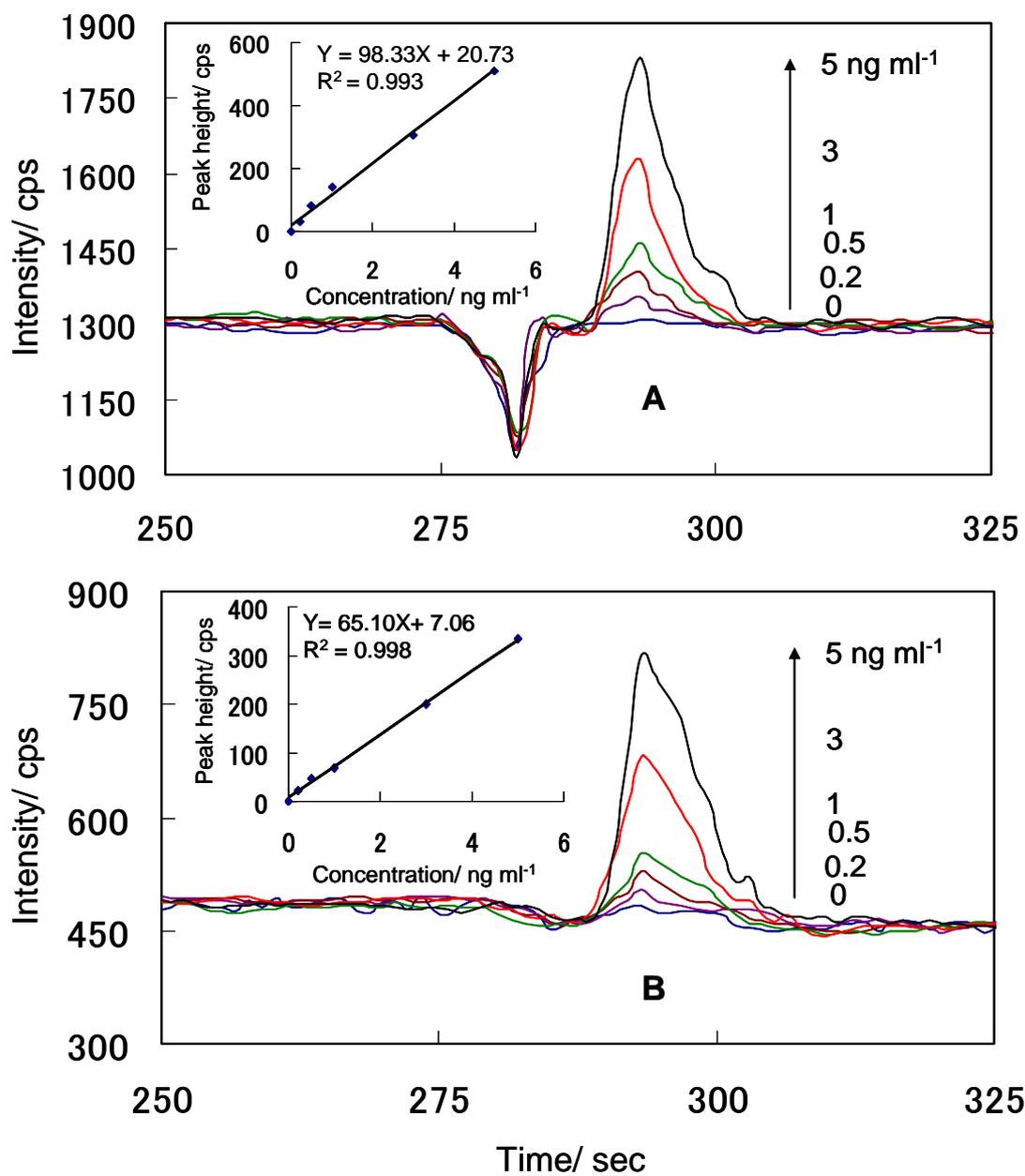Sample: 5 ng ml^{-1} Pb^{2+} (5 ml), other conditions are the same as in Table 1 and Table 2

Fig. 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