# Determination of Ultra-Trace Amounts of Lead in River Water by Flow Injection Analysis Coupled with Computer-Controlled Auto-Pretreatment System Using Solid Phase Extraction Procedure

Ye Yin<sup>1</sup>, Toshio Takayanagi<sup>2</sup>, Mitsuko Oshima<sup>2</sup>, Koji Oshita<sup>3\*</sup>, Shoji Motomizu<sup>2</sup>, Yoshiyuki Murata<sup>1</sup>

<sup>1</sup> Graduate School of Natural Science and Technology, Okayama University, 1-1-1 Tsushimanaka, Okayama 700-8530, Japan
<sup>2</sup> Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushimanaka, Okayama 700-8530, Japan
Department of Interpretional Conservation Studies for Cultural Preparties. Faculty of Cultural Pre-

<sup>3</sup> Department of International Conservation Studies for Cultural Properties, Faculty of Cultural Properties, Kibi International University, 8 Igamachi, Takahashi, Okayama 716-8508, Japan

# Abstract

Flow injection analysis (FIA) system coupled with a computer-controlled auto-pretreatment (Auto-Pret) system (MGC Auto-Pret 018S) was newly developed for the determination of ultra-trace amounts of Pb(II) in aqueous samples. The solid phase material, Analig Pb-01 (GL Sciences), was packed in a mini-column (2 mm i.d. x 40 mm length), which was installed in the Auto-Pret system. In the mini-column, ultra-trace amounts of Pb(II) were selectively adsorbed and concentrated on Analig Pb-01, and Pb(II) adsorbed was eluted with an eluent (3 M KCl). After the eluent passed through the column, the sample zone of Pb(II) in the effluent was retained in the loop of a sample injection valve in the FIA system; then it was introduced in a carrier stream (CS), which was merged with a reagent solution (RS) containing 4-(2-Pyridylazo)resorcinol (PAR) as a coloration reagent (pH 10.2). The absorbance of the colored Pb(II) chelate with PAR was measured at 530 nm, and recorded as a peak with a chart recorder. The concentration efficiency of lead by the proposed FIA system coupled with the Auto-Pret system was 3 with a 5-mL sample and 15 with a 20-mL sample. The limit of detection (LOD) corresponding to 3  $\sigma$  of reagent blanks was 0.5 x 10<sup>-9</sup> M using a 20-mL sample, and the lower limit of quantification (LOQ) was 1.0 x 10<sup>-9</sup> M. The proposed technique was applied to the determination of trace Pb(II) in a river water sample; 4.3 x 10<sup>-9</sup> M Pb(II) was determined; the result of recovery tests were 99% to 101%. The proposed FIA system coupled with the Auto-Pret system waters (0.1 mg/L), environmental waters (0.01 mg/L) and WHO Guidelines of lead in drinking water (0.01 mg/L).

**Keywords** FIA system, Mini-Column, Solid phase extraction, Analig Pb-01, Auto-Pretreatment (Auto-Pret) system, Pb(II), PAR, Spectrophotometry

# 1. Introduction

Lead has been widely used in industrial productions and daily necessities, such as the production of lead-acid batteries, solder and alloys etc. Such lead materials have been widely spread in environment and exist in environmental waters, soils and sediments etc. The uptake of lead is hazardous to human and other creatures because of its high toxicity even at trace levels.

Trace amounts of lead have been determined mainly by spectroscopic methods, such as frame atomic absorption spectrometry (F-AAS) [1-8], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [9-11] and inductively coupled plasma-mass spectrometry (ICP-MS) [12-17] and electro thermal atomic absorption spectrometry (ET-AAS) [18-19]. These spectroscopic systems without pretreatment and preconcentration cannot be easily applied to the trace analysis because only trace amounts of lead exists in environment samples containing high concentrations of matrices. Therefore, some pretreatment techniques using a mini-column packed with solid phase materials, which are based on sequential injection (SI) technique, are used for the collection and concentration prior to the measurement. For determining trace lead at ppt levels, the pretreatment system is coupled with ICP-MS and ET-AAS [20-22]. These are powerful

techniques for measuring trace lead, whereas these spectroscopic systems are too expensive and large in size, which makes applications to on-site analysis difficult. In order to overcome the problems, the pretreatment systems coupled with anodic stripping voltammetry (ASV) for the determination of Pb, Cd, and Zn have been reported [23, 24], whereas the sensitivity improvements of these techniques are necessary for the determination of trace lead in environmental samples. Therefore, the development of a more sensitive measurement system and a more effective pretreatment technique is significant.

Flow injection analysis (FIA) is one of the powerful and sensitive measurement techniques. The analytical technique uses inexpensive instrument and well-established techniques, which allow simple, rapid and reproducible analysis because such FIA systems can be composed of UV/VIS detectors. In order to determine lead by a UV/VIS detector, 4-(2-Pyridylazo)resorcinol (PAR) has been widely used as a coloration reagent. However, PAR is selective for lead, and reacts with Co(II), Ni(II), Cu(II), Cd(II) and Pb(II). The limits of quantification (LOQ) by a UV/VIS spectrophotometric technique and by an FIA technique equipping with a UV/VIS detector for Pb(II) are about  $10^{-7}$  M and  $10^{-8}$  M, respectively. Therefore such an FIA system using a UV/VIS detector cannot be applied to the determination of trace lead in environmental samples due to low selectivity and sensitivity.

For improving the selectivity and sensitivity in lead detection,

<sup>\*</sup> Corresponding author

E-mail: oshita@kiui.ac.jp

many different solid phase materials have been developed for lead detection [25]. Analig Pb-01(GL Sciences) is one of the selective solid phase materials for lead. Its adsorbent is applied to the pretreatment technique for the selective collection and concentration of lead prior to ICP-AES, liquid electrode plasma-atomic emission spectrometry (LEP-AES) and UV/VIS spectrometry [26-28].

In this study, a flow injection analytical (FIA) system coupled with a computer-controlled auto-pretreatment (Auto-Pret) system, which is based on the sequential injection (SI) technique, was newly developed for the determination of ultra-trace amounts of Pb(II) in aqueous samples. An Analig Pb-01(GL Sciences) as the solid phase material for the selective collection and concentration of trace lead was packed in a mini-column (2 mm i.d. x 40 mm length), which was installed in the Auto-Pret system (MGC Auto-Pret 018S). The Auto-Pret system was combined with the FIA system with PAR as a coloration reagent.

# 2. Experimental

### 2.1 Reagents

The solid phase extraction material, Analig Pb-01, was purchased from GL Sciences, which was packed in the mini-column (2 mm i.d. x 40 mm length). The standard solutions of Pb(II) were prepared with a single element standard solution for atomic absorption spectrometry (1000 mg L<sup>-1</sup>, Wako Pure Chemical Industries Ltd., Osaka, Japan). Nitric acid (Wako Pure Chemical Industries, Ltd., special grade) for column conditioning, and potassium chloride (Kanto Chemical Co. Inc., special grade) for preparing an eluent solution and a carrier solution (CS) were used after dissolving with ultrapure water. For the detection of lead, 4-(2-Pyridylazo)resorcinol (PAR, Kanto Chemical Co. Inc., first grade) and 5, 10, 15, 20-Tetrakis(4-sulfophenyl)porphyrin (TPPS, Wako Pure Chemical Industries, Ltd.) were prepared as a reagent solution (RS) after dissolving with ultrapure water. Also, tetraborate-sodium hydroxide sodium and ammonium chloride-ammonia solutions were used for each buffer solution, which is added to the RS, respectively. Ultrapure water (18.3 M $\Omega$  cm<sup>-1</sup>), prepared by an Elix 3 / Milli-Q Element (Nihon Millipore, Tokyo, Japan), was used throughout this experiment.



**Fig. 1** Flow diagram of the proposed FIA system combined with Auto-Pret system for determining Pb(II). SP, syringe pump; HC, holding coil; SLV, eight-way selection valve; S, Sample; SWV, six-way switching valve; CS, carrier solution; RS, reagent solution; V, valve for sample injection; RC, reaction coil; D, detector; R, recorder.

#### 2.2 Apparatus

The proposed system for measuring trace lead consists of an FIA system and an Auto-Pret system shown in Fig. 1. The FIA system is composed of a double plunger-type pump (Sanuki Industry Co. Ltd, RX-703 T), a 6-way valve (Sanuki Industry Co. Ltd) with a sample loop, a spectrophotometer (Soma Optics Ltd., S-3250) as a detector, some connectors and PTFE tubing. PTFE tubing (0.5 mm i.d.) was used for preparing all flow lines. A reaction coil (RC: 1.0 m length, 0.5 mm i.d.) is used for mixing a Pb(II) and PAR solutions. A computer-controlled auto-pretreatment (Auto-Pret) system (MGC Auto-Pret 018S, M&G Chematex Japan, Okayama) was used for the mini-column pretreatment, and consisted of a syringe pump (5 mL), an 8-port selection valve, a 6-way switching valve with a mini-column, and a holding coil (5.5 mL). It was combined with the FIA system. After the preconcentration of Pb(II) by the Auto-Pret system, the lead concentrations in the effluent were measured by the FIA system. The Auto-Pret system was operated by MGC LMPro software (ver. 2.5, M&G Chematex Japan).

### 2.3 Procedures

The Auto-Pret system was operated in six major steps (conditioning, collecting, rinsing, eluting, washing and eluting). Each solution was aspirated and propelled at flow rate of 45  $\mu$ L s<sup>-1</sup> by the syringe pump throughout the pretreatment operations. CS and RS were flowed at 1.0 mL min<sup>-1</sup> throughout the detection operations using FIA system.

*First step (column conditioning)*: After 0.1 M nitric acid (1000  $\mu$ L) was aspirated into HC, it was propelled through the mini-column, and then, ultrapure water (1000  $\mu$ L) was aspirated into HC and was propelled through the mini-column. For the pH adjusting, 1.00 x 10<sup>-3</sup> M nitric acid (2500  $\mu$ L) was aspirated into HC, being propelled through the mini-column.

Second step (lead collecting): A sample solution containing lead (2500  $\mu$ L) was aspirated into HC, and then it was propelled through the mini-column for the Pb(II) collection.

*Third step (matrices rinsing)*: Ultrapure water (1000  $\mu$ L) was aspirated into HC, and was propelled through the mini-column for rinsing the matrices remaining in the mini-column.

Forth step (lead eluting): Eluent (2500  $\mu$ L) was aspirated into HC, and then it was propelled from the reverse direction of the collection of lead into the mini-column. Finally, the effluent was propelled into the sample loop (300 $\mu$ L).

*Fifth step (column washing)*: Ultrapure water (2500  $\mu$ L) was aspirated into HC, and was propelled through the mini-column for washing the mini-column.

Final step (lead detecting): Pb(II) was detected as the following procedure of FIA. The reagent solution (RS) containing the coloration reagent (PAR:  $7.0 \times 10^{-4}$  mol L<sup>-1</sup>, pH 10.2 adjusted with the NH<sub>4</sub>Cl-NH<sub>3</sub> buffer ) and the carrier solution (CS, 3.0 M KCl) were propelled at flow rate of 1.0 mL min<sup>-1</sup>. A sample solution (300 µL) in the sample loop described above in forth step was manually injected into the CS stream by a sample injector. The sample in the CS stream was mixed with RS, which was flowed into the detector (spectrophotometer) through the reaction coil (RC, 1.0 m). The lead was determined by measuring the Pb-PAR chelate at 530 nm.

# 3. Results and Discussion

### 3.1 Conditions of the Auto-Pret procedures

After the preconcentration of Pb(II) by the Auto-Pret system, Pb(II) in the effluent was determined by the proposed system. Trace amounts of Pb(II) was adsorbed on Analig Pb-01 at pH 3.0 selectively, and the Pb(II) adsorbed on it was eluted with the KCl solution effectively. The pH and the volume of a sample solution were fixed at pH 3.0 and 2.5 mL, and the sample volume was adjusted for the preconcentration ratio. The concentration of the KCl solution (2.5 mL) as an eluent was examined by varying its concentrations from 1.0 M to 4.0 M to find a peak maximum at the concentration of 3.0 M; therefore 3.0 M KCl solution (2.5 mL) was used, the volume of which was enough for the quantitative elution of adsorbed Pb(II). The flow rate of each solution was fixed at 45  $\mu L s^{-1}$ , which did not affect the efficiency of adsorption and desorption of Pb(II). The experimental conditions were summarized in Table 1 and Table 2. These optimized conditions of the Auto-Pret system were used throughout this work.

### 3.2 Conditions of FIA system combined with Auto-Pret system

A sample zone containing Pb(II) in the effluent was kept into the sample loop after the preconcentration and elution; then the Pb concentrations of the sample zone in the loop was measured by the FIA system. Firstly, coloration reagents of (a) PAR and (b) TPPS illustrated in Fig. 2 were examined and used for the RS in the FIA system. The molar extinction coefficients of PAR and TPPS are  $4.38 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $2.75 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ , respectively. TPPS is a more sensitive reagent than PAR, easily reacts with alkali metal ions, especially with potassium ion, which interferes with the chelating reaction. Also, when TPPS was used for the RS, the peak profile of TPPS was broader and its tailing was longer than that of PAR as is shown in Fig.3. It is considered that the reaction rate of TPPS with Pb(II) was slower and hydrophobic TPPS was adsorbed on the PTFE tube. On the other hands, PAR does not react with potassium ion, which is contained in the eluent (KCl solution) for eluting the Pb(II) adsorbed on the Analig Pb-01 and in the carrier. As is shown in Fig. 4, the peak profile obtained with PAR was sharper than that of TPPS and its tailing is shorter. Therefore, PAR was used for the coloration of Pb(II) as RS of FIA.



Fig. 2 Coloration reagents examined for detecting Pb(II).

 
 Table 1
 Optimal conditions of auto-pretreatment procedures with mini-column and flow injection measurements.

| Auto-Pret system      |  |  |
|-----------------------|--|--|
| System                | M&G Chematex Japan, Auto-Pret 018S   |  |
| Operating program     | M&G Chematex Japan, LMPro Ver. 2.5   |  |
| Column size           | 2.0 mm i.d. x 40 mm length   |  |
| Resin                 | Analig Pb-01   |  |
| Flow rate             | 45 μL s <sup>-1</sup>  |  |
| Conditioning solution | 0.1 M nitric acid (1 mL), ultrapure water (1                               |  |
|                       | mL), 1.0 x 10 <sup>-3</sup> M nitric acid (2.5 mL)                         |  |
| Sample                | 20 mL, pH 3  |  |
| Rinsing solution      | Ultrapure water (1 mL)   |  |
| Eluent                | 3 M KCl (2.5 mL, pH 7)   |  |
| Washing solution      | Ultrapure water (2.5 mL)   |  |
| FIA system            |  |  |
| Pump                  | double plunger-type,   |  |
|                       | Sanuki Industry Co. Ltd, RX-703 T  |  |
| Detector              | Spectrometer, Soma Optics Ltd., S-3250                                     |  |
| Sample                | 300 µL   |  |
| Temperature           | 25 °C  |  |
| Flow rate             | 1.0 mL min <sup>-1</sup>   |  |
| Reaction Coil (RC)    | 1.0 m  |  |
| Reagent solution (RS) | 7.0 x 10 <sup>-4</sup> M PAR, NH <sub>4</sub> Cl-NH <sub>3</sub> , pH 10.2 |  |
| Carrier solution (CS) | 3.0 M KCl  |  |
| Detection             | 530 nm   |  |

 Table 2 Operating procedure of the Auto-Pret system for the preconcentration of Pb(II).

| Solutions                                 | Aspirate <sup>1</sup> | Dispense <sup>1</sup>       |  |  |
|---|-----------------------|-----------------------------|--|--|
| First step (column con                    | ditioning)            |                             |  |  |
| 0.1 M HNO3                                | 1000 µL to HC         |                             |  |  |
|   |                       | 1000 µL to column           |  |  |
| Ultrapure water                           | 1000 µL to HC         |                             |  |  |
|   |                       | 1000 µL to column           |  |  |
| 1.0 x 10 <sup>-3</sup> M HNO <sub>3</sub> | 2500 µL to HC         |                             |  |  |
|   |                       | 2500 µL to column           |  |  |
| Second step (lead collecting)             |                       |                             |  |  |
| Sample solution                           | 20 mL to HC           |                             |  |  |
|   |                       | 20 mL to column             |  |  |
| Third step (matrices rinsing)             |                       |                             |  |  |
| Ultrapure water                           | 1000 µL to HC         |                             |  |  |
|   |                       | 1000 µL to column           |  |  |
| Forth step (lead eluting)                 |                       |                             |  |  |
| 3.0 M KCl                                 | 2500 µL to HC         |                             |  |  |
|   |                       | 2500 µL to sample loop      |  |  |
|   |                       | through column <sup>2</sup> |  |  |
| Fifth step (column was                    | hing)                 |                             |  |  |
| Ultrapure water                           | 2500 µL to HC         | —                           |  |  |
|   |                       | 2500 µL to column           |  |  |

<sup>1</sup> The flow rate is 45  $\mu$ L s<sup>-1</sup> by Auto-Pret system.

<sup>2</sup> The solution is propelled into the sample loop in the FIA system.



**Fig. 3** Flow signals of Pb(II) by the FIA system without Auto-Pret system using TPPS. Sample,  $0.0 - 8.0 \times 10^{-7}$  M Pb(II); sample loop, 100 µL; CS, water; RS,  $1.0 \times 10^{-5}$  M TPPS and buffer (pH 10.2); flow rate of CS and RS, 0.6 mL min<sup>-1</sup>; RC, 3.0 m x 0.5 mm i.d.; Detector, 464 nm.



**Fig. 4** Flow signals of Pb(II) by the FIA system without Auto-Pret system using PAR. Sample,  $0.0 - 8.0 \times 10^{-7}$  M Pb(II); sample loop, 300 µL; CS, water; RS,  $7.0 \times 10^{-4}$  M PAR and buffer (pH 10.2); flow rate of CS and RS, 0.6 mL min<sup>-1</sup>; RC, 1.0 m x 0.5 mm i.d.; Detector, 530 nm.



**Fig. 5** Effect of sample volume as an effluent volume kept in the loop from Auto-Pret system. Conditions are the same as in the section of 2.3 Procedures.

Secondly, the experimental conditions, such as flow rate, RC length, sample volume, PAR concentration and pH, of the FIA system were optimized as follows: The effect of the flow rate on the peak profiles was examined by varying it from 0.4 mL min<sup>-1</sup> to 1.4 mL min<sup>-1</sup>. The peak height increased along with an increase in the flow rate, then leveled off at the flow rates more than 1.0 mL min<sup>-1</sup>. The length of RC was examined by varying it from 0.5m to 3.0 m. The peak height was maximum at a RC length of 1.0 m and decreased with an increase in the RC length more than 1.0 m. The flow rate and RC length were affected by the diffusion of the sample zone and the reaction time between PAR and Pb(II). The flow rate and RC length were fixed at 1.0 mL min<sup>-1</sup> and 1.0 m respectively. The sample volume, which corresponds to the size of sample loop in the FIA system, was examined by varying it from 50  $\mu L$  to 400  $\mu L$  as shown in Fig. 5. The peak height increased with an increase in the sample volume up to 300  $\mu$ L, and then the peak heights became almost steady for further increases. As a result, the sample volume was fixed at 300 µL for further experiments.

The optimal concentration of PAR was examined by varying it from  $1.0 \ge 10^{-4}$  to  $9.0 \ge 10^{-4}$  M. The peak height was almost the same in the range of the examined concentrations of PAR, although the peak profile was unstable and became less reproducible with an increase in the concentration of PAR. Therefore, the PAR concentration was fixed at  $7.0 \ge 10^{-4}$  M, which was enough for reaction with Pb(II) in samples. Also, the pH of the reagent solution was examined by varying it from 9.8 to 10.6. The peak height observed at pH more than 10 was higher than that at the lower pH range, showing a little effect on pH above 10. In further experiments, the pH of RS was fixed at 10.2. Temperature of the reaction coil was not any significant factor for the reproducibility of the peak profiles, as long as it was kept constant (room temperature,  $25^{\circ}$ C).

### 3.3 Effect of foreign ions on measuring trace amounts of lead

Several metal ions, Na<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2+</sup>, were examined to see their effect on the determination. As in the present analytical procedures, lead(II) was concentrated on the solid phase material, Analig Pb-01 and was eluted with 3 M KCl. Then, the Pb(II)-PAR chelate was detected with a spectrophotometer. The effect of metal ions was examined by adding each metal ion to the sample solution, and the absorbance at 530 nm was monitored by the proposed FIA system combined with the Auto-Pret system. The recovery values of Pb(II) are shown in Table 3, in the presence of the foreign ions,  $Na^{+}$ ,  $Mg^{2+}$ ,  $Al^{3+}$ ,  $K^{+}$ ,  $Ca^{2+}$ ,  $Fe^{3+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cl^{-}$ ,  $NO_{3}^{-}$  and  $SO_{4}^{2+}$ . The recovery values of Pb(II) were 95 - 99%, which means that these metal ions little interfered with the detection of Pb(II), as Analig Pb-01 can adsorb Pb(II) selectively. Therefore, we can safety conclude that the proposed method can be selectively determine lead without any significant interference from ions commonly existing in environmental waters.

### 3.4 Analytical performance and applications

The proposed FIA system was applied to the determination of trace Pb(II) in aquatic samples. The experimental conditions used are shown in Table 1 and Table 2. Typical flow signals at the

| Ions             | Concentration / M      | Pb(II) Recovery / % <sup>1</sup> |
|------------------|------------------------|----------------------------------|
| $Na^+$           | 2.0 x 10 <sup>-3</sup> | 98                               |
| $Mg^{2+}$        | 2.0 x 10 <sup>-3</sup> | 98                               |
| $Al^{3+}$        | 2.0 x 10 <sup>-4</sup> | 99                               |
| $K^+$            | 2.0 x 10 <sup>-3</sup> | 98                               |
| Ca <sup>2+</sup> | 2.0 x 10 <sup>-3</sup> | 99                               |
| Fe <sup>3+</sup> | 2.0 x 10 <sup>-4</sup> | 95                               |
| Cu <sup>2+</sup> | 2.0 x 10 <sup>-4</sup> | 95                               |
| $Zn^{2+}$        | 2.0 x 10 <sup>-4</sup> | 98                               |
| Cl               | 2.0 x 10 <sup>-3</sup> | 99                               |
| NO <sub>3</sub>  | 2.0 x 10 <sup>-3</sup> | 99                               |
| $SO_4^{2-}$      | 2.0 x 10 <sup>-3</sup> | 98                               |

 Table 3 Effect of foreign ions on Pb(II) determination by the proposed technique.

<sup>1</sup> Pb(II), 2.0 x 10<sup>-7</sup> M; Sample volume, 2.5 mL.

**Table 4**Analytical results and recovery values of Pb(II).

| Pb(II) / 10 <sup>-9</sup> M |               | D / 0/       |
|-----------------------------|---------------|--------------|
| Added                       | Measured      | Recovery / % |
| 0.00 (river water)          | $4.30\pm0.01$ | —            |
| 4.30                        | $8.43\pm0.02$ | 98           |
| 12.9                        | $17.3\pm0.01$ | 101          |



**Fig. 6** Typical flow signals of Pb(II) by the FIA system combined with Auto-Pret system. Sample,  $0.0 - 8.0 \times 10^{-8} \text{ mol } \text{L}^{-1}$  Pb(II); sample volume (effluent),  $300\mu$ L; eluent and CS, 3 M KCl; RS, 7.0 x  $10^{-4}$  M PAR.

concentration range from 0.0 x  $10^{-8}$  mol L<sup>-1</sup> to 8.0 x  $10^{-8}$  mol L<sup>-1</sup> are shown in Fig. 6. It shows the sharp peaks and the stable base lines. The regression equation and correlation coefficients (r) were evaluated as follows: y = 0.0145x + 0.02 (y: absorbance, x: lead concentration) and r = 0.996. The negative peaks appearing at the leading edge of each peak arose from the sharp pressure

discontinuity caused by syringe movements. The negative responses little affected the peak height, and hence the Pb(II) determination. The enrichment factors, calculated by comparing the peak height obtained by the FIA system with and without the Auto-Pret system, which were about 3 using 2.5-mL sample solutions and about 15 using 20-mL sample solutions. The limit of detection (LOD,  $3\sigma$ ) and the limit of quantification (LOQ,  $10\sigma$ ) were 0.5 x  $10^{-9}$  M and 1.0 x  $10^{-9}$  M, respectively. The obtained LOD and LOQ values demonstrate that the proposed method can be applied to the determination of trace Pb(II) in tap and river waters.

Finally, the present FIA system was applied to the analysis of a river water, which was sampled at Zasu River near Okayama University. Analytical results and recovery values of Pb(II) are shown in Table 4. Analytical data obtained by the proposed method were highly reproducible for Pb(II)  $(4.30 \pm 0.01) \times 10^{-9}$  M. The recovery test was also performed by using the same samples by adding trace amounts of Pb(II); Pb(II) recovered was  $(8.43 \pm 0.02) \times 10^{-9}$  M and  $(17.3 \pm 0.01) \times 10^{-9}$  M, respectively, when 4.30 x  $10^{-9}$  M and  $12.9 \times 10^{-9}$  M of Pb(II) were added to the sample, indicating that the recovery values were 98% and 101%, respectively.

### 4. Conclusions

The proposed FIA system combined with the Auto-Pret system with the mini-column packed with Analig Pb-01, which is based on the SI technique, was successfully developed for the determination of trace amounts of Pb(II), which is capable of detecting trace amounts of Pb(II) using PAR as a coloration reagent. The LOD and LOQ were  $0.5 \times 10^{-9}$  M and  $1.0 \times 10^{-9}$  M, respectively. The proposed system was applied to the determination of trace lead in real river water samples. The proposed system can be applied to the analysis of the regulated values of waste waters (0.1 mg/L), environmental waters (0.01 mg/L) and WHO Guidelines of lead in drinking water (0.01 mg/L).

# References

- A. I. Cabanero, Y. Madrid and C. Camara, *Anal. Bioanal. Chem.*, **373**, 244 (2002).
- [2] T. Seki, Y. Hirano and K. Oguma, Anal. Sci., 18, 351 (2002).
- [3] M. C. Yebra, L. Rodriguez, L. Puig and A. Moreno-Cid, *Mikrochim. Acta*, 140, 219 (2002).
- [4] V. A. Lemos, M. Guardia and S. L. C. Ferreira, *Talanta*, 58, 475 (2002).
- [5] S. Dadfarnia, A. M. H. Shabani, F. Tamaddon and M. Rezaei, *Anal. Chim. Acta*, 539, 69 (2005).
- [6] R. Chomchoei, M. Miro, E. H. Reis, Hansen and J. Shiowatana, *Anal. Chim. Acta*, 536, 183 (2005).
- [7] B. F. Resi, M. Knochen, G. Pignalosa, N. Cabrera and J. Giglio, *Talanta*, **64**, 1220 (2004).
- [8] A. P. Fernandes, M. de Moraes and J. A. Gomes Neto, *Atom. Spectrosc.*, 24, 179 (2003).
- [9] C. R. T. Tarley and M. A. Z. Arruda, Anal. Lett., 38, 1427 (2005).
- [10] G. A Zachariadis, A. N. Anthemidis, P. G. Bettas and J. A. Stratis, *Talanta*, 57, 919 (2002).
- [11] A. N. Anthemidis, G. A. Zachariadis and J. A. Stratis, Talanta,

58, 831 (2002).

- [12] Y. Li, Y. Jiang, X.-P. Yan, W.-J. Peng and Y.-Y. Wu, Anal. Chem., 74, 1075 (2002).
- [13] A. Wang, L. Guo and H. Zhang, *Fenxi Huaxue*, **33**, 385 (2005).
- [14] M. Soylak, L. Elci, Y. Akkaya and M. Dogan, *Anal. Lett.*, 35, 487 (2002).
- [15] R.G.Wuilloud, J. A.Salonia, J. A.Gasquez, R.A.Olsina and L.D. Martinez, Anal. Sci., 17, 457 (2001).
- [16] M.Zougagh, Garcia de A.Torres, E. V. Alonso and J. M. C.Pavon, *Talanta*, 62, 503 (2004).
- [17] M.S. Bispo, Andrade M. G.Korn, E. S. B Morte and L. S. G. Teixeira, Spectrochim. Acta Part B, 57, 2175 (2002).
- [18] S. N. Willie and R. E. Sturgeon, Spectrochim. Acta B, 56, 1707 (2001).
- [19] S. N. Willie, J. W. H. Lam, L. Yang and G. Tao, Anal. Chim. Acta, 447, 143 (2001).
- [20] R. K. Katarina, N. Lenghor and S. Motomizu, Anal. Sci., 23, 343 (2007).
- [21] A. Sabarudin, N. Lenghor, M. Oshima, L. Hakim, T.

Takayanagi, Y.-H. Gao and S. Motomizu, *Talanta*, **72**, 1609-1617 (2007).

- [22] M.Ueda, N. Teshima, T. Sakai, Y. Joichi and S. Motomizu, *Anal. Sci.*, 26, 597 (2010).
- [23] S. Chuanuwatanakul, W. Dungchai, O. Chailapakul and S. Motomizu, *Anal.Sci.*, 24, 589 (2008).
- [24] S. Chuanuwatanakul, E. Punrat, J. Panchompoo, O. Chailapakul and S. Motomizu, J. Flow Injection Anal., 25, 49 (2008).
- [25] K. Oshita and S. Motomizu, Bunseki Kagaku, 57, 291 (2008).
- [26] A. Sabarudin, N. Lenghor, L-P. Yu, Y. Furusho and S. Motomizu, *Spectroscopy Lett.*, **39**, 669 (2006).
- [27] M. Kumai, K. Nakayama, Y. Furusho, T. Yamamoto, Y. Takamura, *Bunseki Kagaku*, 58, 561 (2009).
- [28] Kyoritsu Chemical-Check Lab., Corp., Pack Test Pb Set (SPK-Pb).

(Received May 6, 2013) (Accepted June 6, 2013)