

Rapid determination of lead extracted by acetic acid from glazed ceramic surfaces by flow injection on-line preconcentration and spectrophotometric detection

Mai Kuramochi, Kenichi Tomioka, Masanori Fujinami, Koichi Oguma*

Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Chiba University, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

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Abstract

A rapid method has been developed for the determination of lead extracted by acetic acid from glazed ceramic surfaces by flow injection analysis without any pretreatment. An aliquot of 4% acetic acid solution, which has been kept in a teacup for 24 h in the dark, is injected into a carrier solution (1 M nitric acid) and passed through a Pb-Spec resin column. After washing the column with an ammonium nitrate solution, the lead adsorbed on the column is eluted with an ammonium oxalate solution and then merged with a 4-(2-pyridylazo)resorcinol (PAR) solution, followed by measurement of the absorbance of the lead–PAR complex at 530 nm. The detection limit, concentration giving a signal equal to three times the standard deviation of the blank signal, is 8 ng ml^{-1} . The relative standard deviation of measurements at the $0.8 \text{ } \mu\text{g ml}^{-1}$ level is 0.35% ($n = 5$). The sample throughput is 12 per hour.

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1. Introduction

Lead is one of the most toxic metals. It adversely affects the central and peripheral nervous systems and the kidney [1]. However, its unique properties make itself to be used as industrial material in diverse fields. Glaze is a typical example of materials containing lead. It is a thin layer of liquid, which is put on a piece of pottery and becomes hard and shiny when the pottery is heated in a hot oven. The possibility of elution of the lead from the surface is, therefore, present in some of glazed ceramic (dinnerware). Hence, the Japan food sanitation law limits the amount of lead released by 4% acetic acid from glazed ceramic (dinnerware) surfaces: the limits for lead specified in the law are $17 \text{ } \mu\text{g cm}^{-2}$ for flatware of the internal depth $<25 \text{ mm}$, 5 mg l^{-1} for hollow ware of the capacity $<1.1 \text{ l}$ and 2.5 mg l^{-1} for hollow ware of the capacity $>1.1 \text{ l}$.

The Japanese official method for the determination of the lead released from the surface of dinnerware is tedious and

time-consuming because the 4% acetic acid solution, which is kept in dinnerware to be tested for 24 h in the dark, must be evaporated up and treated with hydrochloric acid to improve the precision of the determination of lead by FAAS [2]. The aim of the present work is to develop a rapid method for determining the lead extracted by acetic acid from glazed ceramic surfaces.

The various flow injection methods have so far been proposed for the determination of trace lead in diverse samples. Most of the reported methods employed the on-line preconcentration coupled with the appropriate detection. The following examples have been reported for these several years.

Lead in drinking water was preconcentrated as 2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol complexes on a mini-column packed with Amberlite XAD-16 prior to its determination by ICP-AES using pneumatic nebulization [3]. A flow injection method using a mini-column loaded with 8-hydroxyquinoline immobilized on controlled pore glass was also described for the determination of trace lead along with copper, cadmium, zinc, nickel and iron by ion chromatography [4]. On-line preconcentration and simultaneous determination of heavy metal ions in different water samples

* Corresponding author. Tel.: +81 43 290 3502; fax: +81 43 290 3502.
E-mail address: koguma@faculty.chiba-u.jp (K. Oguma).

by ICP-AES was carried out using retention of diethyldithiocarbamate chelates on an octadecyl silica mini-column [5]. Trace lead in a variety of water samples was collected as lead hydroxide precipitates onto the inner walls of a knotted reactor and dissolved by dilute nitric acid to be delivered to FAAS [6]. Ion-exchange for preconcentration and elimination of interferences was also used for the spectrophotometric determination of lead in water samples [7]. Methylthiosilylated silica gel and chitosan were used for preconcentration of lead for ICP-AES determination [8] and spectrophotometric detection of lead–dithizone complex in aqueous medium [9], respectively. Lead in seawater was retained on a mini-column containing Amberlite XAD-4 impregnated with 1-(2-pyridylazo)-2-naphthol [10] or was complexed with 8-hydroxyquinoline-5-sulfonic acid (8-HQS) and then collected on a mini-column filled with florisisil [11]. Total lead and lead isotope ratios in natural waters were determined using sorption of lead complexes with 1-phenyl-3-methyl-4-benzoylpyrazol-5-one on the inner walls of PTFE knotted reactor in advance of the on-line ICP-TOFMS detection [12].

Lead in water and sediment collected as 1-nitroso-2-naphthol complexes on a Diaion HP-20 column for FAAS determination [13]. The simultaneous determination of lead and cadmium in river water and soil was accomplished utilizing in-line cation exchange separation and spectrophotometric detection [14]. Lead in wine and water was preconcentrated on a mini-column filled with polyurethane form modified with 2-(2-benzothiazolylazo)-*p*-cresol [15] or Pb-Spec resin [16] for the FAAS determination of lead. Cadmium, copper and lead in wine were determined by FAAS after solid phase extraction of diethyldithiophosphate complexes on a mini-column filled with C18 bonded silica gel or powdered polyethylene as sorbent [17]. For the determination of lead in environmental samples, the on-line formed lead–pyrrolidinedithiocarbamate complex was sorbed on the polyurethane form, subsequently eluted by 2-methyl-4-pentanone, and determined by FAAS [18]. The determination of lead in biological samples was carried out using a flow injection on-line micelle-mediated preconcentration and separation without phase separation coupled with electrothermal atomic absorption spectrometry (ETAAS) [19]. A chelating resin, Muromac A-1 [20], and a new packing material, acrylic acid grafted PTFE fibers [21], were used for on-line preconcentration of lead in urine, and environmental and biological samples, respectively.

The aforementioned techniques are accurate, but they are time-consuming. The present paper will describe the rapid method for the determination of lead in 4% acetic acid, which had been used to extract lead from the surface of glazed ceramic, by coupling the on-line preconcentration of lead with a Pb-Spec resin (EiChrom Industries, Darien, IL) column with the spectrophotometric detection. In the previous papers, we have already described the flow injection determination of lead in iron and steel [22], river water [23] and seawater [23,24] using Pb-Spec resin for on-line preconcentration of lead and atomic spectroscopic detection. Pb-Spec

resin is prepared by impregnating Amberchrom CG-71md resin (Supelco) with an isodecanol solution of bis-4,4'(5')-[*tert*-butylcyclohexano]-18-crown-6 and exhibits the high selectivity for lead [25].

2. Experimental

2.1. Instrumentation

The block diagram of FIA system used for the spectrophotometric determination of lead is shown in Fig. 1. PTFE tubing (0.5 mm i.d.) was used to construct the manifold. The carrier and washing solutions, eluent and reagent solution were delivered by a pulseless pump PUD-16 (GL Sciences Inc., Tokyo), a mini-chemical pump NP-KX-120U (Nihon Seimitsu, Tokyo) and a double plunger type pump DMX-2000 (Sanuki Kogyo, Tokyo), respectively, and a six-way auto switching valve MPV-6A (GL Sciences Inc., Tokyo) used for sample injection was filled with sample solutions by a peristaltic mini pump SJ-1211 (Atto, Tokyo). The absorbance of the colored lead complex was monitored by a visible detector S-3250 (Soma Optics, Tokyo) and recorded by a chart recorder Shimadzu U-135 (Shimadzu, Tokyo).

An SII 1700 ICP spectrophotometer (Seiko Instruments, Tokyo) was used under the experimental conditions summarized in Table 1 for the measurement of the distribu-

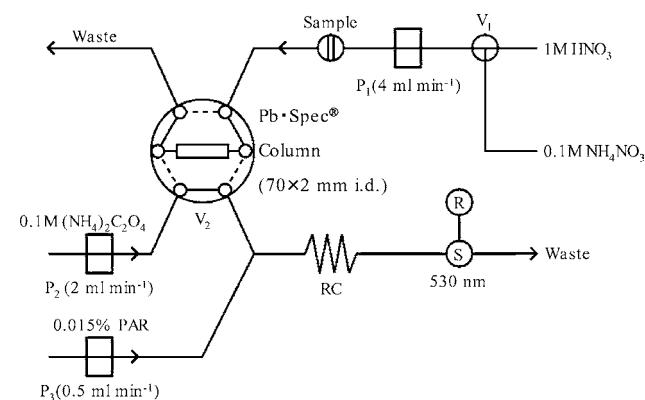


Fig. 1. Flow injection system for the determination of lead. P: pump; V: valve; RC: reaction coil; S: spectrophotometric detector; R: recorder.

Table 1
Operating conditions of ICP-AES^a

Plasma conditions	
Incident RF power (kW)	1.3
Plasma gas (l min ⁻¹)	18.0
Auxiliary gas (l min ⁻¹)	0.5
Carrier gas (l min ⁻¹)	0.45
Sampling conditions	
Observation height (mm)	12
Sample flow rate (ml min ⁻¹)	1.0
Integration time	4 s × 3 times
Wavelength (nm)	220.422

^a Seiko Instruments Plasma Spectrometer SPS 1700HVR.

tion coefficient of lead on Pb-Spec resin in 4% acetic acid medium.

2.2. Reagents

All of the reagents used were of analytical reagent grade and were used as received. Distilled and deionized water was further purified by a Milli-Q Ultrapure water-purification system (Millipore, Bedford, USA).

2.3. Solutions

The stock standard solution of lead(II) ($1000 \mu\text{g ml}^{-1}$) was prepared by dissolving an appropriate amount of lead nitrate in 0.1 M nitric acid. The working solutions were prepared daily by diluting the stock standard solution with 4% acetic acid.

The stock solution of cadmium(II) ($1000 \mu\text{g ml}^{-1}$) was prepared by dissolving an appropriate amount of cadmium powder in 5 ml of 2 M HCl and diluting to 100 ml with water.

The stock solution of zinc(II) ($1000 \mu\text{g ml}^{-1}$) was prepared by dissolving an appropriate amount of zinc sand in 2.5 ml of 4 M nitric acid and diluting to 100 ml with water.

The stock solution of PAR (0.2%) was prepared by dissolving 0.2 g of 4-(2-pyridylazo)resorcinol in 50 ml of ammonia water and diluting to 100 ml with water.

An ammonia–ammonium chloride buffer solution (pH 10) was prepared by dissolving 13 g of ammonium chloride in 40 ml of ammonia water and diluting to 200 ml with water.

A 0.015% PAR solution was prepared by mixing 15 ml of 0.2% PAR solution with 30 ml of pH 10 buffer solution and diluting to 200 ml with water.

2.4. Mini-column for preconcentration of lead

The preconcentration column for on-line use was prepared by packing Pb-Spec resin into a PTFE tube (70 mm long and 2 mm i.d.) and plugging both ends of the tube with cotton wool.

2.5. Methodology

2.5.1. Extraction step

A teacup to be tested was filled with 4% acetic acid solution and allowed to stand in the dark for 24 h. The acetic acid solution was subjected to the flow injection determination of lead without any treatment as described below.

2.5.2. Flow injection analysis step

A 2.4-ml aliquot of the sample solution was injected into the carrier solution (1 M nitric acid; 4 ml min^{-1}) and the lead in the sample solution was adsorbed on the Pb-Spec resin column. The column was washed with 0.1 M ammonium nitrate solution (4 ml min^{-1}) for 1 min and then the lead on the column was eluted with 0.1 M ammonium oxalate solution (2 ml min^{-1}). The eluted lead was mixed with 0.015% PAR

solution (0.5 ml min^{-1}) and the formed Pb–PAR complex was monitored at 530 nm by the spectrophotometric detector. The peak height was used as a measure of the signal.

3. Results and discussion

3.1. Optimization procedure

3.1.1. Effect of acid in sample solutions for FIA

Lead is most strongly adsorbed on Pb-Spec resin from 1 M nitric acid solution [25]. For comparison, 2.4 ml each of 4% acetic acid solution and 1 M nitric acid solution, of which lead concentration was $0.80 \mu\text{g ml}^{-1}$, were injected into the FIA system. The peak heights observed for both solutions turned out to be almost the same as each other. This confirmed that 4% acetic acid solution, which had been left in glazed ceramics, could be injected into the FIA system for the determination of lead without pretreatment.

3.1.2. Effect of acid used as carrier solution

The constant volume (2.4 ml) of 4% acetic acid solution containing $0.80 \mu\text{g Pb ml}^{-1}$ was injected into a carrier solution, 1 M nitric acid or 4% acetic acid. The peak height obtained for 1 M nitric acid was 43% higher than that obtained for 4% acetic acid. Therefore, 1 M nitric acid was used as a carrier solution.

In order to elucidate the reason of the above observation, we measured the distribution coefficient of lead on Pb-Spec resin in 4% acetic acid by a batch method and found that to be about 60. To our knowledge, such a small distribution coefficient is not enough to retain lead on the Pb-Spec resin mini-column used here. Therefore, a residual amount of nitric acid might be trapped in the Pb-Spec resin column during conditioning with 1 M nitric acid and would serve to increase the affinity of lead to Pb-Spec resin when a sample solution of 4% acetic acid is injected into 1 M nitric acid.

3.1.3. Effect of sample volume

The effect of sample volume was examined by injecting 0.8, 2.0, 4.0 or 4.0 ml of $0.80 \mu\text{g Pb(II) ml}^{-1}$ solution. The peak height increased with increase in the sample volume injected, i.e., 4.3 mm for 0.8 ml, 86.0 mm for 2.4 ml and 154.7 mm for 4.0 ml. However, the injection of 4.0-ml sample required longer time, which resulted in a decrease in the sample throughput. The peak height obtained by injecting a 2.4-ml sample was sufficient and accordingly 2.4-ml samples were injected hereinafter.

3.1.4. Effect of carrier solution flow rate

The effect of the flow rate of the carrier solution was studied over the values ranging from 1.0 to 4.0 ml min^{-1} by injecting 2.4 ml of $0.80 \mu\text{g Pb(II) ml}^{-1}$ solution. The peak height increased from 99.2 mm at 1.0 ml min^{-1} to 113.7 mm at 2.0 ml min^{-1} and then remained constant up to 4.0 ml min^{-1} .

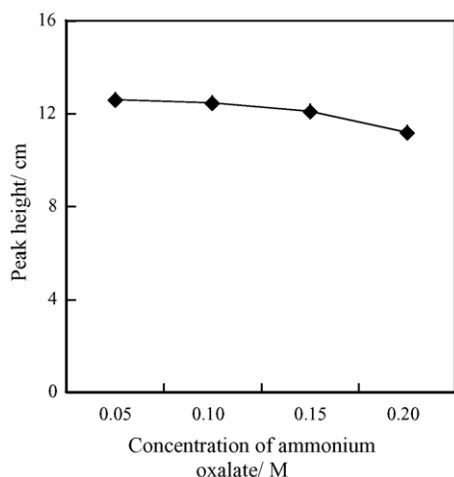


Fig. 2. Effect of ammonium oxalate concentration. Sample: 0.80 $\mu\text{g Pb(II)}$ per ml of 4% acetic acid solution; sample volume: 2.4 ml.

The higher flow rate could give the high sample throughput, but the higher flow rate than 4.0 ml min^{-1} resulted in the leak of the solutions from the joints between the connectors and the PTFE tube. Therefore, the flow rate of the carrier solution was kept at 4.0 ml min^{-1} throughout the work.

3.1.5. Effect of eluent (ammonium oxalate) concentration

Ammonium oxalate was used as the eluent for lead(II) as described in the previous paper [22]. The peak height decreased slightly with increase in the concentration of ammonium oxalate (Fig. 2). An excess amount of oxalate seems to interfere with the reaction of lead(II) with PAR. Both 0.05 and 0.10 M ammonium oxalate solution gave almost the same peak height as each other, but the reproducibility of the peak height obtained was found to be a little better when 0.10 M ammonium oxalate solution was used. Thus, 0.10 M ammonium oxalate solution was selected as the eluent for lead(II).

3.1.6. Effect of PAR concentration

There is no selective chromogenic reagent for lead and PAR was chosen here from the standpoint of sensitivity (molar absorptivity: 3.7×10^4) [26]. The effect of the concentration of PAR ranging from 0.005 to 0.020% was tested. The peak height was found to be almost constant at 0.010% or above (Fig. 3) and 0.015% PAR solution was used as the chromogenic reagent solution.

3.1.7. Effect of reaction coil

The reaction coil length affects the reaction time of lead(II) with PAR and dispersion of the sample zone. The effect of the reaction coil length ranging from 0.5 to 5.0 m was examined and the highest peak was obtained by the coil of 0.5 m (Fig. 4). Therefore, a 0.5-m coil was used as the reaction coil.

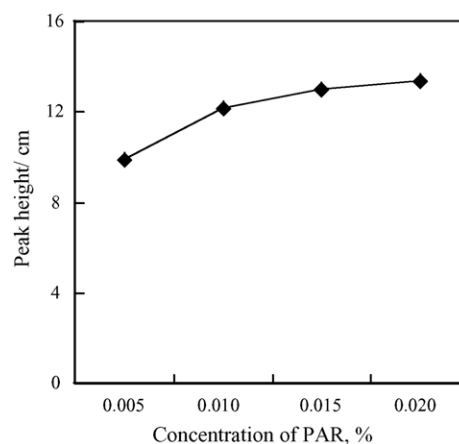


Fig. 3. Effect of PAR concentration. For sample and sample volume, see Fig. 2.

3.1.8. Effect of wavelength

The absorbance of Pb(II)–PAR complex formed at pH 10 is usually measured at 520 nm. The maximum absorbance was actually observed at 520 nm. However, the signal obtained at 520 nm is noisier than that at 530 nm. Thus, the absorbance of Pb(II)–PAR complex was monitored at 530 nm.

3.2. Analytical parameters

A calibration curve of lead, based on optimal conditions ([ammonium oxalate] = 0.10 M, [PAR] = 0.015%, pH 10.0, carrier flow rate = 4.0 ml min^{-1} , eluent flow rate = 2.0 ml min^{-1} , PAR solution flow rate = 0.5 ml min^{-1} , reaction coil length = 0.50 m, sample volume = 2.4 ml, wave length = 530 nm), was obtained. The average calibration equation was peak height (cm) = $12.61 [\text{Pb(II)}, \mu\text{g ml}^{-1}] + 0.12$ (correlation coefficient $r^2 = 0.999$) for 0–1.2 $\mu\text{g Pb(II) ml}^{-1}$.

The preconcentration factor of the Pb-Spec column was found to be 2.5, falling below our expectations. This might

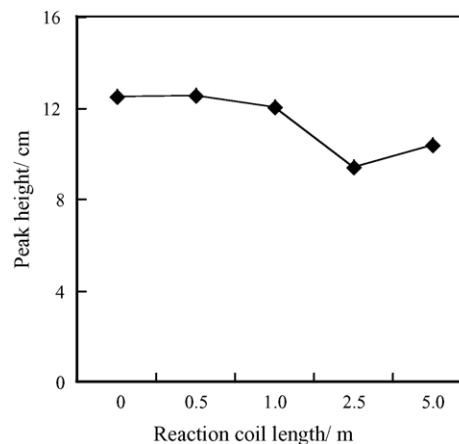


Fig. 4. Effect of reaction coil length. For sample and sample volume, see Fig. 2.

Table 2
Interference study^a

Metal ions	Added ($\mu\text{g ml}^{-1}$)	Pb(II) recovery (%)
Cd(II)	0.08	100 \pm 3
	0.8	102 \pm 0
	8	103 \pm 1
Zn(II)	0.8	100 \pm 0
	8	101 \pm 0
	80	102 \pm 2

^a Pb(II): 0.8 $\mu\text{g ml}^{-1}$, $n=3$.

Table 3
Determination of lead extracted by acetic acid from the glazed ceramic (tea cups) surfaces

Sample	Added ($\mu\text{g ml}^{-1}$)	Found ^a ($\mu\text{g ml}^{-1}$)	Recovery (%)
A ^c	0	N.D. ^b	–
	0.40	0.39 \pm 0.01	98
	0.80	0.80 \pm 0.02	100
B ^d	0	N.D. ^b	–
	0.40	0.39 \pm 0.01	98
	0.80	0.80 \pm 0.00 ₁	100
C ^c	0	N.D. ^b	–
	0.40	0.40 \pm 0.01	100
	0.80	0.81 \pm 0.001	101

^a $n=3$.

^b Not detected.

^c Made in England.

^d Made in Japan.

be because lead is so firmly retained on the Pb-Spec resin and can be removed with a larger volume of the eluent.

The limit of detection, concentration giving a signal equal to three times the standard deviation of the blank signal, is 8 ng ml⁻¹. The relative standard deviation of the measurements at the 0.8 $\mu\text{g ml}^{-1}$ level was 0.35% ($n=5$). The sample throughput is 12 per hour.

3.3. Interference

Interference from zinc and cadmium, often found in real samples, was investigated applying the method to mixed solutions, in the presence of 0.80 $\mu\text{g ml}^{-1}$ lead. As shown in Table 2, both zinc and cadmium do not interfere with the determination of lead even if zinc and cadmium are present at concentrations much higher than those normally present in real samples. This means that lead is effectively separated from zinc and cadmium by the Pb-Spec resin column. The column could be repeatedly used more than 500 times for the preconcentration of lead.

3.4. Application to real samples

The proposed method was applied to the determination of lead extracted from the surfaces of teacups. Lead was not found for all the cups tested (see Table 3). The addition test was therefore attempted and the recovery was found to be

98–101%. Therefore, the proposed method will be applied to the elution test of lead of various glazed ceramic samples.

4. Conclusions

Based on the aforementioned, it is obvious that the proposed method is very simple, rapid, very sensitive, very selective, with high accuracy and eligible to become interference free. Thus, it is highly promising for its application to the routine determination of lead extracted by acetic acid from glazed ceramic surfaces.

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