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Determination of Lead in Aqueous Samples using a Flow Injection Analysis System with On-line Preconcentration and Spectrophotometric Detection

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ABSTRACT

A simple and accurate flow injection analysis systems coupled with spectrophotometric detetection was developed to preconcentration and determination of lead in aqueous samples. The FIA systems based on the reaction of lead (II) with 4-(2-pyridylazo) resorcinol (PAR) in buffer pH 9 with an adsorption maximum at 523 nm. The developed flow system includes a lead preconcentration step in a column packed with Amberlite XAD-7 resin. The optimum preconcentration system, chemical and FIA variables were investigated. The proposed method has a linear calibration range 0.05-0.90 mg L^{-1} of lead with the regression $y = 1.522x–0.031$, $R^2 = 0.9963$, whereas the observed detection limit (3S, n = 20) was 11 μg L^{-1} and the percentage of recovery of 102%. The proposed system show good precision and accuracy with relative standard deviations is 2.4%. The sampling frequency was 12 determinations per hour. The method has been applied to the determination of lead in real water samples with a preconcentration factor of 3.

Keywords: flow injection analysis, Lead, 4-(2-pyridylazo) resorcinol, preconcentration

INTRODUCTION

Human activity may result in increasing level of contamination in environment. Lead is one of the heavy metals frequently determined in waters samples due to high toxicity (United States Environmental Protection Agency, 2001). Lead in water system has influenced on the quality of life seriously especially in developing country. Even small amounts of lead that enter the environment can result in elevated concentrations that can result in adverse effects. A regular absorption of small quantities of lead may cause serious injuries to health such as encephalopathy, kidney damage and several effects in the body (Clarkson et. al., 1998; dos Santos *et.al.*, 2004). In natural water, its typical concentration lies between 2 and 10 ng mL^{-1}, whereas, the upper limit recommened by WHO is less than 10 ng mL^{-1} (Tewari and Singh, 2002). Therefore, lead analysis in water has received attention strongly. At present, the method for the determination of trace lead mainly were atomic absorption spectrometry (requiring a preconcentration step) (Tewari and Singh, 2002; Karadjova *et. al.*, 1998; Vinas *et. al.*, 1997) and the spectrophotometric method based on various reagents (Kilian and Pyrzyńska, 2003; Zaijun *et.al.*, 2003).

However, lead determination in aqueous samples with spectrophotometric detection is not easy because the lead content in these samples is incompatible with the detection limit of this detection. To solve this problem the preconcentration procedures are required. Several methods extensively used for preconcentration include liquid-liquid extraction (Holynska *et.al.*, 1996; Kojima and Katsuzako, 1997), ion exchange (Tao and Fang, 1998; Cuesta and Todoli, 1996) and solid phase extraction (Narin *et.al.*, 2000; Dos Santos *et.al.*, 2004). Solid phase extraction is an attractive technique based on use of a sorbent that retains the analytes. The analytes are eluted from the sorbent using suitable solvent (Uzun *et.al*, 2001). Various sorbents, such as activated carbon (Narin *et.al)*, siliga gel polymeric fiber (Goswami *et.al.*, 2003; Goswami and Singh, 2002) and Amberlite XAD resin (Wen-lu Song *et.al.*, 1997; Tewari and Singh, 2000; Tewari and Singh, 2002; Uzun *et.al.*, 2001; Dos Santos *et.al.* 2004), have been used to preconcentrate trace metal ions from various media. Immobilization of ligand on Amberlite XAD-7 has recently been used by Tewari (Tewari and Singh, 2000; Tewari and Singh, 2002). These system required time consuming for preparing chelating resin and expensive instrument. Furthermore, the lack of papers using pure Amberlite XAD-7 packed in a minicolumn has been reported on the preconcentration of lead.

In this work, the proposed procedure for the determination of lead in aqueous samples by on-line flow injection analysis system coupled with minicolumn containing Amberlite XAD-7 resin with spectrophotometric detection using 4-(2-Pyridylazo) resorcinol (PAR) as complexing agent was also described. The on-line techniques offer more advantage than manual batch precedures, i.e. better reproducibility, accuracy, automated sample management and low consumption of sample and reagents (Yebra *et.al*, 2002). The optimum conditions for the preconcentration step and flow system were carried out using factorial design.

EXPERIMENTAL

Reagents

All the reagents used were of analytical grade, and the solutions were prepared in distilled and deionized water. A 1000 mg L^{-1} of Pb(II) stock solution, obtanied by dilution 1.598 g of lead nitrate (Fluka, switzerland) in deionized water and small amount of nitric acid, was used to prepare lead working standard solutions in the range 0.10- 1.00 mg L^{-1}. 0.02 mol L^{-1} hydrochloric acid (J.T. Beaker, U.S.A.) used as eluent solution was prepared from suitable dilution of the concentrated hydrochloric acid.

A 3×10^{-4} mol L^{-1} 4-(2-Pyridylazo) resorcinol (PAR) (Fluka) solution was obtained by dissolving 0.0192 g of its sodium salt in deionized water. Borate buffer solutions was prepared by dissolve 19.08 g of sodium tetraborate (Ajax Finchem, Newzealand) in 1000 ml of deionized water and the pH adjusted to 9.

Preconcentration column

The acidic and basic impurities of Amberlite XAD-7 resin (20-60 mesh, Acros organic, USA) were removed prior its use as descirbed earlier (Tewari and Singh, 2000). The preconcentration column was prepared by packing a home-made

Perspex tube (1.3 cm×0.1cm) with Amberlite XAD-7 resin. The ends of the tube were fitted with wool to keep the absorbent material inside the tube.

Apparatus and Procedure

A flow injection system is depicted in Figure 1 consists of two pumps (FIAS300 Perkin Elmer, Germany), a six-way valve with a UV-Vis spectrometer (Lamda2S, Perkin Elmer, Germany) as detector, has been described in a previous papers (Klamtet, 2004; Klamtet, 2006). The preconcentration column was incorporated in a six-way valve. The Amberlite XAD-7 was cleaned by passing deionized water into the column. The sample was loaded by passing through it for 4 min with a flow rate 0.9 ml min^{-1}, after this time a 0.20 mol L^{-1} HCl stream was passed to remove the sample with a flow rate 1.5 ml min^{-1}. Then, the eluate was merged with PAR solution and buffer solution at 0.4 ml min^{-1}. The eluate form complex with reagent in the reaction coil and the chelate shows an maximum absorption at 523 nm through a 1-cm path length and 8 µl internal volume flow cell. PTFE tubing was used as flow lines and reaction coil in the system. A model UV-Vis diode-array spectrometer (Specord S10, Perkin Elmer, Germany) was used to scan spectrum.

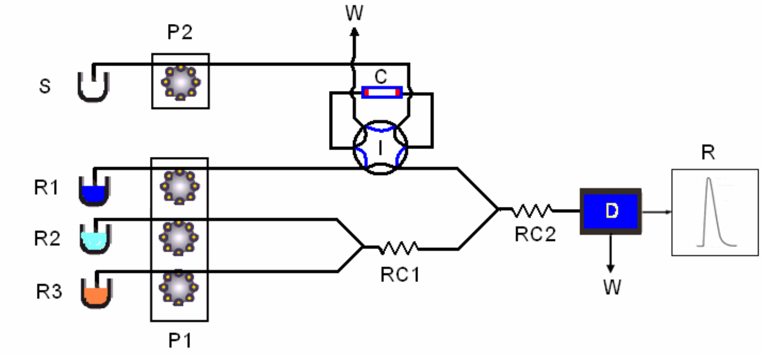

Figure 1 The on-line FIA system. R1, Eluent stream (0.20 mol L^{-1} HCl); R2, Buffer solution; R3, 3.0 × 10^{-4} mol L^{-1} PAR solution; S, sample; P, Peristaltic pump; I, Injection valve; C = minicolumn; RC1, reaction coil 1; RC2, reaction coil 2; D, Detector; W, Waste; R, Recorder or computer.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of the lead-PAR complex and corresponding PAR reagent blank were shown in Figure 2. It can be seen that the complex has the maximum absorption at 523 nm and the reagent blank solution was maximum absoption at 414 nm. The negative absorption value on the lead-PAR spectrum was a result of subtraction its with PAR spectrum. Therefore, analytical wavelength clearly showed an absoption peak at 523 nm.

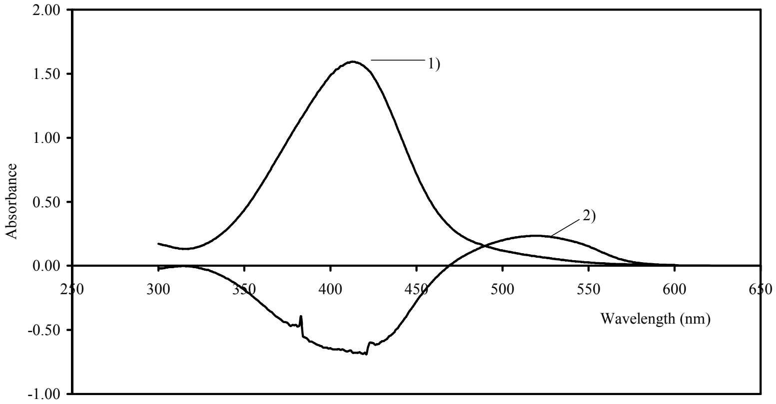

Figure 2 Absorption spectra of 1) PAR solution and 2) Pb(II) – PAR complex : $C_{\mathrm{PAR}} = 3.0 \times 10^{-4}$ mol L^{-1} , $C_{\mathrm{Pb(II)}} = 5.0$ mg L^{-1}, Buffer pH 9.

Preconcentration system

A. Sample loading time and flow rate

The effect of the sample loading time was investigated using 0.10-0.70 mg L^{-1} Pb(II) solutions at a sample flow rate of 1.5 mL min^{-1} into a column (1.3 cm × 1.0 mm) containing Amberlite XAD-7 resin, and the results are shown in Figure 3. The results clearly demonstrated that the sensitivity increase upto 4 min preconcentration time, after which the sensitivity gradually level off, presumably as a result of an insufficient capacity of Amberlite XAD-7 resin. Therefore, the loading time at 4 min was used as an optimum time for subsequent experiments. Variation of sample flow rate was studied ranging from 0.5-1.5 mL min^{-1}. The sample loading flow rate showed that the sensitivity raise almost linear as the loading flow rate increased (Figure 4) but the optimum preconcentration response was obtained at a flow rate of 0.9 mL min^{-1}. However, sensitivity of sample flow rate higher than 0.9 ml min^{-1} showed distortions and a double-peak shape.

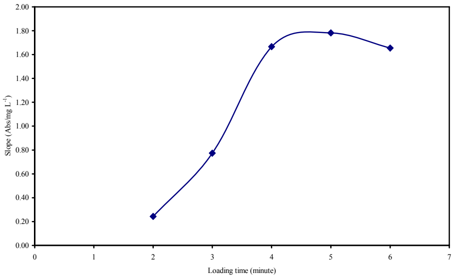

Figure 3 The effect of sample loading time on the sensitivity of Pb(II) determination using 1.3cm×1.0mm column and sample flow rate 1.5 mL min^{-1}.

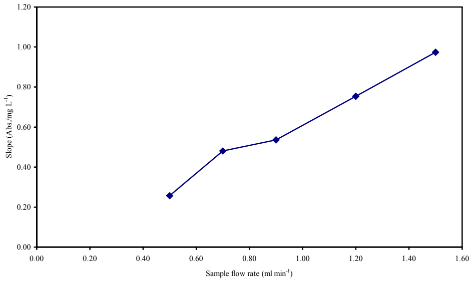

Figure 4 The effect of sample flow rate on the sensitivity of Pb(II) determination using 1.3cm×1.0mm column and sample loading time 4 min.

B. Size of column

The effect of length and internal diameter of the column were studied after preparing four columns of i.d. 0.1 and 0.2 cm with the length 1.0 and 1.3 cm, respectively. Table 1 shows the analytical sensitivity obtained by these minicolumns. As can be seen in Table 1, the sensitivity of 0.1 × 1.3 cm column show higher sensitivity than other column due to limit the amount of resin for adsorption and/or sample volume passing through the column. Thus, the 0.1 × 1.3 cm column was chosen for further experiment.

Table 1 The analytical sensitivity on size of minicolumns

Internal diameter of minicolumn (cm)	Length of minicolumn (cm)	Slope (Abs./mg L^{-1})
0.10	1.00	1.311
0.20	1.00	1.278
0.10	1.30	1.319
0.20	1.30	1.327

C. Elution

The dilute hydrochloric acid was chosen as eluent because its effective elution of the sorbed analyte species and was tested ranging from 0.05-0.25 mol L^{-1}. The results in Figure 5 shown that 0.20 M HCl was suitable concentration for elute Pb(II) without losing sensitivity. The effect of eluent flow rates were also determined (see Figure 6) that 1.5 mL min^{-1} was achieved an optimum elution flow rate.

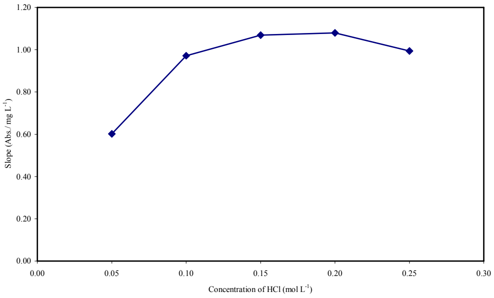

Figure 5 the effect of HCl concentration on the sensitivity of Pb(II) determination using 4 min preconcentration time at sample and elution flow rate 0.9 ml min^{-1}

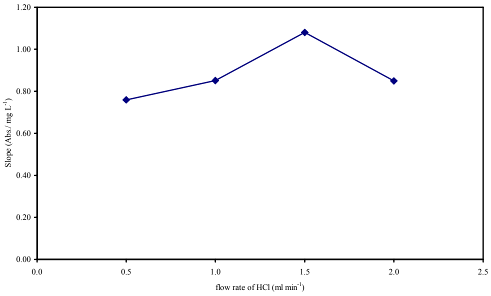

Figure 6 Effect of the elution flow rate on the sensitivity of Pb(II) determination using 4 min preconcentration time at sample flow rate 0.9 ml min^{-1} and 0.20 mol L^{-1} HCl

D. Stability of minicoloumn and sorption capacity

Stability studies were performed under the optimal conditions. Minicolumn with contained Amberlite XAD-7 was kept for 1-30 days at 4°C. The results showed that the minicolumn was stable for at least 30 days.

The sorption capacity of the Amberlite XAD-7 was also determined by passing 0.50 mg l^{-1} of Pb(II) solution through minicolumn for 2-6 min. The results demonstrated that at 5 min. of Pb(II) solution passed through the minicolumn containing 0.05 g of resin has maximum adsorption. Therefore, the resin has sorption capacity 3 μg per 0.05 g of resin.

Optimization of chemical and FIA variables

The operational conditions of the on-line FIA system and chemical variable were optimized in a univariant way in order to achieve high signal and the best reproducibility. Both chemical and flow variables were studied using the flow system shown in Figure 1.

The effect of concentration of PAR and pH of buffer solution was studied in the range 5-11 and the adequate pH for Pb(II)-PAR complex formation was 9. The concentration of PAR was tested between 1.00×10^{-4} and 5.00×10^{-4} mol L^{-1} and the best results were obtained when 3.00×10^{-4} mol L^{-1} PAR was used. Variation of buffer solution and

PAR flow rate was investigated ranging from 0.4 to 1.5 mL min^{-1}. The flow rate lower than 0.4 mL min^{-1} was not used due to avoid the long reaction time. Therefore, 0.4 mL min^{-1} was chosen for the subsequent experiment in order to maintain best sensitivity.

In addition, the internal diameter and length of both reaction coils (RC1 and RC2 in Figure 1) were studied in the range of 0.5-1.0 mm and 200-600 mm. The analytical signals showed that the 1.0 mm/400 mm (i.d/length) RC1 and 0.7 mm/300 mm RC2 were selected for further experiments. The higher internal diameter than 1.0 mm was not used due to high dispersion and doublet peak shape. All these optimum parameters described are shown in Table 2.

Table 2 shows the range over which each parameter was determined and the optimal value obtained by a univariant approach.

Variables	Studied range	Optimum value
Wavelength (nm)	430-560	523
Reaction coil 1 (mm)		
- i.d.	0.5-1.0	1.0
- length	200-500	400
Reaction coil 2 (mm)		
- i.d.	0.5-1.0	0.7
- length	200-600	300
flow rate (ml min^{-1})		
- PAR solution	0.4-1.5	0.4
- Buffer solution	0.4-1.5	0.4

Interference Study

Several interference cations, mainly Zn(II), Cd(II), Mn(II), Fe(II) and Ca(II) were studied. The levels of tolerated concentration of foreign ion was considered as maximum concentration found to cause a change in signal, less than 5 % compared with the signal for lead alone. The maximum ratios lead : interference tested were : Zn(II) and Fe(II) up to 1:1 and Cd(II), Mn(II) and Ca(II) up to 1:0.5. From the results, it is clear that these cations interfere in the preconcentration procedure. On using a mixed solution containing phosphate and citrate, several interferences can be masked coupled with strictly pH controlled to enhance its specificity (Rocha *et.al.* 2001).

Analytical performance

The calibration graph for the determination of Pb(II) was obtained under the experiment conditions above described. The results showed that a good linear relationship was observed in the range of concentration from 0.10 to 0.90 mg L^{-1}. The calibration curve represented by the equation $A = 1.522x - 0.0309$, $r^2 = 0.9963$ where A is the absorbance and x is the concentration of Pb(II) in mg L^{-1}. The detection limit estimated (3S, N= 20) was 11 µg L^{-1}. The repeatability of the method was calculated as the relative standard deviation (RSD) of 20 repilcates containing 0.50 mg L^{-1} Pb(II) injected by dupilcated and the obtained result was 2.4% . The recoveries of lead from water sample collected around the Naresuan University were also studied. As can be seen in Table 3, the recoveries of lead spikes added to the samples ranged from 90 to 117%. The result confirms the validity of proposed method for the preconcentration of lead. Moreover, the analytical sample throughput of this method was 12 samples per hour. The preconcentration factors were calculated by comparing the analytical curve slope obtained from before and after the preconcentration procedure (Nezio *et.al.*, 2004). The preconcentration factor was *ca.* 3 on 3.6 mL of sample volume.

Table 3 The recovery results

samples	Concentration of Pb(II) (mg L^{-1})			
	Found	Added	Detected	% recovery
Natural water	0.021	0.10	0.103	103
		0.30	0.270	90
		0.50	0.502	100.4
		0.70	0.819	117

Determination of lead in aqueous samples

The present method was applied to the preconcentration and determination of lead in the real water samples collected from around the Naresuan University in Phitsanulok province. The levels of the investigated ions are given in Table 4. The results have been calculated by assuming 100% recovery of lead ion. The R.S.D.

was less than 10%. The concentrations of lead in all water samples are less than 0.1 mg L^{-1}.

Table 4 The concentration of lead in the water samples (N=7)

Sample	Concentration of lead (II) (mg L^{-1})
1	0.049 ± 0.002
2	0.089± 0.002
3	0.083± 0.003
4	0.082± 0.005
5	0.021± 0.003
6	0.068± 0.012
7	N.D
8	0.071± 0.027
9	0.063± 0.003
10	N.D

N.D. = not detected

CONCLUSION

The flow injection with on-line preconcentraion provides a simple, precise, accurate and inexpensive method for lead determination. The results can be obtained at least 5 min from the sample introduction. The proposed system achieved a detection limit of 11 µg L^{-1} from the aqueous lead solution at a sampling rate 12 h^{-1}. The preconcentration factor was 3- fold for the 3.6 ml sample loading. This method offers a linear detection range from 0.10 to 0.90 mg L^{-1}. The precision and accuracy of the method were evaluated with a synthetic standard solution and a real sample, the results indicated that the RSD was 2.4% and the recovery of 90-117%. The method was applied successfully to the analysis of different water samples.

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