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Full Paper

A flow injection system for the spectrophotometric determination of lead after preconcentration by solid phase extraction onto Amberlite XAD-4

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Abstract: An on-line flow injection analysis (FIA) system for determination of lead (II) in water samples with a preconcentration step and spectrophotometric detection was investigated. The system is based on preconcentration of lead (II) on a column packed with Amberlite XAD-4 resin and detection by means of 4-(2-pyridylazo)resorcinol (PAR)–lead complex formation with maximum absorption at 523 nm. Chemical and FIA variables influencing performance of the system were optimised. Two linear calibration curves with a range of 0.01 - 0.40 and 0.40 – 0.80 mg L^{-1} were obtained. The developed system allowed a throughput rate of 16 samples h^{-1} with a 9-fold enrichment factor and a detection limit of 7 µg L^{-1}. Relative standard deviation for 10 replicated injections of 0.25 mg L^{-1} was 2.3%. Recoveries of the method were in the range of 80-94 %. The procedure was validated by analysis of lead (II) in real water samples, and the results were statistically compared with those obtained by flame atomic absorption spectrophotometry (FAAS). The results obtained both by the proposed method and by FAAS were in good agreement.

Keywords: flow injection analysis (FIA), determination of lead, 4-(2-pyridylazo)resorcinol, Amberlite XAD-4

Introduction

Lead belongs to those trace heavy metals that are of major interest in environmental protection due to its high toxicity [1]. The determination of lead in environmental samples plays an important role in the monitoring of environmental pollution. Lead is used in storage batteries, cable sheaths, solders and radiation shields and it is widely distributed in the nature [2]. It is confirmed that most of the lead contamination in humans is from foods and drinks consumed. Lead in the water system has a serious influence on the quality of life especially in developing countries. 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 adverse effects in the body [3-4]. In natural water, its typical concentration lies between 2-10 $\mu g\ L^{-1}$, whereas the upper limit recommended by WHO is less than 10 $\mu g\ L^{-1}$ [5]. Due to its toxicity and accumulative power, determination of lead has gained a wide interest. This metal is generally present in small concentrations in environmental samples, therefore sensitive and selective methods for determination of lead are needed. Electrothermal atomic absorption spectrometry (ETAAS) is a frequently used technique for determination of lead and other toxic trace elements. This technique is, however, very expensive and needs a separation and preconcentration procedure to avoid some shortcomings associated with matrix interferences [6]. Flame atomic absorption spectrometry (FAAS) is a more frequently used technique due to its simplicity and lower cost, although this method has a limited sensitivity for lead so a preconcentration step is often required to improve the detection limit [5, 7-9]. Other detection techniques are also used such as inductively coupled plasma mass spectrometry (ICP-MS) [10], hydride generation-inductively coupled plasma-atomic emission spectrometry (HG-ICP-AES) [11], and X-ray fluorescence spectrometry [12]. However, the spectrophotometric method is still one of the most important detection techniques in flow injection analysis for the determination of lead due to its ease of handling and comparatively low cost as well as its speed, precision and accuracy.

However, the lead content in natural water samples is incompatible with the detection limit of the spectrophotometric detection. To solve this problem a preconcentration procedure is required. Solid phase extraction is an attractive technique based on the use of a sorbent that retains the analyte, which is then eluted from the sorbent using a suitable solvent [13]. Various sorbents such as activated carbon [14], silica gel polymeric fibre [15-16] and Amberlite XAD resins [4-5, 13, 17-18] have been used to preconcentrate trace metal ions from various media. However, there is no report in the literature on the use of Amberlite XAD-4 packed in a minicolumn for preconcentration and determination of lead by flow injection analysis with spectrophotometric detection.

This present work reports on the procedure for the determination of lead in natural water samples by an on-line flow injection analysis system coupled with a minicolumn containing Amberlite XAD-4 resin (a non-ionic polystyrene-divinylbenzene polymer with a high surface area of 725 $m^2\ g^{-1}$) which is usually used as solid adsorbent to adsorb hydrophobic molecules from a polar solvent. Amberlite XAD-4 has aromatic moieties in its structure which give the polymeric absorbent excellent physical, chemical and thermal stability [19]. In addition, this resin has a high surface area and a suitable pore size for Pb(II) to be adsorbed before elution. However, the pH of the solution in this determination must be strictly controlled in order to enhance the selectivity. In this present study, the optimisation of conditions for the on-line preconcentration and flow injection determination of lead has been carried out and applied successfully for natural waters.

Materials and Methods

Materials

All the reagents used were of analytical reagent grade, and the solutions were prepared in deionised water. A Pb (II) stock solution (100 mg L^{-1}), obtained by dissolving 0.1598 g of lead nitrate (Fluka, switzerland) in deionised water and 2 mL of concentrated nitric acid then making up the solution to l L, was used to prepare working standard solutions of lead in the range 0.10-0.70 mg L^{-1}. A 0.20 mol L^{-1} hydrochloric acid used as eluent solution was prepared from dilution of 4.27 mL concentrated hydrochloric acid (36%; J.T. Baker, U.S.A.) to 250 mL with deionised water.

A 3×10^{-4} mol L^{-1} 4-(2-pyridylazo)resorcinol monosodium hydrate (PAR) (Fluka) solution was obtained by dissolving 0.0178 g the chemical in 250 mL deionised water. Borate buffer solution (pH 9) was prepared by dissolving 19.08 g of sodium tetraborate (Ajax Finchem, New Zealand) in 1000 ml of deionised water.

Preconcentration column

The acidic and basic impurities of Amberlite XAD-4 resin (Acros Organic, USA) were removed as described earlier [18] prior to its use. The preconcentration column was prepared by packing a small acrylic plastic tube (1.3 cm in length × 1 mm i.d.) with the Amberlite XAD-4 resin. The ends of the tube were fitted with a commercial absorbing cotton to keep the adsorbent material inside the tube.

Apparatus and method

A flow injection manifold is depicted in Figure 1. It consists of two pumps (FIAS300 Perkin Elmer, Germany), a UV-Vis spectrometer (Lamda 2S, Perkin Elmer, Germany) as detector which has been described in previous papers [20-21]. The preconcentration column was incorporated with a six-way valve. The Amberlite XAD-4 was cleaned by passing deionised water into the column. The sample was loaded and passed through the column for 210 s with a flow rate 2.2 mL min^{-1}, after which time the valve was switched to allow HCl (0.20 mol L^{-1}) solution to pass through the column with a flow rate of 2.9 mL min^{-1} to elute the analyte. Then, the eluate was merged with the PAR solution and the buffer solution (pH 9) at the flow rate of 1.0 and 1.8 mL min^{-1} respectively, to form complex with the reagent in the reaction coil. The complex was detected at 523 nm [22] in a flow-through cell (8 µL internal volume). PTFE tubing was used as flow lines and reaction coil in the system.

Results and Discussion

Optimisation of chemical and FIA variables

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

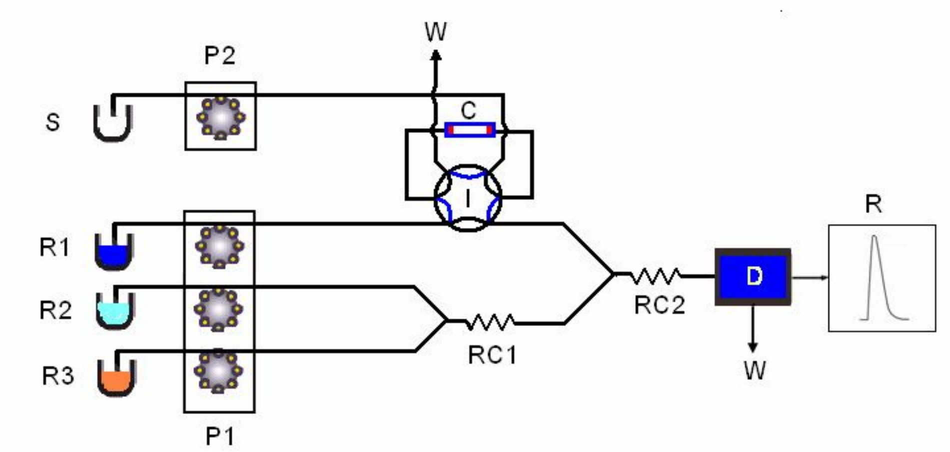

Figure 1. FIA system with on-line preconcentration: R1 = eluent stream (0.20mol L^{-1} HCl), R2 = buffer solution, R3 = 3.0×10^{-4} mol L^{-1} PAR solution, S = sample, P = peristaltic pump, I = injection valve, C = minicolumn, RC1 = reaction coil 1, RC2 = reaction coil 2, D = detector, W = waste, R = recorder or computer

Preconcentration system

A. Sample loading time and flow rate

The sample loading time was investigated using 0.10-0.70 mg L^{-1} Pb(II) solutions at a sample flow rate of 2.2 mL min^{-1}. The result (Figure 2) clearly demonstrates that the sensitivity increases with an increase in preconcentration time and then gradually levels off, implying insufficient capacity of Amberlite XAD-4 resin and concentration of hydrochloric acid as eluent. Therefore, the loading time at 210 seconds was chosen as optimum time for subsequent experiments. The effect of sample loading flow rate was investigated by variation of the flow rate of sample at constant loading time. This means that the amount of Pb(II) passing through the column was changed as a function of flow rate. The result in Figure 3 shows that the best sensitivity and good reproducibility is obtained at a flow rate of 2.2 mL min^{-1}. (The sample flow rate higher than 2.2 ml min^{-1} gave distorted and double-peak signals due to high dispersion of sample zone in the FIA system and insufficient amount of resin for sorption.)

B. Elution

Dilute hydrochloric acid whose concentration was varied between 0.10 and 0.30 mol L^{-1} was selected for the elution of sorbed Pb(II) ions. The result indicated that 0.20 mol L^{-1} HCl was suitable for eluting Pb(II) without losing sensitivity. The optimum eluent flow rate was also determined to be 2.9 mL min^{-1}. All studied variables and their optimum values are listed in Table 1.

FIA system

The influence of PAR concentration, used in pH 9 buffer solution, on complex formation was also studied within the range of 1×10^{-4}-5×10^{-4} mol L^{-1}. As shown in Figure 4, further increase in PAR concentration above 3×10^{-4} mol L^{-1} does not give a significant increase in the sensitivity measured. The PAR concentration of 3 ×10^{-4} mol L^{-1} was therefore chosen.

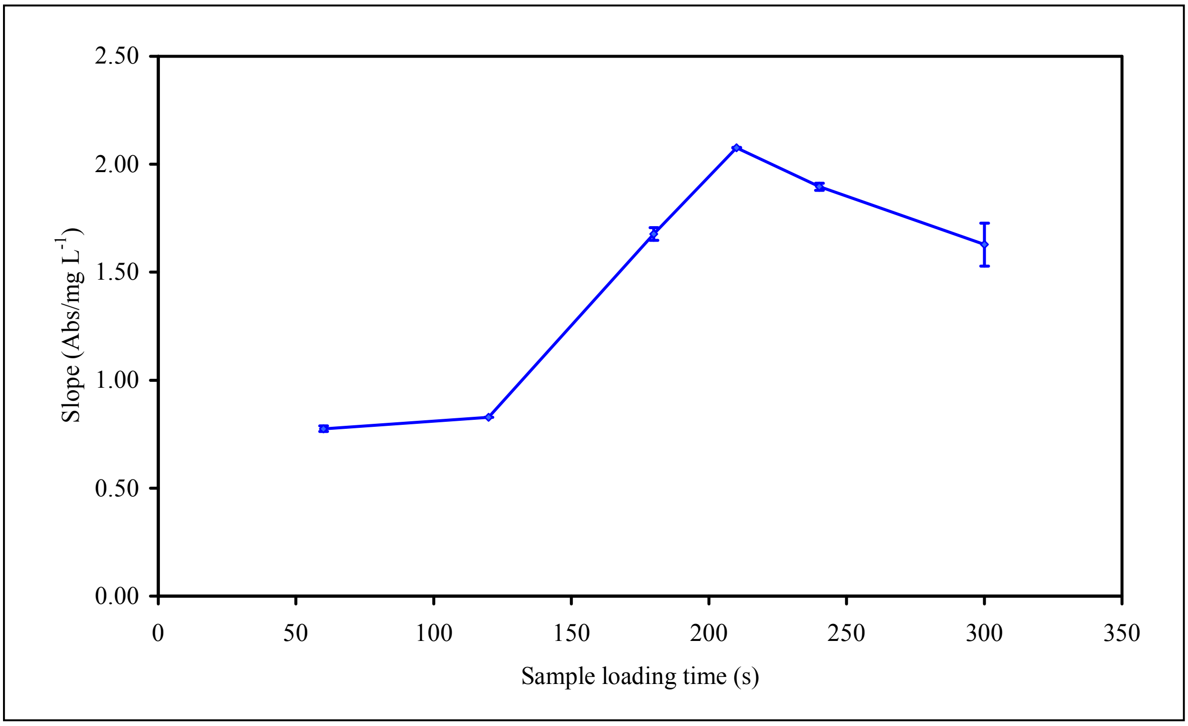

Figure 2. Effect of sample loading time on the sensitivity of Pb(II) determination using 1.3 cm × 1.0 mm column and sample flow rate of 2.2 mL min^{-1}

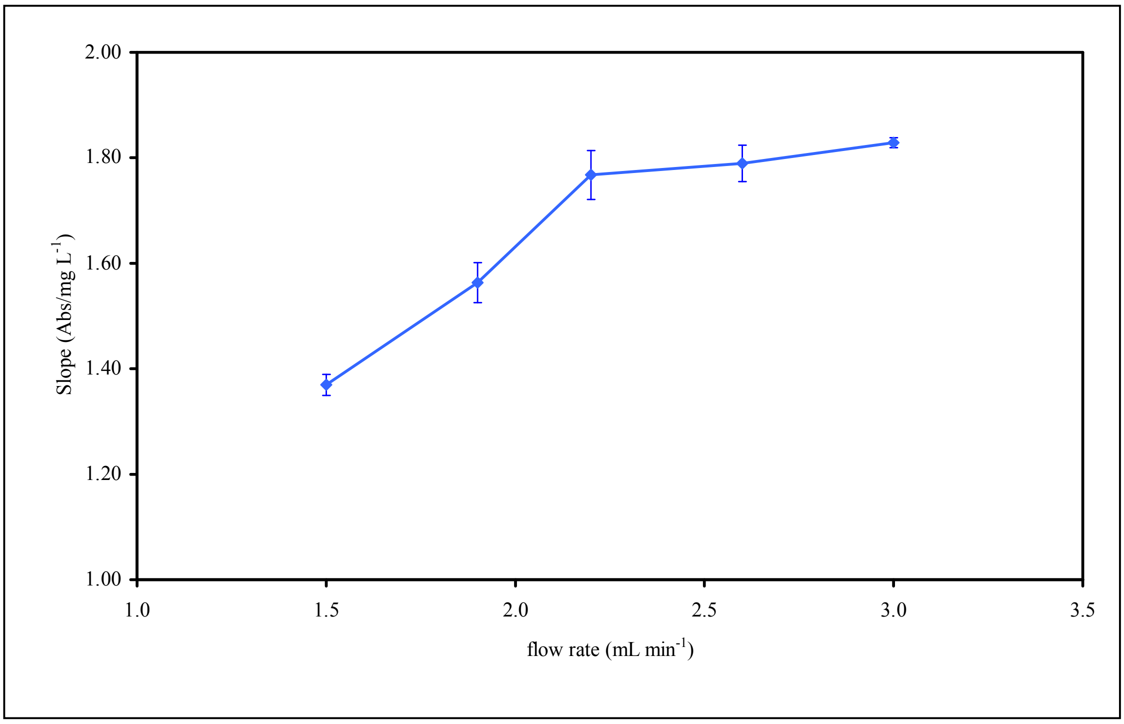

Figure 3. Effect of sample flow rate on the sensitivity of Pb(II) determination using 1.3 cm × 1.0 mm column and sample loading time of 210 s

Variation of the buffer solution and PAR solution flow rates was investigated between 0.8-2.2 mL min^{-1}. The best responses were obtained at a flow rate of 1.0 and 1.8 mL min^{-1} for buffer and PAR solution respectively. The flow rate of higher than 2.2 mL min^{-1} was not used in order to avoid the dispersion and reduce consumption of the reagents.

In addition, the mixing coils were made from PTFE tubing with internal diameter and length of the two reaction coils (RC1 and RC2 in Figure 1) being 0.7 mm/400 mm and 0.7 mm/200 mm respectively. A longer coil and larger diameter gave broad and less intense signals due to excessive dispersion of the reactants into the sample stream. All studied variables and their optimum values are listed in Table 1.

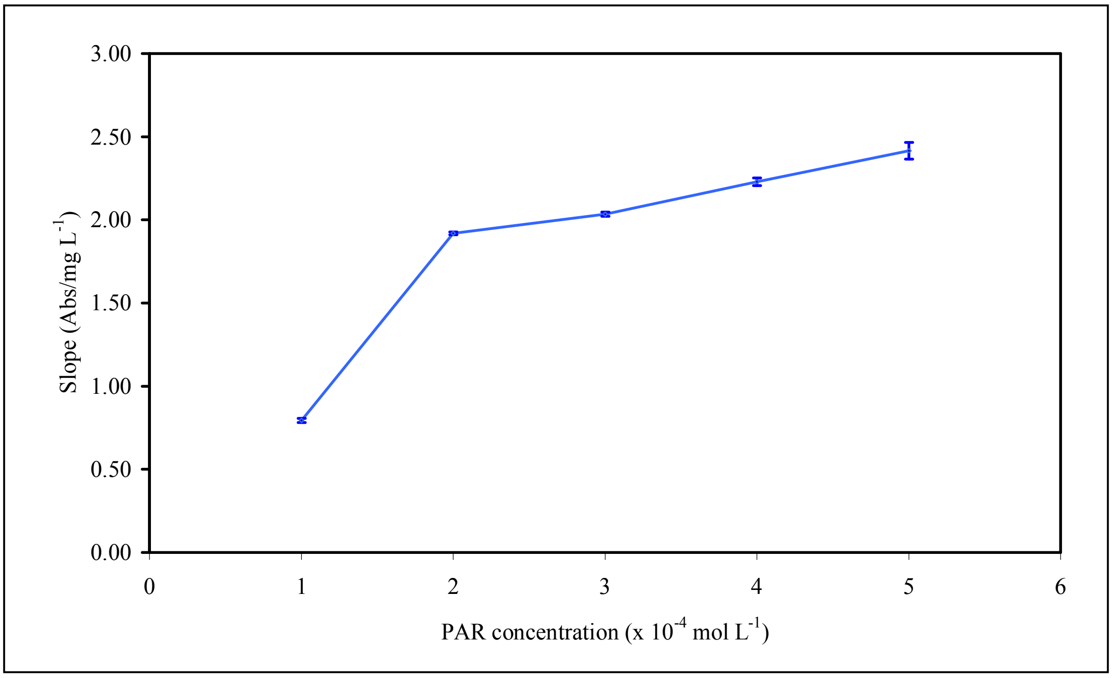

Figure 4. Effect of PAR concentration on the sensitivity of Pb(II) determination

Interference study

Potential interferences present in natural water, mainly Zn(II), Cd(II), Mn(II), Fe(II) and Ca(II), were evaluated. The levels of tolerated concentration of foreign ions were considered as maximum concentration found to cause less than 5 % change in signal compared with the signal for 0.25 mg L^{-1} Pb(II) solution. Fe(II), Ca(II), Cd(II) or Zn(II) up to 10 µg L^{-1} did not interfere with this determination. The maximum allowable values for Mn(II) and Cu(II) were 100 µg L^{-1} and 50 µg L^{-1} respectively. Thus, the pH for the determination of Pb(II) must be strictly controlled to enhance its specificity, coupled with using a solution containing phosphate and citrate to mask several interferences [23].

Analytical performance

The flow system using 210 s preconcentration time shows two linear ranges of concentration from 0.01 to 0.40 and 0.40 to 0.80 mg L^{-1}. The calibration curve is represented by the regression equation A= 2.403x + 0.0111, r^2 = 0.9975 and A= 1.278x+0.530, r^2 = 0.9970 where A is the absorbance and x is the concentration of Pb(II) in mg L^{-1}. The detection limit estimated as three times the standard deviation was 7 μg L^{-1}. The repeatability of the method was calculated as the relative standard deviation (RSD) of the maximum absorbance from 10 replicates of injection of the standard solution containing 0.25 mg L^{-1} Pb(II), which was found to be 2.3%. The sample throughput of this method was 16 samples per hour. The recovery of lead from natural water samples was also studied. As can be seen in Table 2, the recovery of lead spiked to the water samples ranges from 80 to 94%. The result confirms the validity of the proposed method for the preconcentration of lead. Moreover, the preconcentration factor was calculated by comparing the slope of the analytical curve obtained before and after the preconcentration procedure [2], and was found to be *ca.* 9.

Table 1. Optimisation of FIA variables

Variable	Studied range	Optimum value
Sample loading time (s)	60-300	200
Elution time (s)	30-90	60
HCl concentration (mol L^{-1})	0.10-0.30	0.20
PAR concentration (mol L^{-1})	1×10^{-4}-5×10^{-4}	3×10^{-4}
pH of buffer solution	5-11	9
Flow rate (mL min^{-1})		
- sample	1.5-3.0	2.2
- HCl	2.2-3.5	2.9
- PAR	0.8-2.2	1.8
- buffer	1.0-2.2	1.0
Reaction coil 1 (mm)		
- i.d.	0.5-1.0	0.7
- length	200-500	400
Reaction coil 2 (mm)		
- i.d.	0.5-1.0	0.7
- length	200-600	200

Table 2. The recovery results

Samples	Concentration of Pb(II) (mg L^{-1})			
	Found	Added	Detected	% Recovery
3	0.02	0.15	0.14	80
		0.25	0.22	80
5	0.015	0.15	0.15	90
		0.25	0.25	94

Determination of lead in natural water samples

The on-line column preconcentration coupled with FIA method for lead determination was validated against FAAS method. The real water samples were collected from rivers and canals around Naresuan University in Phitsanulok province. To avoid effects of interference ions, the pH for the PAR-Pb(II) complex formation was carefully controlled and the determination carried out by using standard addition method to eliminate any matrix effect in the water samples. The results obtained (Table 3) have been calculated by assuming 100% recovery of lead ions. The statistical pair of *t*-test was used to compare the results from both methods. The results revealed no significant difference ($t_{\mathrm{cal}} = 2.56$ and $t_{\mathrm{critc}\ 95\%,4} = 2.77$) between them.

Table 3. Concentration of lead in real water samples (N=3)

Sample	Concentration of Pb(II) (mg L^{-1})	
	Proposed method	FAAS
1	0.057 ± 0.015	0.045 ± 0.003
2	0.057 ± 0.011	0.034 ± 0.007
3	0.053 ± 0.016	0.051 ± 0.002
4	0.060 ± 0.011	0.038 ± 0.005
5	0.038 ± 0.015	0.037 ± 0.002

Conclusions

A simple, sensitive and low-cost FIA method with on-line preconcentration employing a column containing Amberlite XAD-4 resin has been proposed for the determination of lead in natural water. It gives good accuracy and reproducibility up to a maximum concentration of 0.25 mg L^{-1} Pb(II) with a relative standard deviation of lower than 5%. The result can be obtained in 5 min after the sample introduction and the sample throughput is 16 h^{-1}. The proposed system can achieve a detection limit of 7 μg L^{-1} and a recovery of 80-94%. The preconcentration factor is 9-fold for the 7.7 mL sample loading. This method offers two linear detection ranges from 0.10-0.40 and 0.40-0.80 mg L^{-1}. The method has been applied successfully to the analysis of real water samples and the results obtained are in good agreement with those obtained by FAAS method.

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