Amberlite XAD resin solid phase extraction coupled on-line to flow injection systems using 4-(2-pyridylazo resorcinol) as reagent for preconcentration and determination of zinc in water

Jintana Klamtet*, Wilawan Boonaim and Orapan Songsang
Department of Chemistry, Faculty of Science, Naresuan University,
Phitsanulok, 65000 Thailand
*Corresponding author E.mail: jintanakl@nu.ac.th

ABSTRACT

A determination of Zn(II) in water based on solid phase extraction coupled on-line to a flow injection analysis manifold is described. The method employs on-line preconcentration of Zn(II) onto a 1.3 cm × 1.0 mm (length × i.d.) column packed with Amberlite XAD-4 or Amberlite XAD-7 resins. The Zn(II) are subsequently eluted from the resin into a flowing system by 0.02 and 0.01 M HCl solution for Amberlite XAD-4 and XAD-7, respectively. Then the eluted analytes were quantified spectrophotometrically at 492 nm as the products of reaction with 4-(2-pyridylazo) resorcinol in buffer pH 11. The proposed methods have a linear calibration in range of 0.05-0.20, 0.20-0.80 mg L^{-1} for Amberlite XAD-4 and 0.05-0.40, 0.60-1.40 mg L^{-1} for Amberlite XAD-7, respectively. Detection limit of 0.016 and 0.013 mg L^{-1} and sample throughput of 30 and 26 h^{-1} were obtained for Amberlite XAD-4 and XAD-7, respectively. The procedure was successfully applied to the determination of Zn(II) in water sample, and the results were statistically compared with flame atomic absorption spectrometry.

Keywords: Flow injection analysis, Zinc, 4-(2-pyridylazo resorcinol), Preconcentration

INTRODUCTION

Zinc is a very important metal to human health and occurs exclusively in +2 oxidation state. It was found in air, soil, water and foods. Zinc is an essential element for a healthy body but large amounts of zinc can be harmful. It can cause stomach cramps, anemia, and changes in cholesterol levels (Agency for Toxic Substance and Disease Registry, 2006). Most of zinc is released into the environment by human activities such as mining, steel production, coal burning, and burning of waste. The Environmental Protection Agency (EPA) recommends that the concentration of zinc in drinking water should not more than 5 milligrams per liter (Agency for Toxic Substance and Disease Registry, 2006). Several reagents was proposed for the determination of zinc by spectrophotometric detection, such us 4-(2-pyridylazo) resorcinol (PAR) (Jezorek and Freiser, 1979), 5,8-dihydroxy-1,4-napthoquinone (Sedaira, 2000) and 5,10,15,20-tetrakis(4-carboxyl) porphyrin (Kilianc and Pyrzńyska, 2003). 4-(2-pyridylazo) resorcinol is one of the most interesting reagent it is water soluble and form soluble complexes with large number of metal ions. In addition, several FIA systems for the determination of zinc approaches using different procedures, reagents and solvents have been proposed (Jesus *et al*., 1998; Bin Abas *et al*., 2002; Kendűzler and Tűrker, 2002). However, an investigation on preconcentration of Zn(II) using unmodified Amberlite XAD resin coupled onto flow injection analysis system with spectrophotometric detection has a

few reports (Klamtet *et al.*, 2008). In this recently paper, the spectrophotometric-flow injection systems for preconcentration and determination of zinc using Amberlite XAD as solid adsorbent were investigated. The sample was loaded into a mini-column containing Amberlite XAD resin which inserted into the FIA manifold for enrichment of the desired sample. By introducing a small sample volume, zincs were enriched onto the column. The elution was taken by using HCl solution, rapid desorption can be achieved. The proposed procedure does not require complicated instrumentation and the operating is simple and fast. The optimum conditions of the proposed method based on the reaction between Zn and PAR is presented with emphasis on sensitivity. The developed optimal conditions were applied to the determination of zinc in water sample.

EXPERIMENTAL
Reagents

All the reagents used were of analytical grade, and the solutions were prepared in deionized water. A Zn(II) stock solution containing 1000 mg L^{-1} (Ajax) was used as purchased. The analytical solutions containing 0.50-2.00 mg L^{-1} of Zn (II) were prepared daily by successive dilution from the stock solution.

A buffer solution pH 11 containing 0.05 moL L^{-1} Na_2CO_3 was prepared by dissolving 5.30 g of Na_2CO_3 in water. A stock solution of 4-(2-Pyridylazo) resorcinol (PAR) containing 0.01 moL L^{-1} was obtained by dissolving 0.2372 g of 4-(2-Pyridylazo) resorcinol monosodium salt monohydrated (Fluka) in 100 mL deionized water. A 0.05×10^{-3} moL L^{-1} PAR solution was prepared by dilution from the PAR stock solution with buffer solution.

Preconcentration column

The resin used was Amberlite XAD-4 and Amberlite XAD-7 (Acros organics, USA). The acidic and basic impurities of Amberlite XAD-4 and Amberlite XAD-7 resin were removed prior to use as described earlier (Tewari and Singh, 2000). The preconcentration column was prepared by packing a small acrylic plastic tube of 1.3 cm length × 1.0 mm i.d. with Amberlite XAD-4 or Amberlite XAD-7 resin. The ends of the tube were fitted with a commercial absorbent cotton to keep the absorbent material inside the tube.

Apparatus and method

The flow injection system is depicted in Figure 1, consisting of a Unicam model 8625 spectrophotometer (Cambridge, UK) equipped with a 80 μl Hellma flow cell (Germany) set at wavelength of 492 nm coupled to a home-made software. The preconcentration column was incorporated with an upchurch scientific six-way valve (model V-451 Oak Harbor, WA). A masterflex C/L^{TM} peristaltic pump (USA) furnished with Tygon tubes were used to propel all solutions into the flow system. The Amberlite XAD-4 or Amberlite XAD-7 was cleaned by passing deionized water into the column. The sample was loaded by passing through it for 60 s with a flow rate 0.7 and 0.6 mL min^{-1}, after this time a valve was switched to allow HCl (0.01-0.02 moL L^{-1}) solution that passed through the column with a flow rate of 0.9 and 1.4 mL min^{-1} for Amberlite XAD-4 and Amberlite XAD-7, respectively, to elute the analyte. Then, the eluate was merged with PAR in buffer pH 11 solution at the flow

rate of 0.8 mL min^{-1} to form complex with reagent in the reaction coil. All connections were made using fittings unions and tee made of PEEK materials. PTFE tubing was used as flow lines and reaction coil in the system.
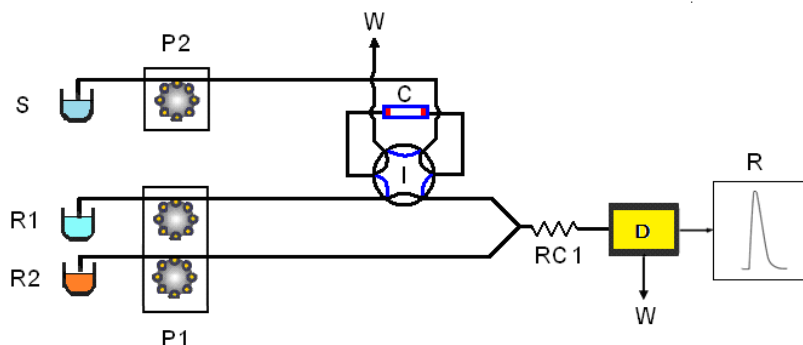

Figure 1 FIA system with on-line preconcentration. R1, eluent stream (HCl 0.02 and 0.01 M); R2, 8.0×10^{-5} moL L^{-1} PAR in buffer solution; S, sample; P, peristaltic pump; I, injection valve; C = minicolumn; RC, reaction coil; D, detector; W, Waste; R, recorder or computer.

RESULTS AND DISCUSSION

Absorption Spectra of the reagent and Zn (II)-PAR complexes

The spectra of reagent and complex produced in the reaction between Zn(II) and PAR at pH 11 was studied over the range 300-580 nm. From the spectra it is clear that the absorption spectra of the PAR reagent and Zn(II)-PAR complex had a maximum absorption at 414 and 492 nm, respectively. The reagent had minimum absorbance at the maximum absorbance of the complex. Therefore, 492 nm is chosen as the optimum wavelength for the future studies.

Optimization of chemical and FIA variables

Flow injection and chemical variables were optimized for the proposed flow injection method to achieve the sensitive and selective determination of zinc(II). Various parameters were studied by altering each variable in turn while keeping the other constant.

A. Preconcentration system

The on-line preconcentration systems proposed for Zn(II) determination by spectrophotometry have several experimental factors. However, in this case, the variables chosen for optimization were sample loading time, sampling flow rate and eluent flow rate and concentration. The sample loading time was investigated using 0.50-2.00 mg L^{-1} Zn(II) solutions at a sampling flow rate between 0.7 and 1.7 mL min^{-1} into a column (1.3 cm × 1.0 mm i.d.) packed with Amberlite XAD-7 and Amberlite XAD-4 resin, respectively. Hydrochloric acid was chosen as eluent and the concentration was varied from 0.01 to 0.03 moL L^{-1}. The eluent flow rates were

changed between 0.6 and 2.0 mL min^{-1}. The optimum conditions are shown in Table 1.

Table 1 Optimization of FIA variable for column containing Amberlite XAD-4 and XAD-7 resin.

Variables	Studied ranges	Optimum values	
		Amberlite XAD-4	Amberlite XAD-7
Sample loading time (s)	60-180	60	60
Sample flow rate (mL min^{-1})	0.5-1.7	0.7	0.6
Elution flow rate (mL min^{-1})	0.6-2.0	0.9	1.4
HCl concentration (mol L^{-1})	0.01-0.03	0.02	0.01

B. FIA system

The first parameter considered for the FIA system performance was concentration of PAR dissolved in buffer solution pH 11. The PAR concentration was examined over the range 5.0×10^{-5} to 14.0×10^{-5} moL L^{-1} for both resins used; Amberlite XAD-4 and Amberlite XAD-7. As shown in Figure 2, the sensitivity of both resin increases rapidly up to 8×10^{-5} moL L^{-1} PAR, further increases in PAR concentration showed no significant increase in the sensitivity measured. Therefore, the PAR concentration of 8×10^{-5} mol L^{-1} was chosen for following experiment.
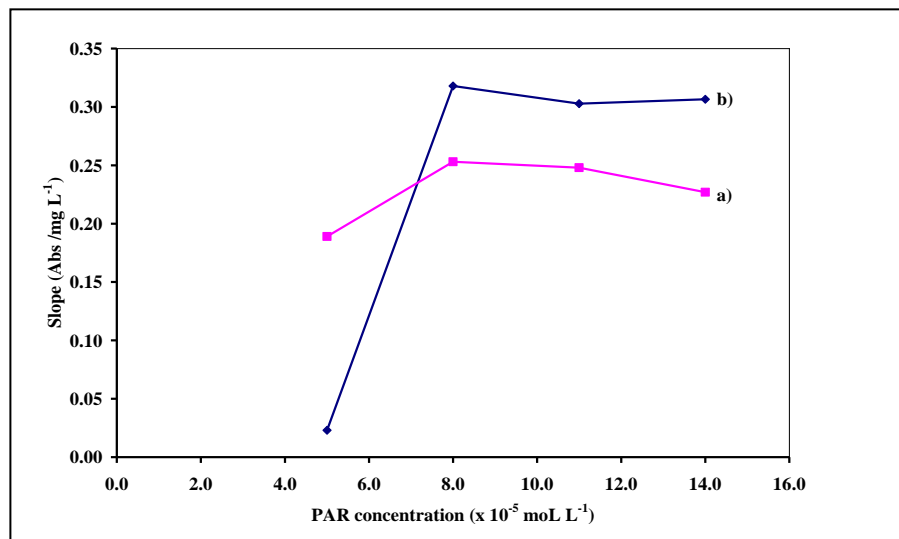

Figure 2 The effect of PAR concentration on the signal for the determination of zinc by using column containing a) Amberlite XAD-4 and b) Amberlite XAD-7.

Variations of reagent flow rate were tested ranging from 0.4 to 2.0mL min⁻¹. The Amberlite XAD-4 and Amberlite XAD-7 resin showed the same results which the optimum flow rate is 0.8 mL min⁻¹.

In addition, the influence of reaction coil volume on the complexation of zinc was investigated in terms of coil length and diameter. The reaction coil (RC in Figure 1) was made from PTFE tubing. The experiment showed that the sensitivity increased with the increment of the coil length until 300 mm and 400 mm for Amberlite XAD-4 and Amberlite XAD-7, respectively, after which, the sensitivity decrease slightly (Figure 3). It might be caused by the dispersion of the reactants into the sample stream. On the other hand, sensitivities were slightly decreased as a diameter increased in both resins, caused by dispersion in the flow systems (Figure 4). Therefore, the optimum coil lengths and diameters of Amberlite XAD-4 and Amberlite XAD-7 of 200 mm/0.5 mm and 300 mm/0.5 mm were selected for subsequent experiments in order to enhance the sensitivity of this determination.
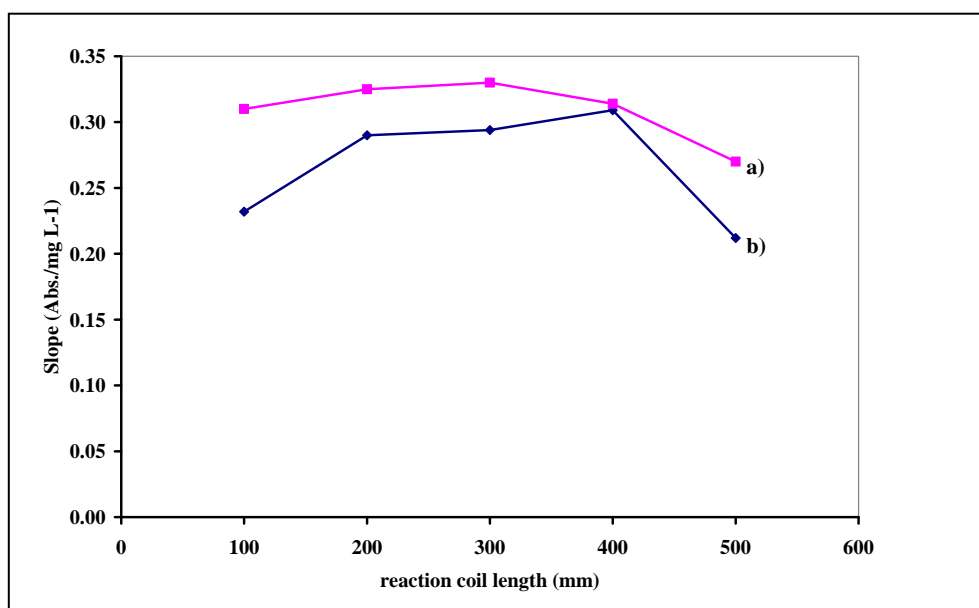

Figure 3   The effect of reaction coil length on the signal for the determination of zinc by using column containing a) Amberlite XAD-4 and b) Amberlite XAD-7.
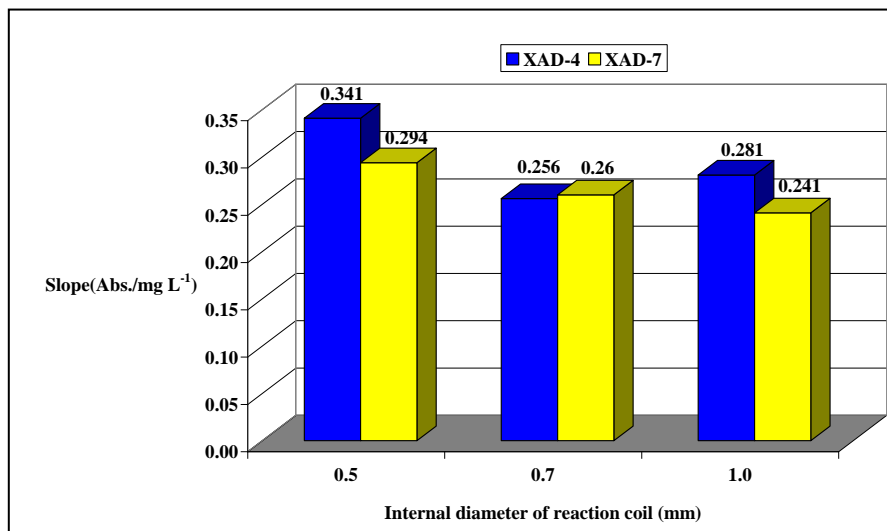
Figure 4 The effect of internal diameter of reaction coil on the signal for the
                determination of zinc by using column containing   Amberlite XAD-4
                and Amberlite XAD-7.

Interference study

　　　　Potential interferences presented in natural water, mainly Ca(II), Cd(II),
Cu(II), Fe(II), Fe(III) and Pb(II), were investigated by analyzing a standard solution
of 0.50 mg L^{-1} Zn(II) to which the increasing amount of interference species were
added. The results of tolerable limit concentrations of several ions in the
determination of Zn(II) are listed in Table 2. The levels of tolerated concentration of
foreign ions was considered as maximum concentration found to cause a signal
change lower than 5% compared with the signal for Zn(II) alone. The results
obtained show that Cu(II) and Pb(II) interfered with in the determination in both
resins. The maximum values of Ca(II) and Fe(II) tested were 0.50 mg L^{-1} for
Amberlite XAD-4 resin and 0.50 and 0.90 mg L^{-1} for Amberlite XAD-7 resin,
respectively. Cd(II) and Fe(III) upto 0.70 and 0.90 mg L^{-1} for preconcentration by
Amberlite XAD-4 did not interfered with this determination. On the other hand, the
results obtained from Amberlite XAD-7 showed that the maximum value of Cd(II)
and Fe(III) upto 0.05 mg L^{-1} and 0.90 mg L^{-1}, respectively, interfered in the
determination. Therefore, the conditions for Zn(II) determination with this reagent
must be strictly controlled to enhance sensitivity.

Table 2 The tolerance limits of interfering ions.

Species	Tolerance limit (mg L^{-1})	
	Amberlite XAD-4	Amberlite XAD-7
Ca^{2+}	0.50	0.50
Cd^{2+}	0.70	<0.05
Cu^{2+}	0.10	<0.05
Fe^{2+}	0.50	0.90
Fe^{3+}	0.90	0.90
Pb^{2+}	0.10	0.10

Calibration and precision

The calibration curves for Zn(II) determination were obtained under the optimum conditions described above using both flow injection preconcentration systems which were compared with FIA system without preconcentration column as shown in Table 3. The detection limits for Zn(II) were determined by passing a 0.20 mg L^{-1} Zn(II) solution through columns of Amberlite XAD-4/7 resins in flow injection system separately. The limit of detection estimated (S/N=3) was 0.016 and 0.013 mg L^{-1}, respectively. Precisions were evaluated by the determination of the relative standard deviation obtained from 10 consecutive sequential analysis of the same solution and the result were 1.4% (Amberlite XAD-4) and 4.4% (Amberlite XAD-7). The sample throughput of Amberlite XAD-4 and XAD-7 resin was 30 and 26 h^{-1}, respectively.

Table 3 The calibration equation, detection limt, precision and preconcentration factor for Zn(II) determination using flow injection analysis systems.

Type of resin	Linear range (mg L^{-1})	Equation*	R^2	detection limit (mg L^{-1})	%RSD	PF	Sample volume (μL)
Without resin	0.50-3.00	y = 0.2251x-0.0073	0.9992	0.16	4.2	-	100
Amberlite XAD-4	0.05-0.20	y=1.032x+0.0455	0.9997	0.016	1.4	4.6	70
	0.20-0.80	y = 0.3305x + 0.205	0.9991				
Amberlite XAD-7	0.05-0.40	y=1.0138x+0.0271	0.9974	0.013	4.4	4.5	60
	0.60-1.40	y = 0.2605x+0.3533	0.9971				

*y is the absorbance
*x is the concentration of Zn(II) in mg L^{-1}
PF is preconcentration factor

Application to water sample

   The recovery studies were performed in natural water sample which the results presented in Table 4. Natural water samples from the different sites around the Naresuan University in Phitsanulok province were analysed by on-line preconcentration FIA systems and were validated against the FAAS method. The analytical results from 3 methods compared favorably, as summaries in Table 5, with were proved with t-test to show that the results were not significantly different ($t_{cal,XAD-4} = 0.50$, $t_{cal, XAD-7} = 0.18$ and $t_{critic(95\%;4)} = 2.78$).

Table 4 The recovery results.

Type of resin	Zn(II) added (mg L^{-1})	Zn Found (mg L^{-1})	Recovery ± s (%)
Amberlite	0.00	0.117	-
XAD-4	0.10	0.212	95.0 ± 0.5
	0.20	0.308	95.5 ± 0.4
Amberlite	0.00	0.507	-
XAD-7	0.60	1.109	100.3 ± 0.5
	0.80	1.378	108.9 ± 0.3

Table 5 The concentration of Zn(II) in the water samples (N=3).

Resin	Sample	Zn concentration (mg L^{-1})	
		FIA	FAAS
Amberlite	1	0.0641±0.0009	0.0569±0.0003
XAD-4	2	0.0544±0.0009	0.0409±0.0004
	3	0.0641±0.0009	0.0502±0.0002
	4	0.0651±0.0005	0.0494±0.0004
	5	0.0728±0.0005	0.0531±0.0010
Amberlite	1	0.0957±0.0017	0.0569±0.0003
XAD-7	2	0.0832±0.0009	0.0409±0.0004
	3	0.0948±0.0011	0.0502±0.0002
	4	0.0963±0.0000	0.0494±0.0004
	5	0.0960±0.0004	0.0531±0.0010

CONCLUSION

Alternative speedy, simple and low cost on-line FIA procedures were developed for the determination of Zn in natural water. The results can be obtained at least 5 min from the sample introduction. The limit of detection of both resins obtained was not different with the sampling rate 30 (Amberlite XAD-4) and 26 (Amberlite XAD-7) h^{-1} and recovery between 95.0 and 108.9%. The preconcentration factor of both resins was about 4.5. These methods were applied successfully to the analysis of real water samples. The results obtained with proposed method are in good agreement with that obtained by FAAS method.

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