Asian Journal of Chemistry; Vol. 24, No. 7 (2012), 3078-3086

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Simultaneous Spectrophotometric Determination of Zinc, Cadmium and Lead by Xylenol Orange Using the Partial Least Squares Method After Their Preconcentration by 5,10,15,20-*Tetrakis*(4-Carboxylphenyl)porphyrin on Amberlite IRA-402 Resin

MOHAMMAD SABER TEHRANI[1], JAHAN B. GHASEMI[2] and MOHAMMAD TAGHI BAHARIFARD[1,*]

[1]Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran
[2]Chemistry Department, Faculty of Science, K.N. Toosi University of Technology, Tehran, Iran

*Corresponding author: Fax: +98 2144869761-2; Tel: +98 2144869761; E-mail: baharifardmt@gmail.com

(*Received*: 8 July 2011; *Accepted*: 16 February 2012) AJC-11070

A new solid phase extraction method for separation and preconcentration of trace amounts of zinc, cadmium and lead in water samples is proposed. The procedure is based on the adsorption of complexes of Pb, Cd and Zn with 5,10,15,20-*tetrakis*(4-carboxylphenyl)porphyrin (TCPP) on anionic Amberlite IRA-402 resin prior to their simultaneous spectrophotometric determination with xylenol orange, using partial least squares method. The enrichment factor for preconcentration of zinc, cadmium and lead was found to be 10. The precision of the method, evaluated as the relative standard deviation obtained by analyzing a series of 10 replicates, was below 4 % for Pb, Cd and Zn. A selective method for group separation of Pb, Cd and Zn in the presence of interfering ions was applied. The practical applicability of the developed method was examined using synthetic natural waters and alloy samples.

Key Words: Zinc, Cadmium, Lead, 5,10,15,20-*Tetrakis*(4-carboxylphenyl)porphyrin, Solid phase extraction.

INTRODUCTION

Heavy metals and specially zinc, cadmium and lead are highly toxic for living organisms. So it is needed simple and rapid methods for their determination in different matrices. Some techniques such as polarography, mass spectrometry, inductively coupled plasma atomic emission, voltammetry, liquid chromatography, X-ray spectrometry, atomic fluorescence spectrometry and atomic absorption spectrometry have been used for the simultaneous determination of zinc, cadmium and lead in aqueous media[1-6].

The simultaneous determination of these ions by the common UV-Visible spectrophotometric techniques using conventional metallochromic indicators in aqueous solution is difficult because, generally, the absorption spectra overlap and the superimposed curves are not suitable for quantitative evaluation. Multivariate calibration methods are playing an important role in the multicomponent analysis of mixture by UV-visible spectrophotometry[7,8]. The main advantage of multicomponent analysis using multivariate calibration is the speed of the method.

Xylenol orange (Fig. 1), is an excellent complexo-metric indicator reagent for determination of many metal ions. Xylenol orange is a classical example of a pH dependent, non-specific, non-selective, colour reagent. This means that separation and/or masking steps always have to be considered and included in these analytical procedures, making them slower and more sensitive to operational errors, which ultimately may reflect on the precision and accuracy of the method[9].

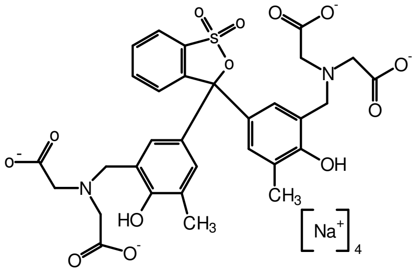
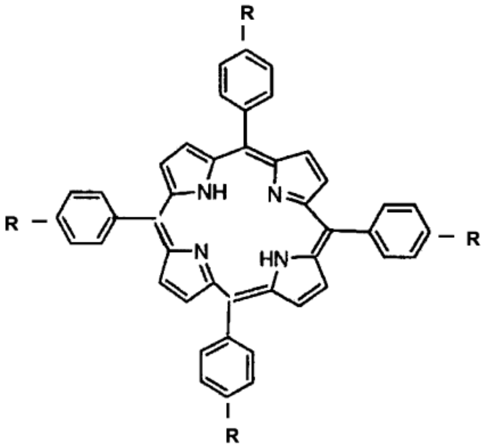


Fig. 1. Chemical structure of xylenol orange

In trace metal analysis, preliminary procedures such as preconcentration of analyte and its separation are frequently necessary in order to improve detection performance and to avoid the interferences caused by matrix components. Among a number of preconcentration/separation techniques reported, solid phase extraction (SPE) methods using chelating sorbents with selective functional groups covalently attached to copolymer matrices as well as ligand-modified resins and using anionic resins for separation of metal complexes have proved to be very effective[10]. Using solid phase extraction for the analysis of trace amounts of metal ions reduces solvent usage and exposure, disposal costs and extraction time and it is a tool for increasing selectivity and group separation of ions from a complex matrix. Various adsorbents, such as octadecyl functional groups bonded on silica gel, C_{18}, glycerol-silica gel, chelating adsorbents, Amberlite XAD and Amberlite IRA resins, chromosorb resins and other sorbents have been used for adsorption of metal chelates in the preconcentration and separation of metal ions[11-17].

The application of anionic resins such as Amberlite IRA for separation and preconcentration of metal complexes has the advantage of controlling the capacity by the appropriate choice of pH and organic reagents, thus controlling the efficiency of the process, easy regeneration for multiple sorption desorption cycles, good mechanical stability and reproducible sorption characteristics[10].

The porphyrins are a class of naturally occurring macrocyclic compounds, which play an important role in the metabolism of living organisms. These have been extensively studied due to their biological importance as well as analytical applications. Particular attention has been given to porphyrins as a highly sensitive chromogenic reagents for spectrophotometric determination of several metal ions[18]. The porphyrin molecule contains four pyrrole rings linked *via* methine bridges (Fig. 2) in the structure shown in Fig. 2 when R=COOH its name is 5,10,15,20-*tetrakis*(4-carboxylphenyl)-porphyrin, (TCPP). It is a good reagent for spectrophotometric determination of some metal cations[19,20].



R = COOH 5,10,15,20-tetrakis(4-carboxylphenyl)porphyrin

Fig. 2. Chemical structure of TCPP

Banks and Bisque' were the first to propose porphyrin as a reagent for zinc in 1957, but little work was done until some twenty years later by Ishii and Yotsuyanagi's groups, who published a series of papers dealing with the use of porphyrins for the determination of Cu, Pb, Cd and Zn[21].

Some porphyrins form stable complexes with transition metal ions. Porphyrins and their metal chelates generally exhibit characteristic sharp and intensive absorption bands in the visible region. The region from 400 to 500 nm, which is called the Soret band. The Soret band is widely used for spectrophotometric determination of metalloporphyrins[22]. Recentiy some porphyrins has been used as chelating agents for metal preconcentration and separation on anionic resin[10,23]. The porphyrin ring can be destroyd by intense visible or UV light due to ring opening[18].

In this paper, we introduce a procedure for the group separation and preconcentration of trace amounts of zinc, cadmium and lead ions in water and industrial samples using. The anion-exchange resin Amberlite IRA-402 as support for TCPP-metal complexes prior to their simultaneous spectrophotometric determination by xylenol orange using partial least squares.

Theory: Partial least squares (PLS) modeling is one of the most powerful multivariate statistical tools that has been applied to the quantitative analysis[24-27]. Several multicomponent determination of inorganic substances based on the application of these methods to spectrophotometric data has also been reported[28-33]. Partial least squares is a quantitative spectral decomposition technique that is closely related to principal component regression. However, in partial least squares the decomposition is performed in a slightly different fashion. Partial least squares actually uses the concentration information during the decomposition process. Thus, the eigenvectors and scores calculated using partial least squares is quite different from those of principal component regression. The main idea of partial least squares is to get as much concentration information as possible into the first few loading and score vectors[34,35]. There are actually two version of the partial least squares algorithm; PLS1 and PLS2. The differences between these methods are subtle but have very important effects on the results. In PLS1 a separate set of scores and loading vectors are calculated for each constituent of interest. In this case, the separate set of scores and loading vectors are specifically tuned for each constituent and therefore, should give more accurate predictions than principal component regression and PLS2. Here we used a PLS1 method and we denote it as partial least squares in all over of text. The basic principle of partial least squares is as follows:

Principal component analysis of the absorbance matrix $A_{a\times p}$ for n mixtures at p wavelengths and the concentration matrix $C_{n\times m}$ for m components of n mixtures gives the equations[36]:

$$A_{a\times p} = T_{n\times a}\cdot P_{a\times p} + E_{n\times a} \quad (1)$$

$$C_{n\times m} = U_{n\times a}\cdot Q_{a\times m} + F_{n\times m} \quad (2)$$

where, T and U are characteristic matrices, P and Q are loading matrices, E and F are error matrices, n, m, p and a are the sample number, component number, number of wavelength points and abstracted factor number, respectively. The deviation of A usually occurs for the same reason as those of C. Variations in C are related to those of A. Their factor lengths are different, but their factor directions are the same. Thus, one may obtain:

$$U_{n\times a} = T_{n\times a}\cdot B_{a\times a} \quad (3)$$

where, B is a diagonal matrix indicating the internal relation between the latent dimension matrices T and U, P, Q and B are determined according to the calibration models. For n unknown samples:

$$A_{n\_\times p} = T_{n\_\times a}\cdot P_{a\times p} \quad (4)$$

Then the characteristic variable matrix U of C is evaluated:

$$U_{n\_\times a} = T_{n\times a}\cdot B_{a\times a}. \qquad (5)$$

Therefore, the evaluated concentration matrix C is[37]:

$$C_{n\times m} = T_{n\times a}\cdot B_{a\times a}\cdot Q_{a\times m}. \qquad (6)$$

The development of each complex as a light absorbing moiety depends on the experimental conditions. One of the most important factors is pH that has a large effect on selectivity and sensitivity in metal ion determination based upon metal complexes formation using metallochromic indicators.

The effect of pH on the sensitivity and selectivity was studied according to the net analyte signal (NAS, a portion of the signal of each component that is orthogonal to the rest signal of other components) for each component in first-order system[38-40]. The net analyte signal (NAS) is defined as:

$$NAS = (I - R_nR^{+}_n)r_n \qquad (7)$$

where, I is the identity matrix, R_n the matrix of pure spectra of all constituent except the nth analyte, R^{+}_n the pseudo inverse or general inverse of R_n and r_n the spectrum of the analyte. The NAS is a vector and is related to the regression vector as depicted in the following equations:

$$C = Rb + e \qquad (8)$$

$$b = \frac{NAS}{\|NAS\|_2} \qquad (9)$$

where, $\|NAS\|_2$ designates the square root of the sum of squares of each element in the vector b, c the analyte concentration and e the error vector. Sensitivity (SEN) and selectivity (SEL) were calculated using following equations:

$$SEN = \frac{1}{\|b\|_2} = \|NAS\|_2 \qquad (10)$$

$$SEL = \frac{1}{\|b\|_2\|r_n\|_2} = \frac{\|NAS\|_2}{\|r_n\|_2} \qquad (11)$$

EXPERIMENTAL

All the chemicals used of analytical reagent grade and deionized water was used throughout. Stock solutions of zinc(II), cadmium(II) and lead(II) (10^{-3} M) were prepared from their commercial nitrate salts and standardized titrimetrically with EDTA in the presence of suitable indicator. The EDTA standardized titrimetrically against solution, which prepared from vacuum dried calcium carbonate. Stock solutions of diverse elements were prepared from the high purity salts of the cations (all from Merck, Germany). Amberlite IRA-402 (styrenedivinylbenzene copolymer, strongly basic anion exchanger Cl^- form total capacity > 1.0 mmol/mL) was supplied by Sigma. 5,10,15,20-*tetrakis*(4-carboxylphenyl)porphyrin (TCPP) from Fluka (grade of 98 %) was used without further purification. Stock solutions (10^{-3} M) of TCPP was prepared by dissolution of reagent in 20 mL of 10 mM sodium hydroxide and further dilution with deionized water up to 25 mL and then store in darkness. A stock xylenol orange solution (1.58 × 10^{-3} M) was prepared by dissolving reagent in deionized water. Buffer solutions (pH = 6.00) was prepared using KH_2PO_4 (0.05 M) as buffer No.1 and H_2PO_4 (0.1 M) + $Na_2B_4O_7.10H_2O$ (0.05 M) as buffer No. 2 and a universal buffer solution (phosphoric, acetic and boric acid each 0.04 M) as buffer No. 3 and a sodium tetraborate 0.05 M as a pH = 9 buffer.

Atomic absorption measurements were performed by using a Varian AA240 apparatus with flame (air-acetylene) atomization and deuterium background correction. The instrumental settings of the manufacturers were followed. Absorption measurements were carried out on a Carry 100 spectrophotometer (slit width: 0.2 nm, scan rate: 500 nm/min) using 1.00 cm quartz cells. All absorbance spectra were digitized and stored at wavelengths from 350 to 700 nm in steps of 1 nm and then transferred in ASCII format to a Pentium IV (2 Gb RAM) computer for subsequent manipulation by partial least squares program. Measurements of pH were made with a Metrohm 827 pH meter using a combined electrode. The data pretreatment was done with MATLAB for windows (Mathworks, Version 7.6). Partial least squares program for calibration-prediction and experimental design was written in MATLAB according to the algorithm described by Martens and Naes[41] and partial least squares routine of partial least squares toolbox (Eigenvector Company, Version 7.6).

Recommended procedure for spectrophotometric determination without solid phase extraction: A solution containing no more than 0.0535 mg of Zn(II), 0.22 mg of Cd(II) and 0.205 mg of Pb(II) was transferred into a 10 mL of volumetric flask and 2 mL of 1.58 × 10^{-3} M xylenol orange solution was added and the volume was made up to the mark with buffer No. 2 solution and the solution was mixed. The absorption spectra were recorded between 350 and 700 nm against a blank in a 10 mm cell.

Recommended procedure for combined solid phase extraction and spectrophotometric determination: The general procedure for the extraction of Zn(II), Cd(II) and Pb(II) ions on the resin is as follows: The column containing 1 g of resin (prepared and dried as mentioned before) was first washed with 30 mL water. Then 100 mL of the sample solution containing of Zn(II), Cd(II) and Pb(II) complexes with TCPP in borate buffer pH 9, was passed through the column with a flow rate of 1 mL min^{-1}. The extracted complexes were then stripped from the column using 5.0 mL of a 0.2 mol L^{-1} solution of nitric acid with a flow rate of 0.5 mL min^{-1} into a suitable test tube. Then the test tube was exposed to UV radiation for 25 min. The solution was transferred to a 10 mL volumetric flask and after neutralizing its excess acid with 4M NaOH, 2 mL of 1.58 × 10^{-3} M xylenol orange solution was added. The volume was made up to the mark with No. 2 buffer and the solution was mixed. And the absorption spectra were recorded between 350 and 700 nm against a blank in a 10 mm cell.

RESULTS AND DISCUSSION

Spectra of Zn, Cd and Pb complexes with xylenol orange: The spectra of Zn, Cd, Pb complexes with xylenol orange and also mixture of them were recorded against a blank (Fig. 3). The complexes of Zn-xylenol orange, Cd-xylenol orange and Pb-xylenol orange exhibited absorption maximum at 573, 580 and 578 nm respectively.

Effect of pH on complex formation: The complexation reaction of xylenol orange with metal ions are well known to be strongly dependent on the pH. The effect of the pH of the solution on the absorption spectra of metal complexes were studied over the pH range 2-10 and then using NAS based relations, sensitivity and selectivity for each analyte at different pH values were calculated (Fig. 4). Therefore, pH 6 was selected as the optimum value.

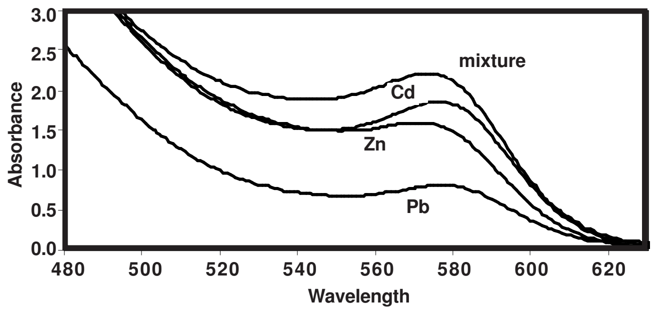


Fig. 3. Absorption spectra of Zn-xylenol orange (2.14 ppm), Cd-xylenol orange (8.2 ppm), Pb-xylenol orange (5.6 ppm) and the mixture (Zn 2.29, Cd 6.29, Pb5.8 ppm) at pH = 6

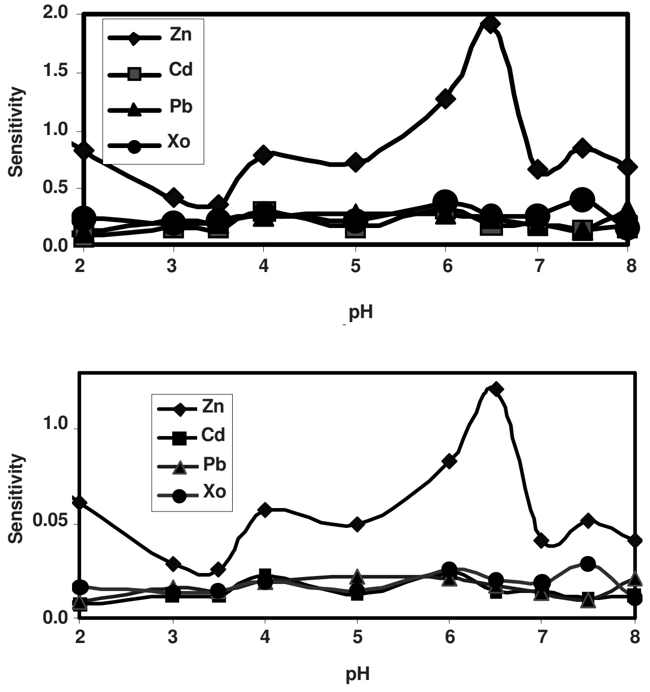


Fig. 4. Dependency of the selectivity and sensitivity to pH

Buffer selection: The effect of buffer kind on the sensitivity of the determinations was also investigated. Three buffer solution No.1 to No.3 as indicated in experimental section were used for pH = 6 adjustment. Fig. 5 shows variation in sensitivity with different buffer. According to these results the No. 2 buffer was selected for all pH 6 adjustment in procedures.

Univariate calibration: To ensure of linear behaviour of each metal complex and to obtain the linear dynamic range for each metal ion, an individual calibration curve was constructed with several points at λ_{max} of each complex as absorbance value *versus* metal ion concentration. The linear ranges are 0.8-20.5, 0.93-22 and 0.3-5.35 ppm for lead, cadmium and zinc respectively. Linear regression results, line equations and R^2 are: Abs = $0.049C_{Pb}$ + 0.8133 (R^2 = 0.9981), Abs = $0.0788C_{Cd}$ + 0.8201 (R^2 = 0.9994) and Abs = $0.3502C_{Zn}$ + 0.8234 (R^2 = 0.9988) for lead, cadmium and zinc, respectively.

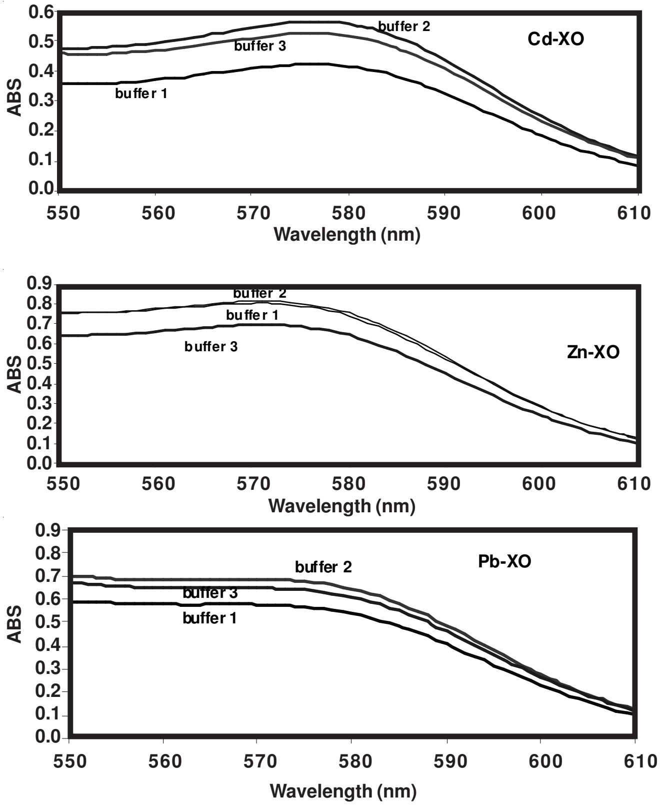


Fig. 5. Absorption spectra of metal-xylenol orange complexes in different buffer. Buffer No. 1 to No. 3, $C_{cation} = 1.6 \times 10^{-5}$ M $C_{xylene\ orange} = 1.26 \times 10^{-4}$ M

Mixture design: Multivariate calibration methods such as partial least squares require a suitable experimental design of the standard belonging to the calibration set in order to provide good prediction ability. A mixture design for three component mixtures was used for calibration[42-44]. A synthetic set of 36 solutions of mixtures of Zn^{2+}, Cd^{2+} and Pb^{2+} was prepared as a calibration set (Table-1). The spectral region between 480 and 630 nm, which implies working with 151 experimental points (λ) per spectrum, was selected for analysis. In this spectral region, the maximum spectral information is shown (Fig. 2.). The spectral data were just mean centered. The compositions of the calibration mixtures were selected according to a (3,7) simplex lattice design. For model assessment, 10 test mixtures inside the linear range of each metal ion according to Table-2 were used as a prediction set. The concentrations of each cation in test mixtures were inside the calibrations space by inspection of their scores in the first PC *vs.* second PC's plot shown in Fig. 6.

Number of significant factors: A cross-validation method leaving out one sample at a time can be used in the partial least squares algorithm to specify the number of significant factors (latent variables or pairs of score and loading vectors) without over fitting[45]. As the training set comprized 36 spectra, the partial least squares calibration, using first pair of score and loading vectors (*i.e.* the first significant factor), were performed on 35 of them and the concentration of the sample left out was predicted. The process was repeated

36 times (once for each sample), using this calibration datum model. The concentration of all components in each sample was compared with the known concentration of the components in this reference sample and the prediction residual error sum of square (PRESS) was calculated according to eqn. (12).

$$\text{PRESS} = \sum_{i=1}^{N}(C_i^{\text{added}} - C_i^{\text{found}})^2 \qquad (12)$$

TABLE-1
THIRTY SIX DESIGNED SAMPLE SOLUTIONS BY USING (3, 7) SIMPLEX LATTICE DESIGN FOR CALIBRATION AND PREDICTION SET

Solution No.	Zn conc. (ppm)	Cd conc. (ppm)	Pb conc. (ppm)
0	0	0	0
1	5.36	0.00	0.00
2	0.00	22.03	0.00
3	0.00	0.00	20.51
4	0.00	9.44	11.81
5	0.00	6.29	14.71
6	0.00	15.74	5.80
7	0.00	18.88	2.90
8	0.00	12.59	8.70
9	0.00	3.15	17.61
10	1.50	0.00	14.71
11	2.29	0.00	11.81
12	4.58	0.00	2.90
13	0.78	0.00	17.61
14	3.79	0.00	5.80
15	3.07	0.00	8.70
16	1.50	15.74	0.00
17	3.79	6.29	0.00
18	4.58	3.15	0.00
19	2.29	12.59	0.00
20	3.07	9.44	0.00
21	0.78	18.88	0.00
22	3.07	6.29	2.90
23	2.29	6.29	5.80
24	1.50	6.29	8.70
25	0.78	6.29	11.81
26	2.29	9.44	2.90
27	1.50	9.44	5.80
28	2.29	3.15	8.70
29	3.79	3.15	2.90
30	1.50	12.59	2.90
31	0.78	15.74	2.90
32	0.78	9.44	8.70
33	0.78	12.59	5.80
34	0.78	3.15	14.71
35	3.07	3.15	5.80
36	1.50	3.15	11.81

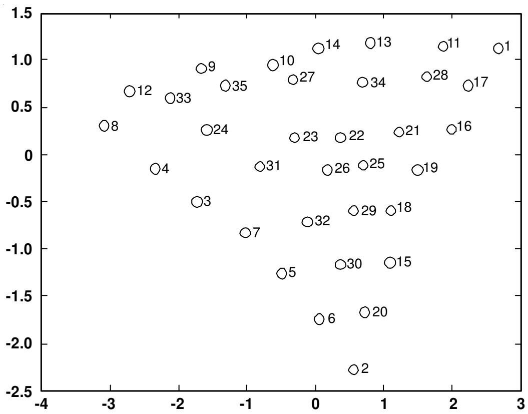


Fig. 6. Score plot of calibration set solution as PC2 *vs*. PC1

The prediction residual error sum of square (PRESS) was calculated in the same manner each time that a new factor was added to the partial least squares model. One reasonable choice for the optimum number of factors would be that number, which yields the minimum prediction residual error sum of square. However, using the number of factors (h^*) that yields the minimum prediction residual error sum of square , usually lead to some over fitting. A better criterion for selecting the optimum number of factors, involves the comparison of prediction residual error sum of square (PRESS) from model which is not significantly greater than prediction residual error sum of square from the model with h^* factors. Haaland and Thomas[46] empirically determined that an F-ratio probability of 0.75 is a good choice. So, we also selected the optimum number of factors for the prediction residual error sum of square value that the F-ratio probability of which drops below 0.75. The maximum number of factors used to calculate the optimum prediction residual error sum of square was selected as 18 (half the number of standard plus one)[42]. The prediction residual error sum of square values are minimum in the number of 4, 5 and 7 for zinc, cadmium and lead, respectively. In Fig. 7 the prediction residual error sum of square obtained by optimizing the calibration matrix of the absorbance data with partial least squares method is shown.

Figures of merit: Some parameters can be used to test the prediction ability of the model for simultaneous determination of zinc, cadmium and lead by the constructed model. The root mean square difference (RMSD) (eqn. 13), the square of the correlation coefficient (R^2) (eqn. 14) and the relative error of prediction (REP) (eqn. 15).

TABLE-2
ACTUAL AND PREDICTED CONCENTRATIONS OF PREDICTION SET

Solution number	Zn(II) (mg/L)			Cd(II) (mg/L)			Pb(II) (mg/L)		
	Actual value	Prediction value	RE (%)	Actual value	Prediction value	RE (%)	Actual value	Prediction value	RE (%)
1	3.07	3.0792	100.3	6.29	6.0815	96.7	2.90	3.1842	109.8
2	1.50	1.543	102.87	15.74	15.6718	99.6	0.00	-0.0854	91.46
3	4.58	4.5919	100.2	3.15	3.0061	95.43	0.00	-0.3085	69.15
4	0.78	0.7204	92.36	15.74	15.7521	100.08	2.90	2.7977	96.47
5	0.78	0.7204	92.36	9.44	9.5966	101.66	8.70	8.5788	98.61
6	3.79	3.7622	92.27	3.15	2.7849	88.4	2.90	3.0219	104.2
7	1.50	1.5742	104.9	3.15	3.3421	106.1	11.81	12.60	106.7
8	0.00	0.0992	109.9	15.74	15.7464	100	5.80	5.4438	93.85
9	0.00	-0.1781	82.19	6.29	6.3211	100.47	14.71	14.3987	97.88
10	2.29	2.3634	103.2	0.00	0.0833	108	11.81	11.6692	98.81

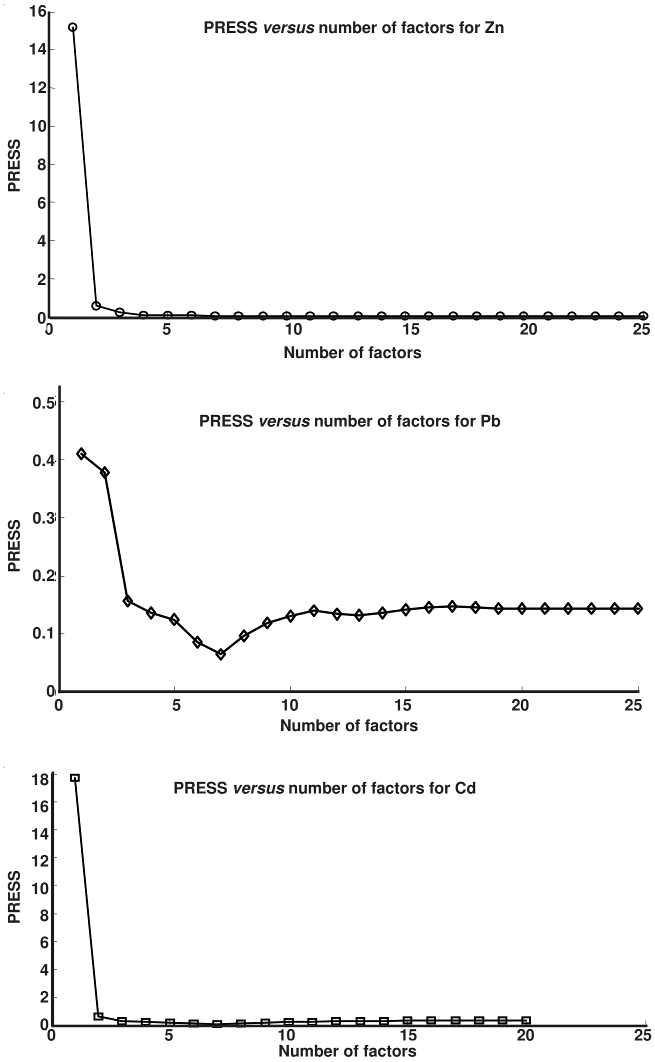


Fig. 7. The prediction residual error sum of square value as a function of the number of factors

$$\text{Room mean square difference} = \left[\frac{1}{n}\sum_{i=1}^{n}(\hat{x}_i - x_i)^2\right]^{0.5} \tag{13}$$

$$R^2 = \frac{\sum_{i=1}^{n}(\hat{x}_i - \bar{x}_i)^2}{\sum_{i=1}^{n}(x_i - \bar{x}_i)^2} \tag{14}$$

$$\text{Relative error of prediction (\%)} = \frac{100}{\bar{x}}\left[\frac{1}{n}\sum_{i=1}^{n}(\hat{x}_i - x_i)^2\right]^{0.5} \tag{15}$$

where, x_i is the true concentration of the analyte in the sample i, $\hat{x}_i$ represents the estimated concentration of the analyte in the sample i, x_i the mean of true concentration in the prediction set and n the total number of samples used in it. The concentration data of the prediction set and the values of room mean square difference (RMSD), relative error of prediction (REP), R^2, number of factors and prediction residual error sum of square are summarized in Table-3.

Analysis of real samples: After the proposed method was found to provide good results in the determination of zinc, cadmium and lead in laboratory-made samples, the method was applied to the determination of zinc, cadmium and lead in water samples. The results of the prediction are summarized in Table-4. The good agreement between these results and known values indicates the successful applicability of proposed method for simultaneous determination of Zn, Cd and Pb in real samples.

TABLE-3
STATISTICAL PARAMETERS FOR THE OPTIMIZED MODEL OF THE PREDICTION SET

Cations	Number of factors	PRESS (ppm^2)	RMSD (ppm)	REP (%)	R^2
Zn^{2+}	4	0.1	0.0333	1.520	0.9865
Cd^{2+}	5	0.25	0.1933	2.387	0.9632
Pb^{2+}	7	0.07	0.1808	3.94	0.9808

[a]Number of factors

Effect of foreign ions: One of the striking points of any new method is its interfering limit of the potential interferences. By definition interferring particle share with the desired one to the instrumental responses in contrast to effect of matrix, which reduce the sensitivity of the method. So to check and evaluate the tolerance limit of different interferes for the proposed model, the interferences due to several cations and anions were studied in detail. For this study, different amounts of the ionic species were added to a mixture of zinc, cadmium and lead. The starting point was 800 ppm of interference metal ions in presence of zinc, cadmium and lead, the tolerated limits were taken as those concentrations causing change not greater than ± 5 % in the concentration of each metal ion in mixtures. The cations and anions tested and their interfering limits are listed in Table-5.

TABLE-5
INFLUENCE OF FOREIGN IONS ON THE SIMULTANEOUS DETERMINATION OF ZINC, CADMIUM AND LEAD AT 2.29, 6.29 AND 5.8 ppm, RESPECTIVELY

Ion	Tolerance limit (ppm)
Na^+, K^+, NO_3^-, ClO_4^-	1800
Hg^{2+}	33.5
Co^{2+}, Ni^{2+}, Sn^{2+}	3.9
Cu^{2+}	6.4
Cr^{3+}	6.9
Mg^{2+}	100
Ba^{2+}, Sr^{2+}, Ca^{2+}	654
Mn^{2+}, Ai^{3+}, Ag^+, Pd^{2+}	5.5
Fe^{3+}	3.0

TABLE-4
SYNTHETIC REAL SAMPLE ANALYSIS BY XYLENOL ORANGE METHOD

Sample	Added (mg L^{-1})			Found (mg L^{-1})			Recovery (%)		
	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb
Tap water	4.6	9.5	3	4.52	9.59	2.98	98.3	101	99.3
	0.8	3.2	8.7	0.832	2.86	9.13	104	89.5	105
Well water	3.0	15.8	5.8	2.76	15.6	5.70	92.0	98.8	98.3
	3.8	6.3	11.8	3.74	6.6	10.58	98.5	105	89.7

Optimum condition for solid phase extraction

Effect of pH on metal-TCPP complex formation: In the preliminary experiments, complex formation of TCPP with Zn, Cd and Pb in different pH values (adjusted by nitric acid and sodium hydroxide) were examined. Fig. 8 shows the absorption spectra of the individual, zinc, cadmium and lead complexes with TCPP at different pH.

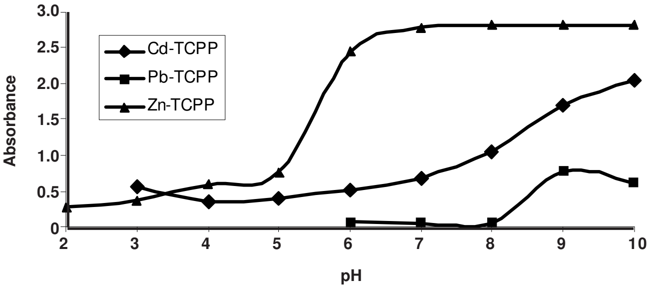


Fig. 8. Effect of pH on complex formation of Zn, Cd, Pb with TCPP at 2 × 10^{-5} M TCPP and Zn, Cd and Pb concentration of 6 × 10^{-6} M

As this figure shows pH = 9 was found to be the optimum pH for complex formation of TCPP with Zn, Cd and Pb, to compromise the sensitivity and selectivity of all three metal ions. So pH = 9 adjusted with 0.05 M borate buffer was chosen.

Complex formation of ions in optimum pH : Complex formation of 19 cations including 3 main cations (Zn, Cd and Pb) and 16 other cations with TCPP were studied in optimum condition (pH = 9 buffer borate 0.05). In addition to Zn, Cd and Pb, only Hg and Sn form complex with TCPP in this condition. The results are summarized in Table-6 and Fig. 9, so this is a good situation for performing a selective method and removing interfering cations in preliminary isolation of interfering ions before spectrophotometric determination of Zn, Cd and Pb, by xylenol orange. In this group separation, according to the table, only Sn and Hg, if present in the solution, could interfere in determination of Zn, Cd and Pb cations in this conditions and should be eliminated or mask with a particular method.

TABLE-6
METAL CATIONS COMPLEX FORMATION BY TCPP AT pH 9 (BORATE BUFFER 0.05 M)

Complex forming cations	Cations that don't form complex
Zn, Cd, Pb, Hg, Sn	Cr, Cu, Fe, Ni, Mn, Co, Al, Pd, Bi, Ag, Mg, Ca, Ba, Sr

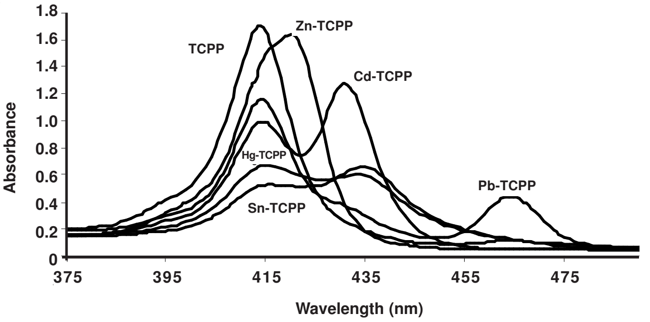


Fig. 9. Spectra of Zn, Cd, Pb, Sn, Hg complexes with TCPP at pH = 9 borate buffer 0.05 M pH 9

Effect of tryptophan: The formation and rate of formation of some metalloporphyrins can be catalyzed and enhanced by catalytic and accelerating effect of some amino acids such as phenylalanine, tryptophan, glycine, alanine, valine and tyrosine. From these amino acids the tryptophan has the most catalytic and accelerating effect[20].

Among Cd, Zn and Pb only the formation of Zn-TCPP is slow and needs at least 1 h time for completeness. So in order to accelerate formation of Zn-TCPP and reducing the time of analysis, the effect of tryptophan on the complex formation in present study cations and diverse ions with TCPP was investigated. Zn, Cd, Pb, Cr, Cu, Fe, Ni, Mn, Co, Al, Pd, Bi, Ag, Mg, Ca, Ba, Sr, Hg and Sn cations were investigated. The tryptophane showed an accelerating and catalytic effect on Zn-TCPP formation, but the Mn and Co form complex in the presence of tryptophan also (they don't form complex with TCPP without presence of tryptophan in this condition). From the results (Fig. 10), it can be seen that the catalytic effect of tryptophan can be used for reducing the time of analysis for the samples that have not Mn and Co as interfering ions.

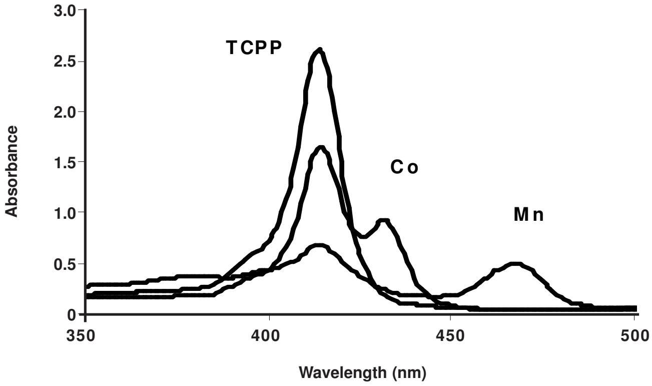


Fig. 10. Catalytic effect of tryptophan on the reaction of Co and Mn with TCPP. [TCPP] = 2 × 10^{-5} M ; [Mn] = 4 × 10^{-6} M ; [Co] = 4 × 10^{-6} M; [Try] = 2 × 10^{-5} M ; pH = 9; borate buffer 0.05 M

Preparation of resin: Amberlite IRA-402 obtained from the supplier contained organic and inorganic impurities. To remove the contaminants, it was washed successively with methanol, water, 1 mol L^{-1} HNO_3, water, 1.0 mol L^{-1} NaOH and water. And then set to dry in room temperature for 6 h. For column use, the ready to use resin were loaded in a glass column (7 cm long and 0.7 cm i.d.) and washed and conditioned with deionized water at least 20 min before use.

Retention of metal ion complexes on resin as a function of pH: The pH of the sample solution is an important factor in the chelation. It determines the value of conditional stability constant of the metal complexes. The sorption behaviour of metal complexes on anionic resins is also highly dependent on pH. The sorption of metal complexes on resin was investigated by batch method. Here 0.5 g dry anionic resin amberlite IRA-402 (prepared for use as previously explained) was gently shaken for 1 h with 25 mL of 1 × 10^{-5} M Pb or Cd or Zn with TCPP at a concentration of 2 × 10^{-5} M in borate buffer 0.05 M in each solution and appropriate pH.

Value adjusted with concentrated HNO_3 or NaOH. The concentration of metal ions were then determined in filtrate spectrophotometrically. The resulting per cent sorption -pH plot are shown in Fig. 9, which indicate that sorption is maximum and quantitative in pH range of 9 to 9.5 for all 3 metal cations. This is in agreement with optimum pH of complex formation of cations with TCPP. Consequently a solution pH of 9 was used for both complexation and retention of complexes of cations on resin, for further experiments.

As it is shown in Fig. 11, the sorption of TCPP-complexes on amberlite IRA-402 is highly dependent on pH. Generally the investigated metal complexes show higher retention at higher pH due to higher conditional formation and having negatively charge and better changing with anions on resin. This method can be used not only for separation, but also for removal of some trace metals from large volume of aqueous solution.

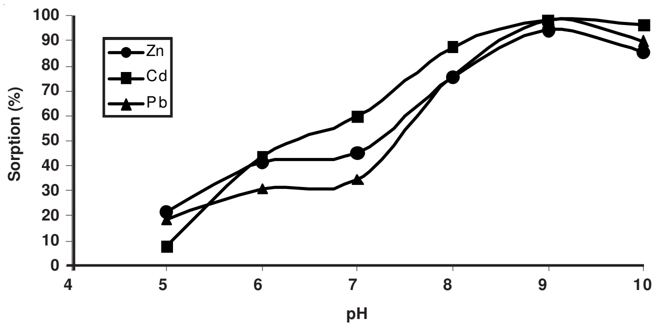


Fig. 11. Sorption of metal-TCPP complexes on amberlite IRA-402 as a function of pH.

Eluent selection: It is important to know the condition for total elution or release of complexes or metal ions from the sorbent in order to predict its potential application for recovery and separation of metal ions. The strong mineral acids are good choice for this purpose. The use of sulfuric acid and hydrochloric acid as eluent was avoided due to their ability to form precipitate with Pb. So nitric acid was choosed for stripping the metal complexes from the resin. In order to choose a proper concentration of HNO_3 for the release of retained complexes, after extraction of 1×10^{-4} mmol of Zn, Cd and Pb complexes in a 25 mL solution by 1 g resin in column. The Pb, Cd and Zn ions were stripped with 5 mL of different concentration of HNO_3 as eluent. The concentration of metal cations in eluent measured by AAS. The results are listed in Table- 7. The results revealed that a 5 mL of 0.2 M concentration of HNO_3 could afford the quantitative elution of Zn, Cd and Pb from the column. Subsequent elutions were carried out with 0.2 M concentration of HNO_3 solution. Subsequent elution of metal-TCPP complexes were carried out with 0.2 M HNO_3.

TABLE-7
PER CENT RECOVERY OF Zn, Cd, Pb-TCPP COMPLEXES FROM THE AMBERLITE IRA-402 RESIN, USING DIFFERENT HNO_3 CONCENTRATION

HNO_3 concentration M	Recovery (%)		
	Zn	Cd	Pb
0.05	74.2	65.0	73.0
0.10	88.7	84.5	89.5
0.20	98.5	99.2	99.8

Total sorption capacity of resin: The capacity of ion exchanger amberlite IRA-402 for metal -TCPP complexes sorbed on it determined by static method. Here, 0.2 g of ready to use resin was equilibrated with each metal ion complex solution (25 mL, 4×10^{-4} M complex of M-TCPP for 1 h at the optimum pH) then, the metal ions were stripped off from the resin with 25 mL of 0.2 M HNO_3 and their concentrations were determined by atomic absorption spectroscopy. The sorption capacities calculated for zinc, cadmium and lead ions were found to be 0.028, 0.025 and 0.022 mmol g^{-1}, respectively.

Effect of flow rate: The effect of flow rate of the sample and stripping solutions through the amberlite IRA-402 column on the retention and recovery of Zn and Cd and Pb complexes was investigated. It was found that, in the range of 0.5-1 mL min^{-1}, the retention of Zn and Cd and Pb, TCPP complexes in resin is good and because of slow rate of exchange on resin, gradually efficiency of retention reduces in greater sample flow rate. On the other hand, quantitative stripping of Zn and Cd and Pb complexes from the column was achieved in a flow rate range of below 0.5 mL min^{-1}, using 5 mL of 0.2 M nitric acid. At higher flow rates, larger volumes of 0.2 M nitric acid were necessary for quantitative stripping of cations.

Photodecomposition of TCPP complexes: During elution of the retained complexes on resin by HNO_3, cations and some TCPP may be eluted with stripping solution and this eluted TCPP can be an interfering species in spectrophotometric determination of cations by xylenol orange and therefore it should be eliminated from the solution. The porphyrin ring system can be destroyed by intense visible light or UV radiation due to ring opening[18]. So the stripping solution passed through the column were exposed to UV radiation for different time during photodecomposition experiments, samples were exposed from 10 cm distance to UV (from mercury lamp) light and protected against heating by intensive cooling with a fan. Reference samples that were not exposed to light were stored in a dark chamber. The results are shown in Fig. 12 for a sample of Zn complex eluted from the column. According to this experiment, eluted samples from column should be exposed to UV light at least for 25 min before spectrophotometric determination with xylenol orange to avoid interference of eluted TCPP in determinations.

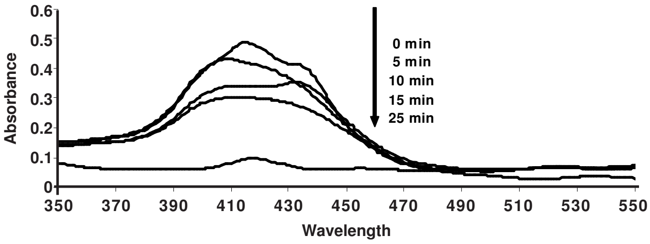


Fig. 12. Changes in absorption spectra (indicated by arrow) of TCPP during exposure to uv for solution of desorbed TCPP-Zn by 5 mL 0.2 M HNO_3 from the resin

Effect of diverse ions on the recovery: In order to assess the possible analytical applications of the recommended procedure, the effect of foreign ions on the separation and preconcentration of zinc, cadmium and lead ions was studied.

TABLE-8
DETERMINATION OF ZINC, CADMIUM AND LEAD IN THE ALLOY SAMPLES (n = 3)

Alloy name	Compositions (%)[B]	Zn found	Recovery (%)	Cd found	Recovery (%)	Pb found	Recovery (%)	Method[A]
Eutectic fusible alloy	Bi(52), Pb(40), Cd(8)	-	-	8.4	105.0	38.5	92.2	2
Eutectic fusible alloy	Zn(32), Pb(40), Cd(28)	33.5	104.7	27.0	96.4	41.5	103.8	1
Hardware bronze	Cu(89), Zn(9), Pb(2)	8.5	94.5	-	-	1.8	90.0	2
Aluminum solder	Zn(75), Cd(20), Al(5)	76.8	102.4	19.3	96.5	-	-	2

A: method 1: without SPE method 2: with SPE; B: for synthetic dissolved alloy nitrate salt of cations were used

A fixed amount of analytes was taken with different amounts of foreign ions and the recommended procedure was followed. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding ± 5 % in the determination of investigated analyte ions by the combination of the column solid phase extraction and the spectrophotometric method. Cr, Cu, Fe, Ni, Mn, Co, Al, Pd, Bi, Ag, Mg, Ca, Ba, Sr cations up to 300 ppm added to sample was examined. Zn, Cd and Pb cations can be recovered by combination of the column solid phase extraction and the spectrophotometric method by the error of below 5 % and only Hg and Sn with concentration greater than 10 and 30 ppm can interfere.

Precision studies: The reproducibility of the proposed method for extraction and determination of 0.037 mg zinc, 0.0315 mg cadmium and 0.029 mg lead from 50 mL water (n = 10) was also studied. The relative standard deviations (R.S.D.) of these determinations were 3.12 % for zinc, 2.7 % for cadmium and 3.97 % for lead.

Applications: The accuracy of the proposed method was tested by separation and determination of zinc, cadmium and lead ions in some synthetic dissolved alloy. The results obtained are shown in Table-8. As is evident, the zinc, cadmium and lead ions added can be quantitatively recovered and determined from the solution matrices.

Conclusion

A new method for the preconcentration and simultaneous spectrophotometric determination of zinc, cadmium and lead using solid phase extraction and partial least squares method is proposed. The results demonstrate that anionic resine Amberlite IRA-402 is an effective sorbent for selective absorption of trace amounts of Zn(II), Cd(II) and Pb(II) ions as their complexes with TCPP and can be used for their preconcentration or removal from their dilute sample solutions after complexation of them with TCPP. Only Hg and Sn can be a serious interfering ion. After extraction of metal complexes they can be determined simultaneously by using xylenol orange as a metallochromic indicator by spectrophotometric method. The proposed preconcentration and determination method gives a good R.S.D. values. The developed solid phase extraction method possesses a high potential for the group separation of these cations from host of coexisting alkali, alkaline earth, transition and heavy metal ions. The method can be successfully applied to the separation and determination of of zinc, cadmium and lead in water and some alloys.

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