

Simultaneous Separation and Preconcentration of Trace Amounts of Cd^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+} and Fe^{2+} on to Modified Amberlite XAD-4 Resin that Loaded with Pyrocatechol Violet

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In this work, a procedure for simultaneous separation and preconcentration of trace amounts of Cd^{2+} , Mn^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Fe^{2+} has been proposed. It is based on the adsorption of these ion solutions on to a column of amberlite XAD-4 resin that modified with benzyldimethyltetradecylammonium chloride and loaded with pyrocatechol violet reagent. These ions are quantitatively retained on the column in the pH range of 7.4–8.2 at a flow rate of 3 mL min^{-1} . The retained analyte on the resin recovered with 10.0 mL of 4 mol L^{-1} nitric acid with a flow rate of 1 mL min^{-1} and then the ions were determined by flame atomic absorption spectrometry. In this case, $0.50 \mu\text{g}$ of cadmium, $0.60 \mu\text{g}$ of manganese, $3.0 \mu\text{g}$ of nickel, $0.40 \mu\text{g}$ of zinc and $2.0 \mu\text{g}$ of iron can be concentrated in the column from 850 mL of aqueous sample whose preconcentration factor is 85. The interference of a large number of anions and cations has been studied and the optimized conditions developed were utilized for the trace determination of these ions in various standard samples. Determination of the ions in standard samples indicated that the method has good accuracy.

Key Words: Simultaneous separation, Preconcentration, Trace ions, XAD-resins, Pyrocatechol violet.

INTRODUCTION

Cleanup of analytical samples prior to determination of various metal ions has been a long standing problem in chemical analysis. This sample pretreatment has two main goals. One is to separate the target metal ions from large amounts of salt, organic material, dirt or other sample substances that would interfere in analytical measurement step. A second goal is to preconcentrate the metal ions to be determined to a point where their analytical determination is facilitated¹.

Trace heavy metal analysis is an important part of the studies in analytical chemistry. The determination of these ions in various materials from the industrial samples to environmental samples has been performed continuously². The concentration of metal ions in the environmental samples is lower than can be determined by flame atomic absorption spectrometry without preconcentration and interference of some ions for determination of these ions' exit. Therefore, whether the procedure contains separation and preconcentration of the metal ions is necessary before determination of these ions³. Several works exit for separation and preconcentration of these ion solutions alone but is necessary for simultaneous separation and preconcentration. Several methods extensively used for preconcentration include liquid-liquid extraction, ion exchange, solid-phase

extraction and chelating materials. However, solvent extraction suffers with problems like handling of large sample volume, slow attainment of equilibrium, mutual solubility of two phases, poor selectivity and emulsion formation. Multistage extraction is required several times for quantitative recovery. Consequently, in the last two decades, the use of chelating resins for metal enrichment has increased very significantly⁴⁻⁷. Their advantages include good selectivity, preconcentration factor, binding energy and mechanical stability, easy regeneration for multiple sorption-desorption cycles and good reproducibility in the sorption characteristic. At this time the most common technique for separation and preconcentration of trace amount ions is solid phase extraction. For this technique different sorbents were used such as activated carbon⁸, adsorption resins⁹, cellulose¹⁰, microcrystalline naphthalene¹¹⁻¹³, amberlite XAD-2 resins¹⁴, octadecylsilica membrane disk¹⁵, synthetic zeolites¹⁶, natural analcime zeolite¹⁷ and modified kaolinite¹⁸. In this work, modified XAD-4 amberlite resin for the simultaneous separation and preconcentration of trace amounts of several ions has been investigated. Benzylidimethyltetradecylammonium chloride surfactant was used for modification of resin and then the resin was modified with pyrocatechol violet reagent as a suitable reagent for complex formation with metal ions. This surfactant increased the sorption capacity of XAD-4 resins for the pyrocatechol violet reagent. Therefore, modified resin was suitable for simultaneous separation and preconcentration of several metal ions. The method is economical, sensitive and selective.

EXPERIMENTAL

A Varian model Spectra A 220 flame atomic absorption spectrometer was used. The conditions and instrumental settings were as in Table-1. A Beckman pH-meter was used for pH measurements. A funnel-tipped glass tube (100 × 20 mm) was used as column for preconcentration. All glassware and columns were washed with a mixture of concentrated hydrochloric acid and concentrated nitric acid (1 : 1) before use.

TABLE-1
CONDITION AND INSTRUMENTAL SETTINGS

	Pb	Cd	Fe	Mn	Zn
Wavelength (nm)	217.3	222.8	248.3	279.5	213.9
Lamp current (mA)	11	4	5	5	5
Slit width (nm)	1.0	0.3	0.2	0.2	1.0
Acetyl flow (L min ⁻¹)	1.5	1.5	1.0	1.0	1.5
Air flow (L min ⁻¹)	3.0	3.5	2.5	2.5	3.5

All chemical reagents used were of analytical grade. A stock solution of each studied cation solution (1000 ppm) was prepared and standardized with known methods¹⁹, the other solutions were made from this. Buffer solution with pH 7.0–10.0 was prepared by mixing an appropriate ratio 0.5 mol L⁻¹ ammonia and 0.5 mol L⁻¹ ammonium acetate solution. A solution of pyrocatechol violet reagent

(0.1%) in ethanol was prepared. A solution of tetradecyldimethylbenzyl ammonium chloride (0.01 mol L^{-1}) was prepared by dissolving in water. Solutions of various metals were used to study the interference of ions.

Preparation of amberlite XAD-4 column loaded with pyrocatechol violet

Amberlite XAD-4 was treated with ethanol, hydrochloric acid and water (2 : 1 : 1) solution overnight and then modified by tetradecyldimethylbenzyl ammonium chloride solution at 70°C for 12 h while being stirred. The adsorbent in this form was dried at 110°C in an oven and stored in calcium chloride desiccators until used. Each time for preparation of column, 1 g of modified resin was added to the column and then the resin was washed with deionized water until pH was neutral. Packing of the column must be done using ethanol as eluent since water makes resin beads float. The resin was saturated with the reagent by passing 5 mL of a 0.1% pyrocatechol violet solution in ethanol at a flow rate of 0.5 mL min^{-1} . Afterwards it was washed with water until excess reagent was eliminated from the resin. All experiments were done in a funnel-tipped glass tube ($100 \times 20 \text{ mm}$) that was used as a column for preconcentration. It was plugged with polypropylene fibres and then filled with XAD-4. Before sample loading the column must be preconditioned by passing a buffer solution. Then the column could be used repeatedly for twenty times at least.

RESULTS AND DISCUSSION

The reaction conditions were investigated with $5 \mu\text{g}$ of each ion. The sorption of ions on the column was found to be a maximum in the pH range of 7.4–8.2 (Fig. 1). In subsequent studies, the pH was maintained at *ca.* 7.8. The flow rate of sample was varied from $0.5\text{--}6 \text{ mL min}^{-1}$ and the results showed that a flow rate of $0.5\text{--}4 \text{ mL min}^{-1}$ did not affect adsorption. A flow rate of 3 mL min^{-1} was recommended in all experiments. The flow rate of eluent solution was varied from $1\text{--}3 \text{ mL min}^{-1}$ and the results showed that a flow rate $0.5\text{--}2 \text{ mL min}^{-1}$ is sufficient for recovery of these ions from column; therefore a flow rate of 1 mL min^{-1} was recommended. The volume of the aqueous phase was varied in the range of 50–1500 mL under optimum conditions, keeping the other variable constant. It was observed that the absorption was almost constant up to 850 mL. However, for convenience, all the experiments were carried out with 50 mL of aqueous phase. Preliminary observations indicated that these ions were completely desorbed from the column with 10.0 mL nitric acid (4 mol L^{-1}).

Sorption capacity of modified resins

The sorption capacity of modified resins for these ions was evaluated. In this case, the column containing 1.0 g of modified resins that loaded with pyrocatechol violet was used and different volume (100 mg L^{-1}) of these ions was passed through the column. Each time, the solution after passing the column was determined for ions until the solution showed each of the ions. The modified resins have a sorption capacity of 0.33, 0.45, 0.34, 0.47 and 0.54 mg of Cd^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+} and Fe^{2+} per g of modified resins, respectively.

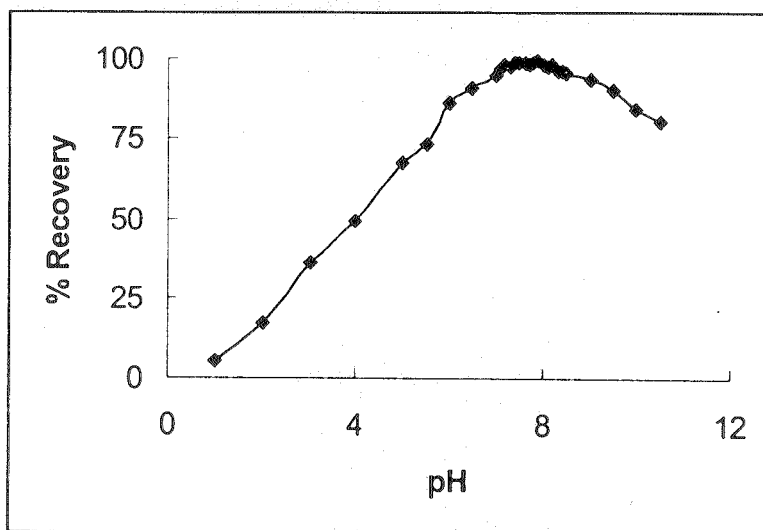


Fig. 1. Effect of pH on adsorption of these ions (Conditions: each of the ions (Cd^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+} and Fe^{2+}) is $5.0 \mu\text{g}$ in final solution; flow rate of sample 3 mL min^{-1} ; eluent was $10 \text{ mL } 4 \text{ mol L}^{-1}$ nitric acid with a flow rate of 1 mL min^{-1} ; instrumental settings were same as in Table-1)

Calibration and sensitivity

Under the optimized conditions, calibration curves were constructed for the determination of these ions according to the general procedure. Linearity in final solution was maintained between $0.05\text{--}2.0 \mu\text{g mL}^{-1}$ for cadmium, $0.06\text{--}4.0 \mu\text{g mL}^{-1}$ for manganese, $0.3\text{--}7.0 \mu\text{g mL}^{-1}$ for nickel, $0.04\text{--}1.5 \mu\text{g mL}^{-1}$ for zinc and $0.2\text{--}6.0 \mu\text{g mL}^{-1}$ for iron with correlation factors 0.9996, 0.9901, 0.9949, 0.9983 and 0.9982, respectively (Fig. 2). Eight replicate determinations of a mixture of $0.5 \mu\text{g mL}^{-1}$ cadmium, $0.5 \mu\text{g mL}^{-1}$ manganese, $2.0 \mu\text{g mL}^{-1}$ nickel, $0.5 \mu\text{g mL}^{-1}$ zinc and $3.0 \mu\text{g mL}^{-1}$ iron in final solution, give relative standard deviations ± 1.4 , ± 1.5 , ± 2.1 , ± 1.1 and $\pm 1.7\%$, respectively. The detection limits were 30 ng mL^{-1} for Ni^{2+} , 4.5 ng mL^{-1} for Cd^{2+} , 5 ng mL^{-1} for Zn^{2+} , 8 ng mL^{-1} for Mn^{2+} and 25 ng mL^{-1} Fe^{2+} in the final solution. In this case we can preconcentrate $1.0 \mu\text{g}$ of Ni^{2+} from 850 mL of solution whose concentration was 3.53 ng mL^{-1} in the original solution. The lowest concentration can be concentrated and then determined by flame atomic absorption spectrometry as follow: Cd^{2+} , 0.58 ng mL^{-1} ; Mn^{2+} , 0.71 ng mL^{-1} ; Zn^{2+} , 0.47 ng mL^{-1} and Fe^{2+} , 2.35 ng mL^{-1} .

Effect of diverse ions

Various salts and metal ions were added individually to a solution containing $5 \mu\text{g}$ of each ion and the general procedure was applied. The tolerance limit was set as the concentration of diverse ion amount required to cause $\pm 4\%$ error in the determination of each ion. The results obtained are given in Table-2. Among the anions examined, most could be tolerated up to milligram level except EDTA; obviously the stability constant of ion-EDTA complex must be near that of the ion-pyrocatechol complex. Most of the metal ions examined did not interfere up to mg level. Thus, the proposed method is selective and can be used for determination of these ions in complex samples without any prior separation.

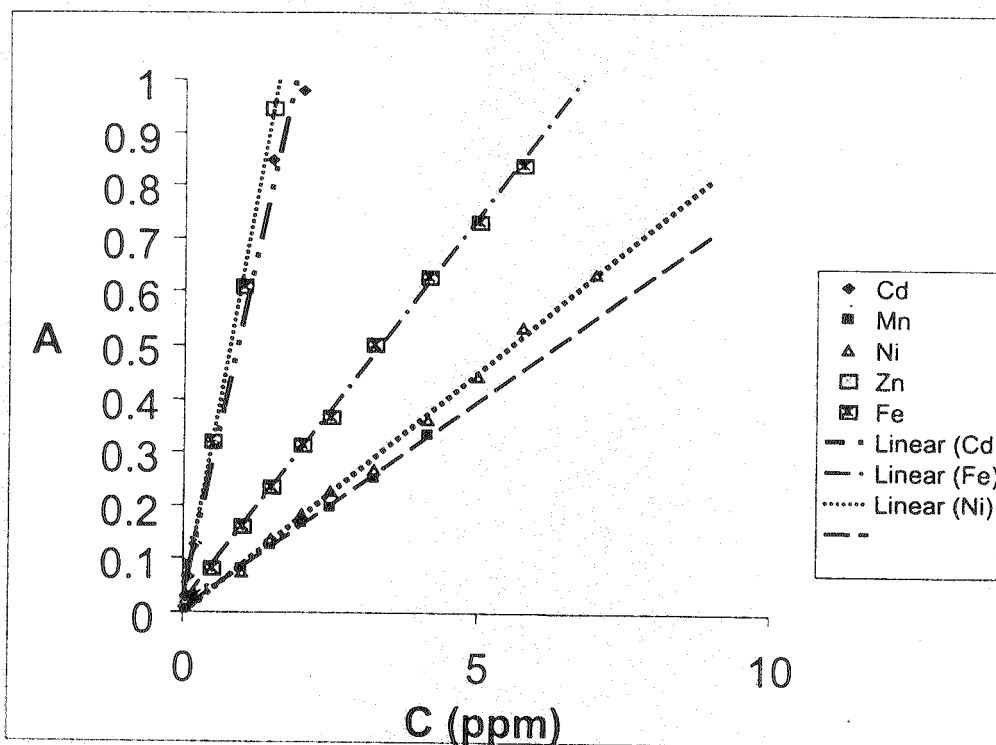


Fig. 2. Calibration curve for ions in final solution (Conditions and instrumental setting were same as Fig. 1: $Y_{Zn} = 0.6134x + 0.0137$, $R^2 = 0.9983$; $Y_{Cd} = 0.5058x + 0.0293$, $R^2 = 0.9901$; $Y_{Fe} = 0.1449x + 0.0153$, $R^2 = 0.9984$; $Y_{Ni} = 0.0907x + 0.0041$, $R^2 = 0.9968$; $Y_{Mn} = 0.078x + 0.0055$, $R^2 = 0.9989$)

TABLE-2
EFFECT OF DIVERSE SALTS AND METAL IONS ON THE
DETERMINATION OF THESE IONS

Salt or ion	Tolerance limit (mg)	Salt or ion	Tolerance limit (mg)
Sb(II), Pb(II)	115	CH ₃ COONa·3H ₂ O, KNO ₃	2000
Cu(II)	13.5	K ₄ SO ₄	450
Al(III)	240	KI	400
Cr(VI)	20	NH ₄ Cl, Na ₃ PO ₄ ·12H ₂ O	750
Ag(I)	13	Sodium potassium tartrate	100
Mo (III)	22	Thiourea, KSCN	120
Pd (II)	18	Sodium oxalate	650
Bi (III)	10	Na ₂ EDTA	0.08
V (V)	21	Mg(II)	740
Hg (II)	70	Ca(II)	850

Sample solution of nitric acid (Conditions: each of the ions (Cd²⁺, Mn²⁺, Ni²⁺, Zn²⁺ and Fe²⁺) is 5.0 µg in final solution, flow rate of sample 3 mL min⁻¹, eluent was 10 mL 4 mol L⁻¹ nitric acid with a flow rate of 1 mL min⁻¹; instrumental settings were same as in Table-1.)
(The sample contained 5.0 of these ions and each amount of the foreign ion in 10.0 mL)

Analysis of these ions in standard samples

The method was applied to the determination of these ions in Nippon Keikinzo Kogyo (NKK) CRM No. 916 and No. 920, NIST SRM 629 zinc alloy, NIES, No. 1 (pepperbush). 0.10 g samples of standard alloy or 1.0 pepperbush was completely dissolved in 10.0 mL of hydrochloric acid and nitric acid (1 : 1) by heating on a water-bath. The solution was filtered and then added to it 10 mL from 0.1 mol L⁻¹ of sodium oxalate and diluted to 100 mL with distilled water in a standard flask. An aliquot of this sample was taken and the procedure was applied. The results obtained are given in Table-3. These results are in agreement with certified values.

TABLE-3
ANALYSIS OF THESE IONS IN STANDARD SAMPLES

Sample	Composition%	Found ^a
NKK CRM No. 916 Aluminum alloy	Si, 0.41; Fe, 0.54; Mg, 0.10; Cr, 0.05; Zn, 0.030; Ti, 0.10; Sn, 0.05; P, 0.04; Sb, 0.01; B, 0.006; Zr, 0.05; Bi, 0.03; Co, 0.03; Ni, 0.06; V, 0.02; Cu, 0.27; Mn, 0.11	Mn, 0.114 ± 0.004; Fe, 0.55 ± 0.01; Zn, 0.038 ± 0.001; Ni, 0.067 ± 0.002
NKK CRM No. 920 Aluminum alloy	Si, 0.78; Fe, 0.72; Mg, 0.46; Cr, 0.27; Zn, 0.80; Ti, 0.15; Bi, 0.06; Ga, 0.05; Ca, 0.03; Co, 0.03; Ni, 0.06; V, 0.02; Cu, 0.27; Mn, 0.11	Mn, 0.111 ± 0.002; Zn, 0.83 ± 0.02; Ni, 0.28 ± 0.01; Fe 0.73 ± 0.02
NIST SRM 629 Zinc alloy	Fe, 0.017; Cu, 1.5; Al, 5.15; Mg, 0.094; Sn, 0.012; Cr, 0.0008; Cd, 0.0155; Ni, 0.0075; Pb, 0.0135; Si, 0.078	Fe, 0.018 ± 0.001; Cu, 1.52 ± 0.06; Ni, 0.0077 ± 0.0003; Cd, 0.0158 ± 0.0008
NIES, No. 1 Pepperbush	Ca, 1.38 ± 0.07%; K, 1.51 ± 0.06%; Mn, 0.203 ± 0.17; Mg, 0.408 ± 0.020; Cd, 6.7 ± 0.5; Ni, 8.7 ± 0.6; Fe, 205 ± 17; Co, 23 ± 3; Pb, 5.5 ± 0.8; Cu, 12 ± 1; Zn, 340 ± 20; Ba, 165 ± 10; Na, 106 ± 13; Rb, 75 ± 4; Sr, 36 ± 4; As, 2.3 ± 0.3; P, 1100; Cr, 1.3; Cs, 1.2; Tl, 0.13; Hg, 0.05 (after K all of µg g ⁻¹)	Cd, 6.9 ± 0.4; Ni, 9.2 ± 0.4

^aMean of five determinations ± standard deviation.

Conclusion

Many methods have been reported for preconcentration and determination of these ions alone but sometimes these ions were together, therefore it was necessary to develop a method for simultaneous separation and preconcentration. The main advantage of this procedure is: (i) Simultaneous separation and preconcentration. (ii) During ions desorption the pyrocatechol violet reagent remains in the resin which allows using the column several times. (iii) A good preconcentration factor (85) can be achieved. (iv) The preparation of the extractor system is

simple, economical and fast. The procedure used for measurement of these ions in standard samples showed a good accuracy. This method was used for the first time for modification of XAD-4 resin with surfactant and the results showed that the modification increased the sorption capacity of resin for organic material.

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