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# Combined cation-exchange and extraction chromatographic method of pre-concentration and concomitant separation of Cu(II) with high molecular mass liquid cation exchanger after its online detection

B. Mandal*, U.S. Roy, D. Datta, N. Ghosh

*Department of Chemistry, Visva-Bharati University, Santiniketan 731235, India*

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ABSTRACT

A selective method has been developed for the extraction chromatographic trace level separation of Cu(II) with Versatic 10 (liquid cation exchanger) coated on silanised silica gel (SSG-V10). Cu(II) has been extracted from 0.1 M acetate buffer at the range of pH 4.0–5.5. The effects of foreign ions, pH, flow-rate, stripping agents on extraction and elution have been investigated. Exchange capacity of the prepared exchanger at different temperatures with respect to Cu(II) has been determined. The extraction equilibrium constant ($K_{ex}$) and different standard thermodynamic parameters have also been calculated by temperature variation method. Positive value of $\Delta H$ (7.98 kJ mol$^{-1}$) and $\Delta S$ (0.1916 kJ mol$^{-1}$) and negative value of $\Delta G$ (−49.16 kJ mol$^{-1}$) indicated that the process was endothermic, entropy gaining and spontaneous. Preconcentration factor was optimized at 74.7 ± 0.2 and the desorption constants $K_{desorption}{}^{1}$(1.4 × 10$^{-2}$) and $K_{desorption}{}^{2}$(9.8 × 10$^{-2}$) were determined. The effect of pH on $R_f$ values in ion exchange paper chromatography has been investigated. In order to investigate the sorption isotherm, two equilibrium models, the Freundlich and Langmuir isotherms, were analyzed. Cu(II) has been separated from synthetic binary and multi-component mixtures containing various metal ions associated with it in ores and alloy samples. The method effectively permits sequential separation of Cu(II) from synthetic quaternary mixture containing its congeners Bi(III), Sn(II), Hg(II) and Cu(II), Cd(II), Pb(II) of same analytical group. The method was found effective for the selective detection, removal and recovery of Cu(II) from industrial waste and standard alloy samples following its preconcentration on the column. A plausible mechanism for the extraction of Cu(II) has been suggested.

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## 1. Introduction

Copper is a harmful toxic element and has got technical importance because of its high thermal and electrical conductance. In trace level heavy metals like Cr(III), Cd(II), Zn(II), Hg(II), Pb(II) and Cu(II) etc., are hazardous to the environment [1]. The removal of heavy metal ions from industrial waste waters is becoming more relevant with the increase of industrialization [2]. Trace level monitoring of metallic toxicant poses a challenging problem to the analytical chemists. However, preconcentration and separation of an analyte is usually necessary before its monitoring. In this regard, the most widely used techniques are solvent extraction [3], coprecipitation [4–6], ion chromatography [7], adsorption [8,9], cloud point extraction [10], electrochemical deposition [11] and solid phase extraction (SPE) [12–14]. But, except SPE all other techniques are extremely expensive, when the metals are in large volumes of relatively low concentrations [15]. SPE [16–18] is an analytical technique for the trace level separation and preconcentration of heavy metals. It is simple, selective, rapid, ecofriendly, cost effective and has high enrichment factor. In our laboratory, Versatic 10 on hydrophobic silica support has been used for the extraction, separation and preconcentration of Bi(III) [19]. But the systematic extraction chromatographic investigation of Cu(II) with HMMCA, Versatic 10 on silanised silica gel for simultaneous detection and separation at trace level after its preconcentration at the column has yet not been reported. Versatic 10, is a mixture of $C_{10}$ isomeric tertiary monocarboxylic acids, had the concentration and purity of 5.2 M and 99% (w/v) respectively [20]. It is soluble in several solvents like benzene, toluene, *n*-hexane, xylene, butanol, carbon tetrachloride, chloroform, nitrobenzene and diisopropyl ether [21,22]. It has a good thermal and chemical stability [20] and efficiently extracts metal ions from aqueous solution over a wide range of pH [23,24]. The present work reports a rapid method for the extraction, preconcentration, detection and separation of microgram level Cu(II) from wide variety of multi-component mixtures

* Corresponding author. Tel.: +91 9474738517; fax: +91 3463261526.
*E-mail address:* bhabatosh_mandal@yahoo.co.in (B. Mandal).

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containing large number of heavy, toxic and conger cations with HMMCA, Versatic 10 on hydrophobic silica support.

## 2. Experimental

### 2.1. Apparatus

Digital Elico L1-120 pH meter combined with glass electrode, 7D-1F thermostat, spectrophotometer (Beckman DU-6 ECIL GS 5700A), Shimadzu FTIR spectrophotometer (model no FTIR-8400S), Simadzu atomic absorption spectrophotometer (model no. 6300), Thermo Scientific (Orion 5 Star Benchtop Multi W/ISE mtr, Singapore) and chromatographic glass column (0.8 cm × 8 cm) were used in the present study.

### 2.2. Reagents

Unless otherwise stated, all chemicals and solvents used in this work were of analytical grade (BDH/E Merck). A liquid cation exchanger, Versatic 10 (Shell Chemical, London, England), a mixture of highly branched aliphatic $C_{10}$ isomeric tertiaty monocarboxylic acid, was used without any further purification. Dimethyldichlorosilane (BDH, Mumbai, India) was used for end capping of silica gel (BDH, Mumbai, India) (120 mesh). A standard stock solution of Cu(II) (1.06 mg cm$^{-3}$) was prepared by dissolving $Cu(NO_3)_2$ (E. Merc, Mumbai, India) in water and estimated complexometrically [25] with EDTA (E. Merc, Mumbai, India) using xylenol orange (BDH, Mumbai, India) as indicator. The solution containing 10.6 μg cm$^{-3}$ of Cu(II) was prepared through appropriate dilution. This concentration (10.6 μg cm$^{-3}$) of Cu(II) has been selected randomly for our present work. Buffer solutions of different pHs were prepared using acetic acid (BDH, Mumbai, India) (0.1 M) and ammonium acetate (BDH, Mumbai, India) (0.1 M) in proper ratio. Lower pH values were adjusted with the help of 0.2 M chloro-acetic acid.

### 2.3. Preparation of ion exchange material

Silica gel (60–120 mesh) was made hydrophobic by exposing it to the vapor of dimethyldichlorosilane (DMDCS) in $N_2$ atmosphere. The DMDCS treated (silanised) silica gel was then washed with anhydrous methanol and dried at 70–80 °C. The silanised silica gel (SSG) was impregnated with Versatic 10 (V 10), diluted in diisopropyl ether (0.2 mL in 100 mL) and was dried in a rotary vacuum evaporator to achieve uniform coating [19]. The surface area of exchanger was determined by standard methylene blue method [26]. The exchanger (SSG-V10) could be used for at least 40 cycles without any loss of its exchange capacity. For ion-exchange paper chromatography, a strip of Whatman No 1 was immersed in a solution of Versatic 10 (0.2 mL was taken in 20 mL diisopropyl ether) to achieve uniform coating and then dried in air. Cu(II) in μg level was spotted on the paper strip containing exchanger and developed with acetate buffer of pH 5.0:acetone (15:2, v/v).

### 2.4. General extraction procedure

An aliquot of Cu(II) solution (10.6 μg mL$^{-1}$) in acetate buffer of pH 5.0 was passed through the column (pre-adjusted pH 5.0) containing ion exchanger (1 g), at a flow rate of 1.0 cm$^3$ min$^{-1}$. After extraction, Cu(II) was stripped with 0.1 M $HNO_3$ and the amount of Cu(II) was determined by ion selective electrode.

### 2.5. Batch procedure

#### 2.5.1. Distribution co-efficient ($K_d$)

A total 100 mg of the dry exchanger was suspended with constant stirring in 400 cm$^3$ Cu(II) solution (10.6 μg cm$^{-3}$) for 30 min at the desired pH value in the range 2.5–7.5. The same experiment has also been made in presence of acetate ion in the range 50–300 ppm at pH 5.0. The supernatant was filtered through a dry filter paper immediately. The amount of Cu(II) in the filtrate was determined by Ion selective electrode.

#### 2.5.2. Adsorption isotherm

A total 100 mg of the dry exchanger was suspended with constant stirring for 30 min in 400 cm$^3$ of Cu(II) solution with different initial concentrations (10–80 μg cm$^{-3}$) at pH 5.0. The amount of Cu(II) adsorbed per unit mass of the adsorbent ($q_e$ in mg g$^{-1}$) was computed using the following equation:

$$q_e = (C_i - C_e) \times \frac{V}{m} \quad (1)$$

Here, $C_i$ and $C_e$ are the initial and equilibrium concentrations (mg dm$^{-3}$), m is the mass (g) of the adsorbent, and $V$ (dm$^3$) is the volume of the solution.

## 3. Results and discussion

### 3.1. FTIR analysis

The decreasing of stretching frequency (1703 to 1660–1540 cm$^{-1}$) in the loaded exchanger indicates the conversion of –COOH group to –COO$^-$ ion [27] and suggests the participation of this functional group in the adsorption of Cu(II) by the exchanger.

### 3.2. Exchange capacity of the prepared exchanger

The exchange capacity of the prepared exchanger was determined [22] at different temperatures by measuring the milliequivalent of sodium ions adsorbed by 1 g of dry exchanger in $H^+$ form. The exchange capacity at pH 10–12 and temperature 27–40 °C was found to be 2.56 mequiv. of $H^+$ g$^{-1}$ of dry exchanger and it is consistent with the literature value [19,28]. It corresponds to the maximum uptake capacity of the exchanger for Cu(II) and it was 1.28 mequiv (81.28 mg g$^{-1}$) at the said pH.

### 3.3. Break through capacity (maximum uptake capacity) and preconcentration factor

The pHs of the exchanger bed and Cu(II) solution (0.053 mg cm$^{-3}$) were adjusted to the desired value with 0.1 M acetate buffer and then Cu(II) solution in buffer was passed through the column containing 1 g of dry exchanger at a flow-rate of 1.0 cm$^3$ min$^{-1}$. The column was saturated with Cu(II) at pHs 4.5, 5.0 and 5.5 on passing 634 cm$^3$ (33.6 mg), 675 cm$^3$ (35.8 mg) and 738 cm$^3$ (39.1 mg) of metal ion solution, respectively. So the maximum uptake capacity of Cu(II) in the column increases with the increase in pH. Here, the working pH (4.5–5.5) is much lower than the required pH (10–12) for full functioning of the exchange site and so the efficiency of the exchanger stands at somewhat reduced level of 41.3–48.1% with respect to Cu(II). After saturation through extraction, Cu(II) was eluted from column with 10 cm$^3$ 0.1 M $HNO_3$. During this continuous extraction, Cu(II) has been accumulated gradually on the column from its influent of lower concentration (0.053 mg cm$^{-3}$) and after elution the effluent (10 cm$^3$) were found to be enriched with higher concentrations (3.34 mg cm$^{-3}$, 3.56 mg cm$^{-3}$, 3.87 mg cm$^{-3}$) (99% recovery) of

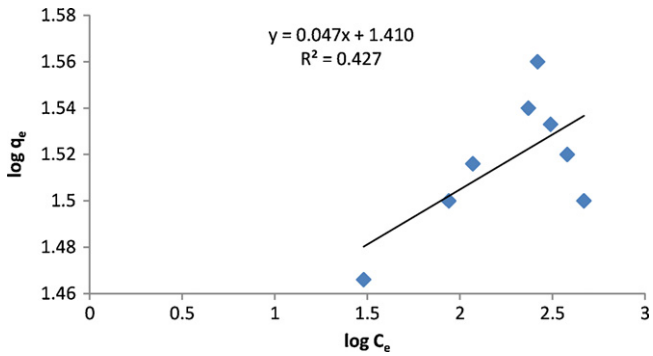



**Fig. 1.** FTIR spectra of (a) the ion exchanger and (b) Cu(II) loaded ion exchanger.

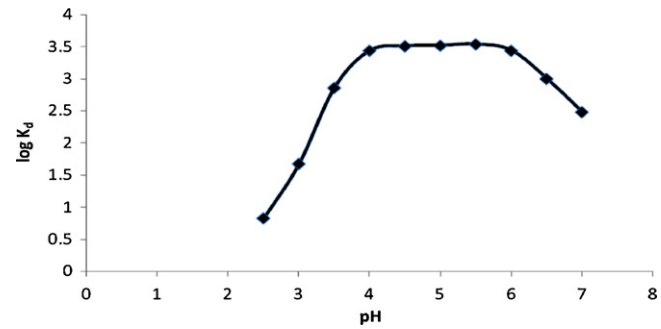



**Fig. 2.** Plot of $\log q_e$ vs. $\log C_e$.

Cu(II). So the developed method preconcentrates Cu(II) in the effluent with a factor of 63, 67 and 73 on milligram levels.

### 3.4. Effect of temperature on extraction

The extraction equilibrium constant ($K_{ex}$) has been computed at different temperatures using the following equation (Eq. (2)) [19] and plot of $\log K_{ex}$ vs. $1000/T$ gives a linear behavior ($y = -0.4169X + 0.002$; $R^2 = 0.9796$).

$$K_{ex} = \frac{E_R}{[(RCOO^-)_2(H^+)_2(S)]^2} \times [H^+] \quad (2)$$

where $[(RCOO^-)_2(H)^+{}_2(S)]$, denotes the concentration of Versatic 10 in its dimeric form participating in ion-exchange process, and $E_R$ is the ratio of extracted metal ion to its un-extracted portion.

The effect of temperature on extraction of Cu(II) has been made for the determination [19] of different thermodynamic parameters at pH 5.0 using the standard van't Hoff equation. The enthalpy change ($\Delta H$) was evaluated from the plot of $\log K_{ex}$ vs. $1000/T$.

The positive $\Delta H$ (7.98 kJ mol$^{-1}$) and smaller $\Delta S$ (0.1916 kJ mol$^{-1}$) rationalize the endothermic nature of the extraction process [29]. The higher negative value of $\Delta G$ (−49.16 kJ mol$^{-1}$) suggests that the adsorption equilibrium was thermodynamically favored and it was chemisorption [29]. The behavior reflects Langmuir adsorption isotherm.

### 3.5. Adsorption isotherm

An experimental linear plot ($y = 0.0295X + 0.0995$; $R^2 = 0.9991$) of $C_e/q_e$ versus $C_e$ for the adsorbent suggests the validity of the Langmuir adsorption (chemisorption) isotherm (Eq. (3)). From the slope and intercept of the linear plot $Q_0$ (maximum adsorption) and b (energy parameter of adsorption) were found to be 33.9 (mg g$^{-1}$) and 0.296 (dm$^3$ mg$^{-1}$) respectively. The observed $Q_0$ value is in well agreement with the experimental breakthrough capacity value (33.6 mg g$^{-1}$).

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

where $C_e$ is the equilibrium concentration (mg dm$^{-3}$) of Cu(II) and $q_e$ is the amount of Cu(II) adsorbed per unit mass of the adsorbent (mg g$^{-1}$). However, the experimental plot (Fig. 1) of $\log q_e$ versus $\log C_e$ gives no linear relation and denies the Freundlich isotherm models (Eq. (5)). Moreover, the value of $1/n$ for the average curve is appreciably lower than unity (0.047). The correlation coefficient for Langmuir (0.9977) is very much higher than that of Freundlich value (0.427). So, it becomes more and more difficult to adsorb additional adsorbates.

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (4)$$

Here, the adsorption constants $k_F$ and $1/n$ were the indicators of adsorption capacity and adsorption intensity, respectively. The dimensionless separation factor [30] $R_L$, was calculated from Langmuir constant (b) (Eq. (5)).

$$R_L = (1 + bC_i)^{-1} \quad (5)$$

where $C_i$ is the initial solute concentration. Using initial solute concentration ranging between 10–80 μg cm$^{-3}$ the values of $R_L$ (0.25–0.04) were calculated. The $R_L$ values lie between 0 and 1, indicating a favorable exchange process.

### 3.6. Effect of volume and flow-rate of the influent, and common anions on extraction

It is observed that the volume of Cu(II) solution up to 0.9 dm$^3$ does not influence the percentage of retention. The complete retention of Cu(II) at the column was found even at a flow rate of 3.5 cm$^3$ min$^{-1}$. Common anions like $Cl^-$, $SO_4{}^{2-}$, $ClO_4{}^-$, $NO_3{}^-$ up to 250 μg cm$^{-3}$ and $CH_3COO^-$ up to 300 μg cm$^{-3}$ did not interfere in the extraction.

### 3.7. Effect of pH on extraction

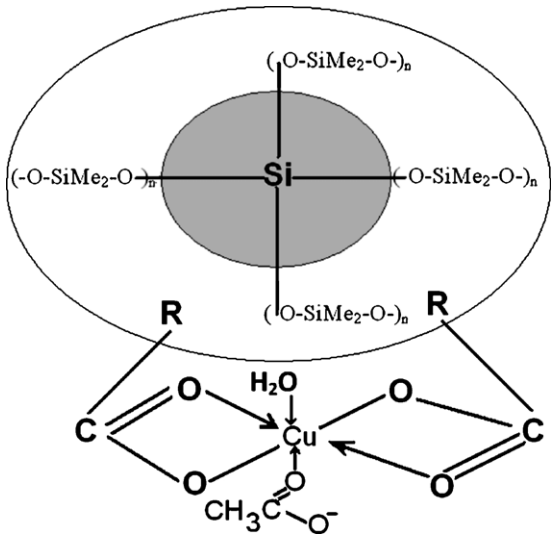
The systematic extraction chromatographic studies on Cu(II) (10.6 μg) ensured its quantitative extraction at an optimum pH range of 4.0–5.5. The extracted Cu(II) renders an intense green colored band at the column. The distribution coefficient ($K_d$) at different pH has been computed using equation 6. The effect of pH on $\log K_d$ of Cu(II) between the adsorbent and solution is depicted in Fig. 2.

$$K_d\ (\text{mL g}^{-1}) = \frac{C_s\,(\mu\text{g g}^{-1})}{C_{sol}\,(\mu\text{g mL}^{-1})} \quad (6)$$

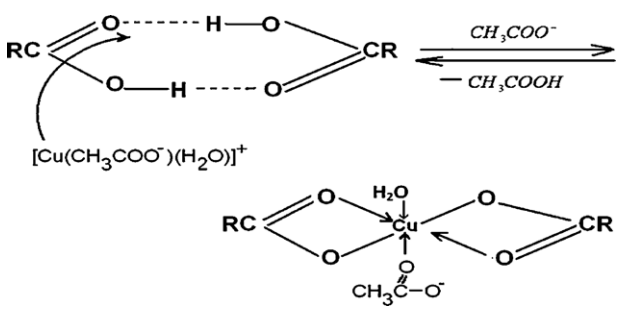
Here, $C_s$ and $C_{sol}$ are concentrations of Cu(II) in the solid phase and in solution phase, respectively.

At low pH values (<4.5), the lower values of $\log K_d$ were attributed to the difficult deprotonation of the carboxylic acid moiety of the exchanger which diminishes the ability of acetate ion to chelate with Cu(II). The low pH values also increase the solubility of Cu(II) in aqueous solution and corroborate the suggested mechanistic path (Eq. (7)). It is observed that $\log K_d$ for Cu(II) (3.6) at pH 5.0 of the modified silica gel with Versatic 10 is much higher than the corresponding value of 1.2 for bare active silica gel.

The surface of the silica gel becomes methylated (hydrophobic) during silanization (Eq. (8)) [24]. The silanised silica surface immobilizes the hydrophobic part of the exchanger through weak hydrophobic interaction [31] and the –COOH group point towards the hydrophilic mobile phase. At the range of pH 4.5–6.5, the exchanger exists as a dimmer through inter molecular hydrogen bonding [32]. The mechanistic path has been shown in Schemes 1 and 2.




**Scheme 1.**




**Scheme 2.**

Taking O···H···O bond length 258 pm, C–O bond length 132 pm and ∠OCO 120° [20], the calculated core radius of the dimmer (114 pm) is comparable with the radius of Cu(II) (87 pm). To elucidate the hardness behavior, the structure of Versatic 10 was optimized by semi-empirical method and from HOMO (−11.10 eV)–LUMO (1.03 eV) gap the global hardness was calculated [33] ($\eta$ = 6.03 eV). Here, Cu(II) is trapped inside the co-ordination sphere of a number of hard donor O-sites (Fig. 7) present in the exchanger core (inherent $\eta$ = 8.27 eV). The distorted $O_h$ complex gives an intense blue color. Both the neutral, $[Cu(CH_3COO)_2]$ and cationic species, $[Cu(CH_3COO)]^+$ are present [34] at pH 4.0–5.5. At pH 5, plot of log $K_d$ against log $C_{[CH_3COO^-]}$ gives a linear relationship ($y = 0.9691X + 1.5909$; $R^2 = 0.9893$) with slope of 0.97 at fixed concentrations of extractant and Cu(II). A linear relationship ($y = 1.9754X + 1.5616$; $R^2 = 0.9812$) with slope = 1.9754 between log $K_d$ and log $C_{[Versatic\ 10]}$ is also obtained at pH 5, at a fixed concentrations of acetate and Cu(II). Thus, the probable composition of the extracted species comes out to be 1:2:1 (metal:extractant:acetate). Bearing this in mind it has been suggested that Cu(II) first produces the monomer, $[Cu(CH_3COO)]^+$ with acetate ion at pH 4.0–5.5. The cationic monomer, having suitable size and charge, moves to the exchange site as per following proposed path:

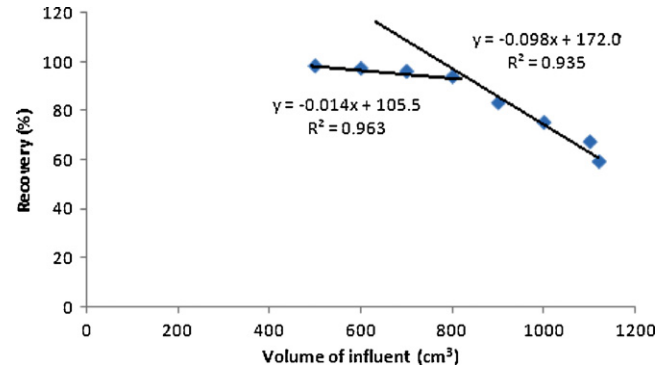



**Fig. 3.** Plot of log $K_d$ vs. pH at fixed concentration of Cu(II) and extractant.

$$(RCOO^-)_2(H^+)_2(S) + [Cu(CH3COO)]^+(Sol.) \rightleftharpoons [Cu(CH_3COO)]^+(RCOO^-) \cdot RCOOH(S) + H^+(Sol.) \quad (7)$$

$$-\overset{|}{\underset{|}{Si}}-O + SiMe_2Cl_2 \overset{HCl}{\rightleftharpoons} \{Si(-O-SiMe_2-O-)\}_n \quad (8)$$

At pH higher than 5.5, Cu(II) undergoes hydrolysis and does not participate in exchange process.

**Table 1**
Stripping behavior of Cu(II) with respect to different eluents [column = 0.8 cm × 8 cm; flow-rate = 1.0 mL min$^{-1}$; Cu(II) taken = 10.6 μg; pH = 5.0].

| Eluents | Conc. (M) | Distance for peak elution, $y$ (cm) | Peak width, $W_{0.6065}$ (cm) | $V_{max}$ (mL) | $V_t$ (mL) | Recovery[a] (%) | Column efficiency, $N$ |
|---|---|---|---|---|---|---|---|
| $H_2SO_4$ | 0.01 | 3.2 | 0.7 | 80 | 120 | 32.8 | 334 |
| | 0.05 | | | 50 | 100 | 67.2 | |
| | 0.1 | | | 12 | 30 | 98.6 | |
| $HNO_3$ | 0.01 | 2.9 | 0.25 | 60 | 100 | 26.2 | 538 |
| | 0.02 | | | 50 | 90 | 48.1 | |
| | 0.03 | | | 25 | 60 | 74.4 | |
| | 0.05 | | | 15 | 25 | 82.6 | |
| | 0.1 | | | 5 | 10 | 98.5 | |
| HCl | 0.01 | 3.8 | 0.45 | 45 | 100 | 18.5 | 285 |
| | 0.02 | | | 45 | 90 | 54.5 | |
| | 0.03 | | | 35 | 80 | 67.6 | |
| | 0.05 | | | 30 | 60 | 86.7 | |
| | 0.1 | | | 15 | 45 | 98.6 | |
| $CH_3COOH$ | 0.2 | 2.6 | 0.35 | 35 | 60 | 8.8 | 221 |
| | 0.5 | | | 25 | 50 | 38.6 | |
| | 1.0 | | | 12 | 30 | 78.4 | |
| | 1.5 | | | 12 | 25 | 98.6 | |

[a] Average of five determinations.

**Table 2**
Effect of Volume, sample concentration and pH on preconcentration factor [flow-rate = 1 $cm^3\,min^{-1}$; pH = 5.0; Cu(II) = 0.03–0.045 $mg\,cm^{-3}$; standard deviation = 0.08].

| pH | Sample conc. ($C_s$) ($mg\,cm^{-3}$) | Sample vol. ($V_s$) ($cm^3$) | Cu(II) (mg) | | Effluent conc. ($C_f$) ($mg\,cm^{-3}$) | Recovery $R_{Cu(II)}$ (%) | PF ($C_f/C_s$) |
|---|---|---|---|---|---|---|---|
| | | | Added | Recovered | | | |
| 4.5 | 0.03 | 500 | 15.0 | 14.72 | 1.472 | 98.1 | 49.1 |
| | | 600 | 18.0 | 17.45 | 1.745 | 97.1 | 58.2 |
| | | 700 | 21.0 | 20.14 | 2.014 | 95.9 | 67.1 |
| | | 800 | 24.0 | 22.48 | 2.248 | 93.7 | 74.9 |
| | | 900 | 27.0 | 22.41 | 2.241 | 83.1 | 74.7 |
| | | 1000 | 30.0 | 22.53 | 2.253 | 75.1 | 75.1 |
| | | 1100 | 33.0 | 22.21 | 2.221 | 67.3 | 74.0 |
| | | 1120 | 33.6 | 19.89 | 1.989 | 59.2 | 66.3 |
| 5.0 | 0.04 | 400 | 16.0 | 15.94 | 1.594 | 99.6 | 39.9 |
| | | 500 | 20.0 | 19.70 | 1.970 | 98.5 | 49.3 |
| | | 600 | 24.0 | 23.35 | 2.335 | 97.3 | 58.4 |
| | | 700 | 28.0 | 26.88 | 2.688 | 96.0 | 67.2 |
| | | 800 | 32.0 | 29.86 | 2.986 | 93.3 | 74.7 |
| | | 895 | 35.8 | 29.75 | 2.975 | 83.1 | 74.4 |
| 5.5 | 0.045 | 400 | 18.0 | 17.94 | 1.794 | 99.7 | 39.8 |
| | | 500 | 22.5 | 22.12 | 2.212 | 98.3 | 49.1 |
| | | 600 | 27.0 | 26.32 | 2.632 | 97.5 | 58.4 |
| | | 700 | 31.5 | 30.30 | 3.030 | 96.2 | 67.3 |
| | | 800 | 36.0 | 33.69 | 3.369 | 93.6 | 74.8 |
| | | 869 | 39.1 | 32.96 | 3.296 | 84.3 | 73.2 |

### 3.8. Effect of Cu(II) concentration for visual color change

The systematic studies on visual change in color at the column have been made with Cu(II) solution of different concentrations (0.05–6 $\mu g\,cm^{-3}$). A distinct color change from colorless to intense green was found for a metal content of 5–7 $\mu g\,mg^{-1}$ of dry exchanger.

### 3.9. Selection of stripping agents

The systematic studies on stripping behavior gave the quantitative elution of Cu(II) with $HNO_3$ and HCl of concentrations ≥0.1 M and with $CH_3COOH$ of concentration ≥0.5 M (Table 1). Column efficiency ($N$) for these eluents has been calculated [19] with respect to Cu(II) ($N_{H_2SO_4} = 334$; $N_{HNO_3} = 538$; $N_{HCl} = 285$; $N_{CH_3COOH} = 221$). During experiment it was found that 0.1 M $HNO_3$ gave the best stripping (least required volume, 10 $cm^{-3}$ and highest column efficiency, $N_{HNO_3} = 538$), hence it was used as stripping agent in the subsequent steps of experiments. Acetic acid dissociates weakly in aqueous solution and that is why it requires relatively higher concentration compared to the strong inorganic acids like HCl or $HNO_3$ for the quantitative elution of Cu(II). Moreover, low level of the mineral acids elute Cu(II) from the exchanger bed through the formation of nitro [34], $Cu(NO_3)^+$ and corresponding chloro cations.

### 3.10. Effect of pH, volume and concentration of influent on recovery and preconcentration factor

The extraction of Cu(II) (0.03–0.045 $mg\,cm^{-3}$) at the range of pH 4.5–5.5 showed that PF increases with increase in volume as expected (Table 2). However, at a particular volume it does not depend on either concentration or pH of the influent. Recovery decreased with increase in influent volume. Up to an influent volume of 800 $cm^{-3}$ recoveries were quantitative (>93.5 ± 0.2%). To reach the break-through values 33.6 $mg\,g^{-1}$(at pH 4.5), 35.8 $mg\,g^{-1}$(at pH 5.0) and 37.1 $mg\,g^{-1}$(at pH 5.5), respectively, 1120, 895 and 869 $cm^3$ of Cu(II) solution were passed through the column. Here, due to volume effect [20] recoveries were much poor (<85%) and PF did not attend its maximum possible values (112, 89.5 and 86.9 at 100% recovery) though it was optimized at a value of 74.7 ± 0.2. Plot of $V_s$ (sample volume) vs. $R_{Cu(II)}$ (recovery of Cu(II)) produces two linear segments ($y = -0.014X \pm 105.5$; $R^2 = 0.963$ and $-0.098X \pm 172.0$; $R^2 = 0.935$) intersecting at a volume of 800 $cm^3$ (Fig. 3). The slopes of the corresponding segments are the measures of desorption efficiency and yielded the desorption constants $K_{desorption}{}^1(1.4 \times 10^{-2})$ and $K_{desorption}{}^2(9.8 \times 10^{-2})$ respectively. After 800 $cm^3$ the rate of desorption is much higher and the recovery would become zero at an influent volume of 1755 $cm^3$ (extrapolated value). That is, at this very condition the influent solvent itself will act as an eluent.

**Table 3**
$R_f$ values and selectivity factors ($\alpha = (R_f)_i/(R_f)_{Cu(II)}$) of different metal ions on Whatman No 1 impregnated with Versatic 10; [time = 2.5 h; pH = 5.0].

| Cations | $R_f$ values | Affinity order (increasing) ↓ | Selectivity factor ($\alpha$) | Cations | $R_f$ values | Affinity order (increasing) ↓ | Selectivity factor ($\alpha$) |
|---|---|---|---|---|---|---|---|
| Ca(II) | 0.95 | Sn(II) | 2.31 | [b]Hg(II) | 0.18 | Cu(II) | |
| Mg(II) | 0.93 | Ca(II) | 2.26 | Cu(II) | 0.42 | Al(III) | [b]1.32 |
| Co(II) | 0.94 | Co(II) | 2.24 | [b]Al(III) | 0.32 | Ga(III) | [b]1.61 |
| Zn(II) | 0.92 | Mg(II) | 2.21 | [b]Ga(III) | 0.26 | Hg(II) | [b]2.33 |
| Cd(II) | 0.86 | Ni(II) | 2.19 | [b]Tl(III) | 0.08 | Bi(III) | [b]3.82 |
| Pb(II) | 0.55 | Zn(II) | 2.19 | [b]Bi(III) | 0.11 | Tl(III) | [b]5.25 |
| Sn(II) | 0.97 | Cr(III) | 2.14 | [a]Fe(III) | 0.41 | [a]Cu(II) | |
| Cr(III) | 0.90 | Cd(II) | 2.05 | [a]Cu(II) | 0.93 | [a]Fe(III) | 2.27 |
| Ni(II) | 0.92 | Pb(II) | 1.31 | [a]Zr(IV) | 0.06 | [a]Zr(IV) | 15.5 |

[a] pH = 2.5; developing solvent = acetate buffer:acetone (25:1), v/v.
[b] $=\alpha^{-1}$.

**Table 4**
Ratio $R_f$ values of Pb(II), Cu(II), Hg(II), Sn(II)and Pb(II), Cu(II), Bi(III), Cd(II) in acetate buffer at different pHs; Time = 2.5 h; Temp. = 25 °C.

| Metal ions | | pH | Distant travels (cm) | | $R_f$ values | Ratio of $R_f$ values |
|---|---|---|---|---|---|---|
| | | | Solute front | Solvent front | | |
| 1. | Sn(II) | 4.5 | 13.2; 9.4; 7.0; 3.2 | | 0.89; 0.63; 0.47; 0.22 | 4.04; 2.86; 2.47; 1 |
| | Pb(II) | 5.0 | 14.4; 8.2; 6.2; 2.6 | | 0.97; 0.55; 0.42; 0.17 | 5.71; 3.23; 2.47; 1 |
| | Cu(II) | 5.5 | 14; 7.2; 5.8; 2.8 | 14.8 | 0.94; 0.49; 0.39; 0.19 | 4.94; 2.58; 2.05; 1 |
| | Hg(II) | | | | | |
| 2. | Cd(II) | 4.5 | 12.6; 9.4; 7.0; 2.2 | | 0.90; 0.63; 0.47; 0.15 | 6.00; 4.20; 3.13; 1 |
| | Pb(II) | 5.0 | 12.8; 8.2; 6.2; 1.6 | | 0.91; 0.55; 0.42; 0.11 | 8.27; 5.00; 3.82; 1 |
| | Cu(II) | 5.5 | 12.4; 7.2; 5.8; 2.0 | 14 | 0.88; 0.49; 0.39; 0.13 | 6.77; 3.77; 3.0; 1 |
| | Bi(III) | | | | | |

### 3.11. Ion-exchange paper chromatography

At pH 5.0, the $R_f$ values and selectivity factors ($\alpha$) (ratio of the $R_f$ values) of metal ions were determined in acetate buffer-acetone mixture (15:2, v/v) on chromatogram (Table 3). Result shows that under this recommended condition Sn(II), Cr(III), Ca(II), Mg(II), Co(II), Zn(II), Cd(II) are very weakly bound ($R_f$ value ~0.9), metal ions like Pb(II), Al(III), Cu(II), Ga(III) are moderately bound ($R_f$ value 0.3–0.6) while Hg(II), Bi(III), Tl(III) is tightly bound ($R_f$ value <0.2) with the stationary phase. At pH 2.5, binding strength of Zr(IV) ($R_f$ value = 0.06) is very much higher than that of Fe(III) ($R_f$ value = 0.41) and under this condition, $[Cu(H_2O)_6]^{2+}$ [35] is very weakly bound ($R_f$ value = 0.93) with the stationary phase. At ~pH 5.0 Sn(II) exists as an anionic complex [36], $[Sn(CH_3COO)_3]^-$ and moves at the fastest rate with the mobile phase. Aqua Cr(III) is quite acidic ($pK_a = 4$) and at pH ~5.0 the hydroxo monomer

**Table 5**
Important binary separations of Cu(II); [flow-rate = 1.0 mL min$^{-1}$; pH = 5.0; Cu(II) = 10.6 μg; standard deviation <0.07].

| Cations | | Wt. of the cations (μg) | | Recovery (%) | Relative error (%) | Eluent Used | Eluent Vol. (mL) |
|---|---|---|---|---|---|---|---|
| | | Added | Recovered[a] | | | | |
| 1. | Mg(II) | 4020 | 4014 | 99.85 | −0.15 | Mobile Phase | 30 |
| | Cu(II) | 10.6 | 10.72 | 101.1 | 1.13 | 0.1 M $HNO_3$ | 10 |
| 2. | Ca(II) | 3768 | 3744 | 99.36 | −0.74 | Mobile Phase | 30 |
| | Cu(II) | 10.6 | 10.8 | 101.8 | 1.88 | 0.1 M $HNO_3$ | 10 |
| 3. | Cr(III) | 3848 | 3811 | 99.04 | −0.96 | Mobile Phase | 30 |
| | Cu(II) | 10.6 | 10.65 | 100.5 | 0.47 | 0.1 M $HNO_3$ | 10 |
| 4. | Cu(II) | 10.6 | 10.51 | 99.15 | −0.85 | Mobile Phase | 20 |
| | Fe(III)[b] | 3874 | 3896 | 100.6 | 0.57 | 0.5 M $H_2SO_4$ | 50 |
| 5. | Zn(II) | 3660 | 3602 | 98.41 | −1.58 | Mobile Phase | 30 |
| | Cu(II) | 10.6 | 10.66 | 100.6 | 0.57 | 0.1 M $HNO_3$ | 10 |
| 6. | Pb(II) | 3266 | 3318 | 101.6 | 1.59 | 0.5 M $CH_3COOH$ | 12 |
| | Cu(II) | 10.6 | 10.46 | 98.68 | −1.32 | 0.1 M $HNO_3$ | 10 |
| 7. | Cd(II) | 3540 | 3501 | 98.89 | −1.1 | Mobile Phase | 15 |
| | Cu(II) | 10.6 | 10.7 | 100.9 | 0.94 | 0.1 M $HNO_3$ | 10 |
| 8. | Cu(II) | 10.6 | 10.67 | 100.7 | 0.66 | 0.1 M $HNO_3$ | 10 |
| | Hg(II) | 3824 | 3798 | 99.32 | −0.68 | 0.3 M $H_2SO_4$ | 30 |
| 9. | Cu(II) | 10.6 | 10.51 | 99.15 | −0.85 | 0.1 M $HNO_3$ | 45 |
| | Bi(III) | 3242 | 3296 | 100.7 | 1.66 | 1 M HCl | 20 |
| 10. | Sn(II) | 3646 | 3614 | 99.12 | −0.88 | Mobile Phase | 30 |
| | Cu(II) | 10.6 | 10.73 | 101.2 | 1.23 | 0.1 M $HNO_3$ | 10 |
| 11. | Cu(II) | 10.6 | 10.74 | 101.3 | 1.32 | 0.1 M $HNO_3$ | 10 |
| | Al(III) | 3864 | 3828 | 98.07 | −0.93 | 1 M $CH_3COOH$ | 50 |
| 12. | Cu(II) | 10.6 | 10.71 | 101 | 1.04 | 1.2 M $CH_3COOH$ | 12 |
| | Ga(III) | 3577 | 3508 | 98.07 | −1.93 | 0.5 M $HNO_3$ | 40 |
| 13. | Cu(II) | 10.6 | 10.76 | 100.5 | 1.51 | 1.2 M $CH_3COOH$ | 12 |
| | In(III) | 4228 | 4189 | 99.07 | −0.92 | 2.5 M $CH_3COOH$ | 30 |
| 14. | Cu(II) | 10.6 | 10.49 | 98.96 | −1.04 | 0.1 M $HNO_3$ | 10 |
| | Tl(III) | 3000 | 3048 | 101.6 | 1.6 | 0.5 M HCl | 20 |
| 15. | Cu(II) | 10.6 | 10.44 | 98.49 | −1.51 | Mobile Phase | 20 |
| | Zr(IV)[b] | 3266 | 3288 | 100.7 | 0.66 | 6 M $HNO_3$ | 15 |
| 16. | Cu(II) | 10.6 | 10.77 | 101.7 | 1.6 | 0.1 M $HNO_3$ | 10 |
| | Ce(IV) | 4140 | 4101 | 99.06 | −0.94 | 0.4 M $H_2SO_4$ | 30 |
| 17. | Cu(II) | 10.6 | 10.78 | 101.7 | 1.69 | 0.1 M $HNO_3$ | 10 |
| | Th(IV) | 3976 | 3919 | 98.57 | −1.43 | 2 M $HNO_3$ | 25 |

[a] Average of five determinations.
[b] pH = 2.5

**Table 6**
Separation of Cu(II) from multi-component synthetic mixtures [column = 0.8 cm × 8 cm; flow-rate = 1.0 mL min$^{-1}$; Cu(II) taken = 10.6 μg; pH = 5.0; standard deviation <0.07].

| Metal ions | | Weight of the metal ions (μg) | | Recovery (%) | Relative error (%) | Eluent used | Eluent volume (mL) |
|---|---|---|---|---|---|---|---|
| | | Added | Recovered[a] | | | | |
| 1. | Fe(III)[b] | 3574 | 3608 | 100.95 | 0.95 | 0.5 M $H_2SO_4$ | 50 |
| | Co(II) | 3266 | 3233 | 98.99 | −1.01 | Mobile Phase | 30 |
| | Cu(II) | 10.60 | 10.78 | 101.7 | 1.69 | 0.1 M $HNO_3$ | 10 |
| | Tl(III) | 3224 | 3269 | 101.4 | 1.39 | 0.5 M HCl | 20 |
| 2. | Fe(III)[b] | 3574 | 3624 | 101.4 | 1.39 | 0.5 M $H_2SO_4$ | 50 |
| | Ni(II) | 4280 | 4206 | 98.27 | −1.73 | Mobile Phase | 30 |
| | Cu(II) | 10.60 | 10.76 | 101.5 | 1.51 | 0.1 M $HNO_3$ | 10 |
| | Tl(III) | 3804 | 3769 | 99.08 | −0.92 | 0.5 M HCl | 20 |
| 3. | Fe(III)[b] | 3574 | 3616 | 101.1 | 1.08 | 0.5 M $H_2SO_4$ | 50 |
| | Cd(II) | 3740 | 3682 | 98.75 | −1.27 | Mobile Phase | 15 |
| | Cu(II) | 10.60 | 10.72 | 101.1 | 1.13 | 0.1 M $HNO_3$ | 10 |
| | Tl(III) | 3804 | 3748 | 98.73 | −1.28 | 0.5 M HCl | 20 |
| 4. | Fe(III)[b] | 3574 | 3626 | 101.45 | 1.45 | 0.5 M $H_2SO_4$ | 50 |
| | Zn(II) | 3160 | 3118 | 98.67 | −1.33 | Mobile Phase | 30 |
| | Cu(II) | 10.60 | 10.44 | 98.49 | −1.51 | 0.1 M $HNO_3$ | 10 |
| | Hg(II) | 3744 | 3696 | 98.72 | −1.28 | 0.3 M $H_2SO_4$ | 30 |
| 5. | Fe(III)[b] | 3574 | 3618 | 101.23 | 1.23 | 0.5 M $H_2SO_4$ | 50 |
| | Cd(II) | 3350 | 3398 | 98.95 | −1.06 | Mobile Phase | 15 |
| | Cu(II) | 10.60 | 10.78 | 101.7 | 1.69 | 0.1 M $HNO_3$ | 10 |
| | Hg(II) | 2788 | 2758 | 98.92 | −1.08 | 0.3 M $H_2SO_4$ | 30 |
| 6. | Fe(III)[b] | 3574 | 3628 | 101.51 | 1.51 | 0.5 M $H_2SO_4$ | 50 |
| | Cr(III) | 3840 | 3886 | 101.19 | 1.19 | Mobile Phase | 30 |
| | Cu(II) | 10.60 | 10.52 | 99.24 | −0.75 | 0.1 M $HNO_3$ | 15 |
| | Hg(II) | 3826 | 3778 | 98.75 | −1.25 | 0.3 M $H_2SO_4$ | 30 |
| 7. | Sn(II) | 3834 | 3898 | 101.67 | 1.67 | Mobile Phase | 50 |
| | Pb (II) | 4764 | 4832 | 101.4 | −1.43 | 0.01 M $CH_3COOH$ | 12 |
| | Cu(II) | 10.6 | 10.79 | 101.7 | 1.79 | 1.5 M $CH_3COOH$ | 15 |
| | Hg(II) | 3000 | 2956 | 98.53 | −1.47 | 0.3 M $H_2SO_4$ | 30 |
| 8. | Cd(II) | 3860 | 3908 | 101.24 | 1.24 | Mobile Phase | 15 |
| | Pb(II) | 2844 | 2894 | 101.7 | 1.44 | 0.01 M $CH_3COOH$ | 12 |
| | Cu(II) | 10.6 | 10.42 | 98.3 | −1.69 | 0.1 M $HNO_3$ | 10 |
| | Bi(III) | 3006 | 2978 | 99.07 | −0.93 | 1 M HCl | 20 |

[a] Average of five determinations;
[b] pH = 2.5

$[Cr(OH)(H_2O)_5]^{2+}$ equilibrates with hydroxo dimmer, $[Cr_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ [37]. These different cationic species probably equilibrate with the exchange site and move at a slower rate in comparison to Sn(II). $K_A$ for Al(III), Ga(III), In(III) and Tl(III) respectively, are $10^{-5}$, $10^{-3}$, $10^{-4}$ and $10^{-1}$. The aqua ion, $[M(H_2O)_6]^{3+}$ protonate quickly the acetate ion and the conjugate base $[M(OH)(H_2O)_5]^{2+}$ is produced [39] with their formation order, $[Tl(OH)(H_2O)_5]^{2+} \gg [Ga(OH)(H_2O)_5]^{2+} > [Al(OH)(H_2O)_5]^{2+}$. These monomers quickly equilibrates with their corresponding dimmers [37], $[M_2(H_2O)_8(\mu\text{-}OH)_2]^{4+}$. It is suggested that these hydroxo species goes to the exchange site at the recommended pH. The most easily formed $[Tl(OH)(H_2O)_5]^{2+}$ binds preferably with the exchange site and its movement in the mobile phase is slowest, while $[Al(OH)(H_2O)_5]^{2+}$ with its lowest formation tendency moves at the fastest rate. Aqua ions of Zn(II), Cd(II) and Hg(II) are quite acidic and their corresponding hydroxo species, $[M(OH)(H_2O)_5]^{+}$ [37] equilibrated during the development of chromatogram. The increasing affinity order is directly related to decreasing order of their hydrated radii (Kielland [38]). At pH 2.5, Cu(II) is not present as $[Cu(CH_3COO)]^{+}$ [34] and does not participates in the exchange process. Under this recommended condition, aqua $[Fe(H_2O)_6]^{3+}$ gives μ-oxo dimmer, $[(H_2O)_5FeOFe(H_2O)_5]^{4+}$ [37], as the main species during its equilibration with stationary phase and moves moderately. While under this high acidic condition (low pH),

**Table 7**
Preconcentration, removal, recovery of Pb(II) and Cu(II) from industrial and alloy samples [pH = 5.0; flow-rate = 1.0 mL min$^{-1}$; column = 0.8 cm × 8 cm; sample volume = 800 mL; elution volume = 10 mL].

| Samples/composition | Separation of Pb(II) | | Separation of Cu(II) | |
|---|---|---|---|---|
| | Found (%) | [a]Recovery (%) | Found (%) | [a]Recovery (%) |
| Lead concentrates (42G)/<br>Pb(II) = 75.6<br>Cu(II) = 0.14 (in %) | 72.23<br>(SD = 0.35)<br>(P.F. = 76.4) | 95.54 | 0.126<br>(SD = 0.41)<br>(P.F. = 72.1) | 90.1 |
| Brass 5g/<br>Pb(II) = 2.23<br>Cu(II) = 67.4 (in %) | 2.11<br>(SD = 0.36)<br>(P.F. = 75.7) | 94.62 | 61.6<br>(SD = 0.34)<br>(P.F. = 73.1) | 91.39 |
| Electroplating waste/<br>Pb(II) = 11.2<br>Cu(II) = 10.0 (in mg dm$^{-3}$) | 10.4<br>(SD = 0.38)<br>(P.F. = 74.3) | 92.85 | 9.18<br>(SD = 0.33)<br>(P.F. = 73.5) | 91.8 |

[a] Average of five determinations.

**Table 8**
Determination of Pb (II) and Cd (II) in water samples [Cu(II) = 40.4 μg cm$^{-3}$; Cd(II) = 40.6 μg cm$^{-3}$; sample volume = 600 cm$^3$].

| Sample | Water | | | | |
|---|---|---|---|---|---|
| | Metal ion | Added (μg) | [a]Found (μg) | Recovery (%) | PF |
| Waste water | Cu(II) | – | 1020 | – | |
| | | 24,240 | 24,060 | 95.25 | 59.6 |
| | Cd (II) | – | ND | – | |
| | | 24,360 | 23,320 | 95.73 | |
| Thermal water | Cu(II) | – | 240 | – | |
| | | 24,240 | 23,722 | 96.9 | 59.2 |
| | Cd (II) | – | ND | – | |
| | | 24,360 | 23,389 | 96.01 | |
| Well water | Cu(II) | – | 840 | – | |
| | | 24,240 | 23,804 | 94.91 | 58.9 |
| | Cd(II) | – | ND | – | |
| | | 24,360 | 23,384 | 96 | |

[a] Average of five determinations.

zirconium(IV) exists as a tetramer [39], $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$. Having high charge density and suitable size the tetramer goes to exchange site quickly and moves at the slowest rate.

### 3.12. Effect of pH on selectivity factor

Systematic studies on selectivity factor at the pH range 4.5–5.5, gave the best separation efficiency at pH 5.0 for the congeners of Cu(II) (Table 4). This justifies the separation of congeners at this particular pH.

### 3.13. Separation of Cu(II) from binary mixtures

Cu(II) was separated from several metal ions in binary mixtures (Table 5). The separations were achieved either by exploiting the difference in pH for extraction or by using suitable stripping agent utilizing the $R_f$ values and selectivity factor, $\alpha$ [19]. Metal ions in binary mixtures were chosen having widely different selectivity factor ($\alpha > 1.31$) and $R_f$ values. When, Cu(II)–Fe(III) and Cu(II)–Zr(IV) binary mixtures were passed through the column at pH 2.5, only Cu(II) ($R_f > 0.93$) from the said mixtures was percolated through the column with the mobile phase. The quantitatively extracted Fe(III) and Zr(IV) were eluted with 0.5 M $H_2SO_4$ and 6 M $HNO_3$ respectively. The acid strength sequence is also expected from their affinity order (Table 3). Binary mixtures containing Cu(II) with Mg(II), Ca(II), Sn(II), Cr(III), Co(II), Ni(II), Zn(II) and Cd(II) when equilibrated with the exchanger at pH 5.0, the diverse ions ($R_f > 0.92$) passed through the column with the mobile phase. However, at pH 5.0, from the binary mixtures, the diverse ions like Pb(II), Bi(III), Al(III), Ga(III), In(III), Tl(III), Hg(II), Ce(IV) and Th(IV) are extracted along with Cu(II) owing to their comparable $R_f$ values (<0.7). From these respective mixtures, Cu(II) was separated by using different selective eluents.

### 3.14. Separation of Cu(II) from multi-component mixtures

In order to assess the possible analytical applications the proposed method was applied to separate Cu(II) from multi-component synthetic mixtures. These synthetic mixtures contain different metal ions commonly associated with Cu(II) in same analytical group, ores and alloy samples (Table 6). Separation of Cu(II) from diverse metal ions in binary and multi-component synthetic mixtures follows the $R_f$ values, Ketell [40] and Kielland principle [38]. The exchanger metal binding can be rationalized in terms of hardness values ($\eta$) of the metal ions. Here, except Hg(II), Cu(II) with its close hardness value ($\eta_{Cu} = 8.27$ eV) to the exchanger ($\eta$ exchanger = 6.03 eV) makes a fairly good complex than most of the other metal ions: $\eta$Cr(III) (9.10 eV), $\eta$Cd(II) (10.29 eV), $\eta$Sn(II) (7.49 eV), $\eta$Co(II) (8.22 eV), $\eta$Ni(II) (8.50 eV), $\eta$Pb(II) (8.46 eV), $\eta$Bi(III) (3.96 eV), $\eta$Hg(II) (7.70 eV). Symbiotic effect enhanced the global hardness of Bi(III) and forms a better complex [19] with the exchanger. [Co(II) and Ni(II)] in acetic acid are present as their anionic complexes [41]and passed through with the mobile phase.

At pH 5.0 when the synthetic mixture containing Pb(II), Cu(II), Sn(II) and Bi(III) was allowed to flow through the column, only Sn(II) passes as anion complex [36], $[Sn(CH_3COO)_3]^-$. Sequential elution of Pb(II), Cu(II) and Hg(II) have been made with 0.01 M $CH_3COOH$, 0.1 M $HNO_3$ and 0.3 M $H_2SO_4$ respectively. Synthetic mixture containing Pb(II), Cu(II), Cd(II) and Bi(III) when equilibrated with the exchanger at pH 5.0, except Cd(II) all the metal ions along with Cu(II) were quantitatively extracted at the column. Sequential elution of Pb(II), Cu(II) and Bi(III) has been made with 0.01 M $CH_3COOH$, 0.5 M $HNO_3$ and 1 M HCl respectively. For all other quaternary synthetic mixtures, metal ions are separated by a two step extraction process. At pH 2.5, from the solution only Fe(III) was extracted while other three ions percolate through the column. The effluent containing the three unextracted ions was again equilibrated with the exchanger at pH 5.0 and separated from each other with selective eluents (Table 5).

### 3.15. Effectiveness and utility of the proposed method

The effectiveness of the proposed method was judged by separating Cu(II) from some standard alloy samples. The feasibility of the process was tested with the effluent obtained from a typical electroplating industry. High degree of preconcentration (800 mL to 10 mL) (>70 fold) with subsequent removal, or recovery (>90%) of Cu(II) and the associated metals with low standard deviation (<0.4) for industrial and standard alloy samples were obtained (Table 7). Separation of Cu(II) and Cd(II) in water (waste, thermal and tap water) samples were performed by applying the proposed method (PF: 59.1 ± 0.3) (Table 8). The amounts of recovered Cu(II) were equated with the average recovery of 97.1 for a sample volume of 600 cm$^3$ (Table 2) and the projected concentrations were calculated to have an idea about the concentrations of the mother samples. The calculated values were highly

**Table 9**
Comparison of the observed conc.(AAS) with the preconcentration technique.

| Sample | Conc. (AAS) | Conc. (predicted) | Relative error (%) |
|---|---|---|---|
| Waste water | 42.10 | 41.30 | 1.9 |
| Thermal water | 40.80 | 41.02 | 0.54 |
| Well water | 41.80 | 40.86 | 2.25 |

compatible with observed values obtained by AAS (relative error <2.5%) (Table 9). In comparison to other matrices (except very few [42,45]) such as Poly(HEMA)-Cibacron Blue F3-GA (PF: 63) [14], XAD-1180-SA (PF: 150) [42], XAD-2-Quinalizarin (PF: 100) [43], XAD-2-o Aminophenol (PF: 50) [44], XAD-2-Triton (PF: 200) [45], Silica gel-N-(3-propyl)-o-phenylenediamine (PF: 100) [46], Merrrifield resin-calix [4]arene-o-vanillinthiosemicarbazone (PF: 100) [47], the present exchanger, Versatic 10-Silanised Silica Gel has got very good value of preconcentration factor ($74.7 \pm 0.2$). After removal, recovery from effluent and alloy samples, Cu(II), Cd(II) and Pb(II) were determined by Ion selective electrode.

## 4. Conclusions

The proposed method is simple, cost effective, rapid and selective and needs only 2.5 h for complete work involving separation and estimation of Cu(II). Clean separation of Cu(II) has been achieved from several toxic and heavy metal ions like Pb(II), Fe(III), Cr(III), Zn(II), Cd(II), Hg(II), Tl(III), Zr(IV), Ce(IV), and Th(IV) having very high $\alpha$ ($\geq$1.31) values. The separation of Cu(II) from these toxic, heavy and congener metals has great importance to the environmental and analytical chemists. The method was found selective at the optimized conditions for Cu(II) and does not need separation of other constituents present in the matrix. Very minute amount (~0.2 mL) of liquid extractant in the developed exchanger can selectively separate Cu(II) from these wide variety of multicomponent mixtures containing large number of heavy, toxic and conger cations (Table 5). The method was also found effective for the selective detection of Cu(II) at microgram level in presence of other similarly behaving heavy and toxic metal ions like Pb(II), Fe(III), Cr(III), Zn(II), Cd(II), Hg(II), Tl(III), Zr(IV), Ce(IV), and Th(IV) as they gave no visual change in color during their adsorption at the column. The developed exchanger is chemically stable (up to 6 M $HNO_3$, 4 M $CH_3COOH$, 4 M HCl and 2 M $H_2SO_4$) and effective over a wide range of pH. It can be used for more than 30–40 cycles without any loss in its exchange capacity.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.06.083.

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