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Factorial design for optimization of experimental variables in preconcentration of copper by a chromotropic acid loaded Q-Sepharose adsorbent

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Abstract

An agarose-based anion exchanger (Q-Sepharose) was loaded with chromotropic acid (CTA) and used for column preconcentration and determination of copper by flame AAS. Preliminary experiments indicated that a sample pH of 5.7–6.5 is best suited for accumulation of copper and a 2.5 ml portion of a $0.02\,\mathrm{mol\,l^{-1}}$ HCl solution can efficiently desorb the analyte from the column. An incomplete factorial design was used for optimization of five different variables that affect recovery of copper. The results indicated that ionic strength, pH and sample volume variables are the most important effects, respectively. Hence, these variables and their possible interactions were studied more carefully. In optimized conditions, the column could tolerate up to $0.18\,\mathrm{mol\,l^{-1}}$ sodium nitrate in the matrix. A 5 ml portion of a $0.02\,\mathrm{mol\,l^{-1}}$ CTA was sufficient for loading of a 0.5 ml column prior to preconcentration of copper from a 150 ml sample solution. Matrix ions of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} and potentially interfering ions of Pb^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+} and Mn^{2+} with relatively high concentrations did not have any significant effect on the recovery of the analyte. A preconcentration factor of 60 and a detection limit of $1.0\,\mu\mathrm{g\,l^{-1}}$ was obtained for the determination of copper by the flame AAS method. A precision better than 2.5%, expressed as R.S.D., was also achieved. Application of the method to tap water and two different river water samples resulted in values well confirmed by direct determinations with ET-AAS.

Keywords: Copper; Chromotropic acid; Q-Sepharose; Preconcentration; Factorial design; Flame AAS

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1. Introduction

Column preconcentration techniques are among the most widely used methods for sensitivity enhancement and matrix separation prior to the determination of heavy metals [1–6]. This is because of their ease of use, the possibility of automation, less sample handling and usually high selectivities observed for them. The determination of heavy metals, particularly metals such as copper that play important roles in biological mechanisms, has been receiving much attention. Problems of a technical or esthetic nature, as well as health effects, especially for bottle-fed children, have been encountered for high copper concentrations [7].

One of the problems with such column preconcentration techniques has been optimization of the several factors that affect a column extraction procedure. In most cases, a classical one-at-a-time method is applied, which may result in wrong conclusions if there are interactions between different factors. On the other hand, use of a method such as factorial design can reduce the number of experiments or provide much more information about the effect of different variables. The interest in the use of such optimization methods has substantially increased in recent years [8–11].

Chromotropic acid (CTA), with the chemical name of 4,5-dihyroxy-2,7-naphtalenedisulfonic acid, is a phenolic compound with the ability to act as a bidentate ligand with the tendency to make complexes with "hard" metals [12]. The two sulfonic groups of CTA dissociate in aqueous solutions to make the molecule as a doubly charged anion.

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CTA is a known spectrophotometric reagent for the determination of nitrate in water [13]. It has been also used for colorimetric determination of formaldehyde in air [14]; separation of Sr^{3+}, Zn^{2+} and Fe^{3+} on a filter paper [15]; determination of Ni^{2+}, Cu^{2+}, Cd^{2+} [16] and Al^{3+} [17] in fluorescence spectroscopy. CTA has been also used in column preconcentration techniques [18–20]. Tewari and Singh reported the use of Amberlite XAD-2 [18] and Amberlite XAD-7 [19] functionalized with CTA for the preconcentration of some metal ions including Cu^{2+}. They covalently linked CTA with the support of an azo spacer. Shao et al. [20] reported the preconcentration of boron on an anion exchanger loaded by CTA before its determination by a spectrophotometric method. The anion exchanger they used was, however, an ordinary ion chromatography packing, with 10 μm particle sizes, which limited the sample flow rate to 0.65 ml min^{-1}.

In previous works [3,21,22] we reported the use of a highly cross-linked agarose (Novarose) as a promising column packing for the preconcentration of metal ions. High sample flow rates were tolerated by an iminodiacetate-Novarose column with still quantitative recoveries [21]. Q-Sepharose is an agarose-based anion exchanger with ternary ammonium groups that shows slightly higher back pressures than Novarose. Recently, we reported the successful use of Q-Sepharose in a dual column system for the speciation of chromium and selective accumulation of Cr(VI) [22].

The aim of this study is the modification of Q-Sepharose with a CTA chelating agent and the application of the modified adsorbent for preconcentration of Cu^{2+}. Modification of an ion exchange column by immobilization of a chelating ligand has the advantage that the column can be used for other ordinary uses as well. Copper is studied here as a representative heavy metal. Since the recovery of the metal ion in the column preconcentration system can depend on a variety of factors whose relative importance are unknown, a fractional factorial design is applied in order to identify the effects of different variables on the recovery of copper and finding out possible interactions between the main factors.

2. Experimental

2.1. Apparatus

A flame atomic absorption spectrometer (Shimadzu AA-670, Japan) employing an air–acetylene flame was used for determination of copper and other elements under the manufacturer's recommended conditions. An ET-AAS (Shimadzu AA6650, Japan) with a deuterium lamp background correction was used for direct determinations of copper in natural water samples. Hollow-cathode lamps were employed as radiation sources. For pH determinations, a Jeneway model 3020 pH meter with a combined glass electrode was used after calibration against standard Merck buffers. Preconcentration columns were polypropylen tubes (Duran, USA) with 6 mm i.d. and two end frits for holding the adsorbent. A peristaltic pump (EYLA, Japan) was used for pumping the solutions through columns.

2.2. Chemicals and reagents

CTA and all other chemicals and reagents were of analytical reagent grade (Merck, Germany) and used as received. Doubly distilled water, prepared by a totally glass Fision (UK) double distiller, was used for all the dilutions. The Q-Sepharose anion exchanger with 40–60 μm particle size was a gift from Pharmacia Bioteck AB (Stockholm, Sweden).

2.3. Methods

Stock Cu^{2+} solution (1000 mg l^{-1}) was prepared by dissolving appropriate amounts of its sulfate salt in 10 ml of concentrated hydrochloride acid, diluted to 250 ml by water and stored in a plastic bottle. Standard and test copper solutions were prepared by dilution of the stock with water. Test solutions were usually buffered with a 0.01 mol l^{-1} acetic acid/ammonium acetate buffer and pH adjusted with dropwise addition of HCl (0.1 mol l^{-1}) or NaOH (0.1mol l^{-1}) solutions.

For the packing of columns, a suspension of the adsorbent particles was pipetted into an empty column with a frit at the bottom. A gentle vacuum was applied for faster settling of the particles before mounting the top frit. The column was then cleaned with some 10–15 ml of 1.0 mol l^{-1} HCl to remove any impurities, followed by the passage of the same volume of water and a 0.1 mol l^{-1} acetate buffer.

Column pretreatment, before each preconcentration experiment, was made by the passage of the following solutions: first, 2 ml of 5 mmol l^{-1} sodium hydroxide in order to transform the anion exchanger support to the –OH form, then 20 ml distilled water to displace excess amounts of the base, and finally, 5 ml of a 0.02 mol l^{-1} CTA solution for immobilization (unless otherwise stated).

Preconcentration and recovery experiments were usually performed by pumping a 5 ml 0.01 mol l^{-1} acetate buffer followed by a buffered test solution through a pretreated 0.5 ml column. The column was then washed with a few ml of a 0.01 mol l^{-1} acetate buffer and eluted by 5 ml 0.05 mol l^{-1} hydrochloric acid (unless otherwise stated). The eluate was collected in small capped vessels and analyzed by flame AAS against matched standards.

All field samples were acidified to pH 2.0 on collection and filtered to remove any particulate matter. These samples were pH adjusted immediately before preconcentration and treated with essentially the same method as test samples. The enriched volume was 150 ml in this case.

2.4. The fractional factorial design test and response surfaces

For performing the factorial design test, five parameters were chosen as variables and tested at two levels. The

Table 1
The factors included in the fractional factorial design

Symbol	Parameter	Low (−)	High (+)	Unit
A	pH	5.0	6.0	–
B	Ionic strength	0.01	0.1	mol l^{-1}
C	Sample volume	30	100	ml
D	CTA concentration	0.025	0.25	mmol l^{-1}
E	Column length	5	10	mm

parameters were pH, ionic strength, sample volume, CTA concentration and column length. The high and low levels defined for them are listed in Table 1.

For five variables with two levels for each variable, there are 2^5 or 32 possible combinations in a full factorial design. An incomplete design allows one to select an effective sample from the total experiments by a procedure based on the advantages of randomized testing and balancing of two-factor interactions [8]. In this case, we selected $2^{5-1} = 16$ experiments using the computer program Statgraphics [23]. We also added three center points in order to have an estimate of the experimental error. Table 2 shows the design matrix for the total 19 experiments. An analysis of variance (ANOVA) test was used in order to identify the effect of individual factors and their second-order interactions. Higher order interactions were assumed to be negligible in the half fraction design applied. The recovery was defined as the dependent variable and the five selected factors as independent variables in this test.

The response surfaces and related contour diagrams were calculated by performing a user-specified design for two experimental factors using the Statgraphics program.

3. Results and discussion

In preliminary experiments, CTA was added to a buffered solution of Cu^{2+} and, after some 10 min, the solution was enriched on a 0.5 ml column packed with Q-Sepharose. It was expected that the column would retain the Cu–CTA negatively charged complexes formed in the solution, but the results did not confirm this. A very poor reproducibility and usually low recoveries were obtained. Different sample pH and CTA to Cu^{2+} mole ratios (up to 1000) also were tested. Only in a high pH of 12.0 a quantitative recovery was achieved. At this pH, however, there is a high risk of Cu^{2+} hydrolysis and a precipitate was collected on the top frit of the column.

A much better reproducibility of the results and quantitative recoveries in reasonably lower pHs was achieved by converting the column to its –OH form before its modification with the ligand. It was also found that addition of CTA to the sample before its enrichment on the modified column does not improve the recovery of Cu^{2+} significantly. It was, however, essential to reload the column with CTA before the enrichment of each sample. This may be explained by the fact that the loaded ligand on the column is partially washed out and replaced by the anions present in the sample or eluent solutions.

3.1. *Effect of pH on the recovery*

Because of the high dependency of the analyte recovery on pH, the effect of this factor was studied separately, keeping other variables constant. Column recoveries of Cu^{2+} in a pH range of 2.8–7.3 are shown in Fig. 1. Triplicate measurements

Table 2
Incomplete fractional factorial experimental design matrix[a]

Factors combination	pH	Ionic strength (mol l^{-1})	Sample volume (ml)	CTA concentration (mmol l^{-1})	Column length (mm)	Cu^{2+} recovery (%)
A	6	0.01	30	0.025	5	103.6
B	5	0.1	30	0. 25	5	10.6
C	5	0.01	100	0.025	5	55.2
D	5	0.01	30	0.025	5	81.5
E	5	0.01	30	0.025	10	52.5
ABE	6	0.1	30	0.025	10	83.6
ADE	6	0.01	30	0.25	10	102.4
BCE	5	0.1	100	0.25	10	1.9
BDE	5	0.1	30	0.25	10	7.6
CDE	5	0.01	100	0.25	10	55.9
ABC	5	0.1	100	0.025	5	14.8
ABD	6	0.1	30	0.25	5	61.4
ACD	6	0.01	100	0.25	5	91.7
ACE	6	0.01	100	0.025	10	71.4
BCD	5	0.1	100	0.25	5	2.9
ABCDE	6	0.1	100	0.25	10	52.4
Center point 1	5.5	0.055	65	0.138	7.5	197.6
Center point 2	5.5	0.055	65	0.138	7.5	103.3
Center point 3	5.5	0.055	65	0.138	7.5	101.3

[a] The factors and combinations listed in this table are not in the order performed.

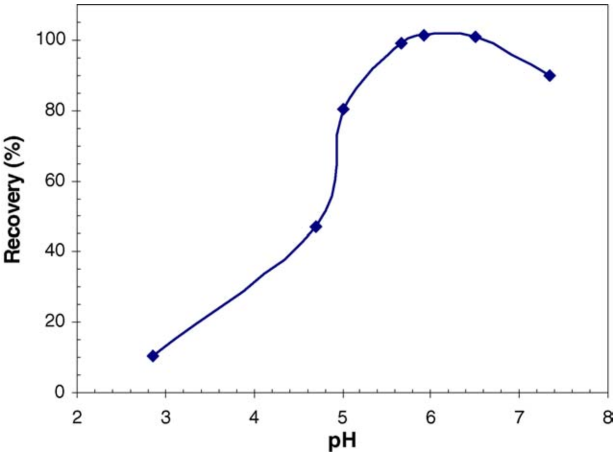

Fig. 1. Effect of pH on the recovery of Cu^{2+} on a 0.5 ml Q-Sepharose column. CTA concentration, 0.02 mol l^{-1} (5 ml); Cu^{2+} concentration, 0.5 mg l^{-1}; sample volume, 40 ml; acetate buffer concentration, 0.01 mol l^{-1}; flow rate, 2.5 ml min^{-1}; eluent, 10 ml HCl (1.0 mol l^{-1}).

for each point indicated that a quantitative recovery of Cu^{2+} is obtained over a pH range of 5.7–6.5. The R.S.D. of the results for each point also was generally less than 2%.

3.2. Effect of type, volume and concentration of the eluent

Since desorption of copper from the column does not have any effect on the extraction efficiency of the analyte on the column, it was decided to ensure complete elution of the analyte from the column before doing further optimization. Using various volumes and concentrations of HCl, a 2.5 ml portion of hydrochloric acid with a minimum concentration of 0.02 mol l^{-1} was found to be satisfactory for a quantitative elution. Table 3 compares desorption of the analyte by different eluents. The results indicate that strong acids can efficiently elute copper from the column, but the recovery is not quantitative when a weak acid is used. The use of hydrochloric acid was continued due to its less oxidizing effects on the adsorbent.

3.3. Optimization with the incomplete factorial method

The relative importance and possibility of interactions between pH, ionic strength, sample volume, CTA concentration and column length factors were studied using the fractional factorial design method. The low and high levels for the factors were selected according to our previous experiences and some preliminary tests. Despite of the individual study of the effect of pH (see Fig. 1), this factor was included in the test to study its possible interactions with other factors. On the other hand, the sample flow rate was omitted, because some flow instabilities at low flow rates and increasing column back pressures at high flow rates were encountered.

Table 3
Effect of eluent type on the recovery of copper[a]

Eluent	H_2SO_4	$HClO_4$	H_3PO_4	CH_3COOH	HNO_3	HCl
Recovery (%)	101.1	101.3	96.1	73.2	100.7	100.0
s (*n* = 3)	1.8	1.2	1.4	2.4	0.7	1.3

[a] Sample volume, 30 ml; sample pH, 6.5; eluent volume, 2.5 ml, eluent concentration, 0.01 mol l^{-1}; other conditions are as in Fig. 1.

Table 4
Results of the ANOVA test for recovery

Factors combination	Sum of squares	d.f.[a]	Mean square	*F*-ratio	*p*[b]
A	6396.27	1	6396.27	4.45	0.1027
B	934821	1	934821	6.50	0.0634
C	1558.31	1	1558.31	1.08	0.3568
D	238.19	1	238.19	0.17	0.7049
E	1.41	1	1.41	0.00	0.9765
AB	262.01	1	262.01	0.18	0.6915
AC	445.13	1	445.13	0.31	0.6077
AD	1.76	1	1.76	0.00	0.9738
AE	307.36	1	307.36	0.21	0.6680
BC	46.77	1	46.77	0.03	0.8657
BD	74.78	1	74.78	0.05	0.8308
BE	741.02	1	741.02	0.52	0.5126
CD	199.88	1	199.88	0.14	0.7283
CE	46.15	1	46.15	0.03	0.8666
DE	119.18	1	119.18	0.08	0.7878
Total error	5755.18	4	1438.80		

[a] d.f.: degrees of freedom.
[b] *p*: probability for *F*-ratio test.

The 19 runs were performed in randomized order. The lowest recovery was obtained for a BCE combination of factors (high levels of ionic strength, sample volume and column length). Quantitative recoveries were obtained for ADE, A and the center point experiments (see Table 2). Table 4 and Fig. 2 show the results of the ANOVA test performed by the Statgraphics program.

The ANOVA table tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. The *R*-squared statistic indicates that the model as fitted explains 77.08% of the variability in recovery. The standard error of the estimate shows the standard deviation of the residuals to be 37.93. The mean absolute

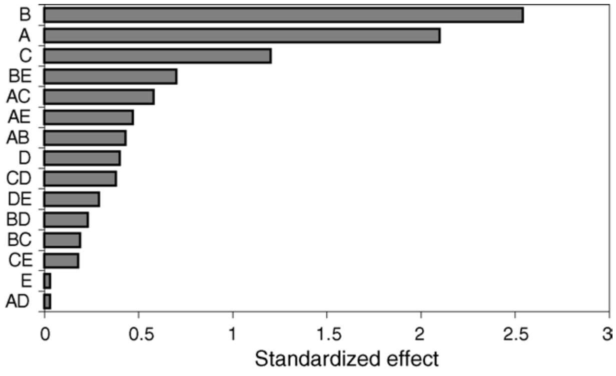

Fig. 2. Standardized Pareto chart for recovery.

error or the average value of the residuals also is 12.16, as calculated by the program.

None of the studied effects have *p*-values less than 0.05, indicating that they are not significant at a 95.0% confidence level. However, the Pareto chart (Fig. 2) indicates that the most important effects are the effects of the individual factors of ionic strength (B), pH (A) and sample volume (C). Therefore, it was decided to study these factors and their interactions more carefully.

3.4. *Effect of ionic strength and its interaction with pH*

The results of the factorial design and the ANOVA test indicates that ionic strength has the most considerable effect on recovery. The effect of this factor is significant in a 90% confidence level (see Table 4). This can be explained by the fact that the column is an anion exchanger, and any kind of anion in large quantities can compete with the Cu(II)–CTA complexes for the column active sites. Optimization of recovery with respect to ionic strength and pH (the second most important factor) was carried out with a designed response surface experiment. Thirteen experiments were performed at three different pHs of 5.5, 6.0 and 6.5 for estimation of the response surface. Fig. 3 indicates the contour diagram of the estimated response surface. The figure clearly indicates the significance of ionic strength and it interaction with pH. In a higher pH, larger salt concentrations can be tolerated, up to 0.18 mol l^{-1} at pH 6.5. This may be explained by the fact that at a higher pH, Cu^{2+} is partially hydrolyzed and converted to $Cu(OH)^+$ or $Cu(OH)_2$. Therefore, Cu(II)–CTA complex will become more negatively charged and more strongly retained by the anion exchanger column.

3.5. *Effect of sample volume and its interaction with pH*

According to the ANOVA table (Table 4), the enrichment sample volume (factor C) is the third important factor. The effect of this factor is not shown to be significant at a high (>90%) confidence level, but, for the achievement of large preconcentration factors, testing large sample volumes would be valuable. Since there was some risk of interaction between sample volume and pH, 14 experiments were performed at 3 different pH levels for optimization of recovery and estimation of the corresponding response surface. Fig. 4 indicates the contour diagram of the estimated response surface. The figure clearly indicates the significance of enrichment volume at high levels and its interaction with pH. In a higher pH, larger sample volumes can be tolerated, up to 150 ml at pH 6.5. The same explanation as above (see Section 3.4) may be given here for the effect of pH.

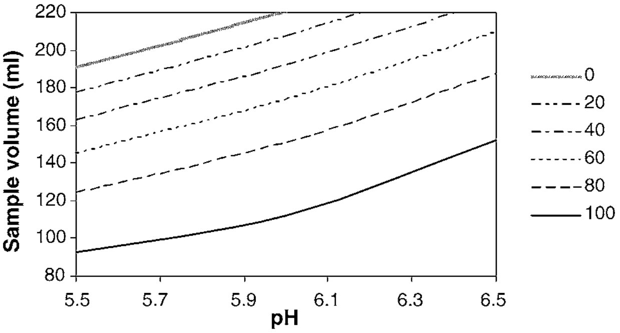

Fig. 4. Contours of estimated response surface for recovery of copper. Column length, 12 mm; sample volume, 30 ml; eluent, 5 ml HCl (0.05 mol l^{-1}); other conditions are as in Fig. 1.

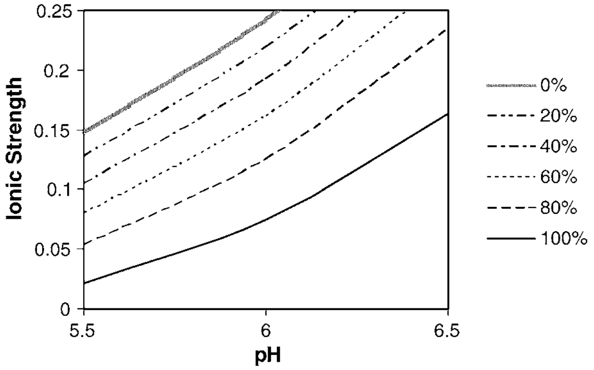

Fig. 3. Contours of estimated response surface for recovery of copper. Column length, 12 mm; sample volume, 30 ml; eluent, 5 ml HCl (0.05 mol l^{-1}); other conditions are as in Fig. 1.

3.6. *Effect of CTA concentration*

The ANOVA table indicates that the CTA concentration (in the range used) has little effect on the recovery. The effect of this factor, however, was studied here in order to find out the minimum amount of ligand that can be loaded on the column for a quantitative recovery. The pH 6.5 was used because of its positive effects on the factors A and C (see Figs. 3 and 4).

Fig. 5 indicates the effect of the amount of CTA ligand loaded on the column before the sample enrichment on recovery. According to the results, a minimum loading value of 0.07 mmol CTA (or 5 ml of 0.014 mol l^{-1} solution) would be sufficient. Since the sample volume used here was 50 ml, a

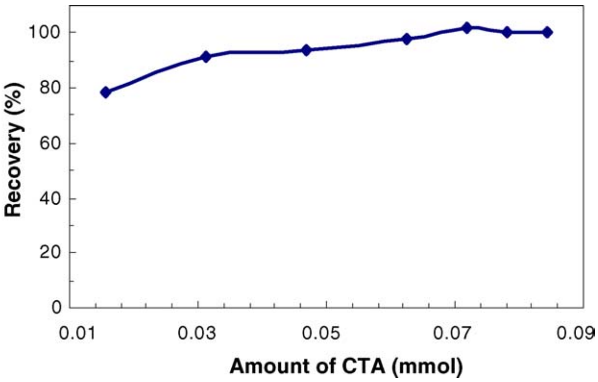

Fig. 5. Effect of CTA amount on the recovery of Cu^{2+} at pH 6. Column length, 12 mm; sample volume, 50 ml; eluent, 5 ml HCl (0.05 mol l^{-1}); other conditions are as in Fig. 1.

Table 5
Effect of some matrix ions on the recovery of Cu^{2+}

Matrix ion	Ion concentration[a] ($mg\,l^{-1}$)	Matrix ion/Cu^{2+} mol ratio	Cu^{2+} recovery (%)	S[b]	Salt used
Ca^{2+}	2000	2523	101.6	1.1	$CaCl_2$
Mg^{2+}	2000	1530	99.3	3.3	$MgNO_3$
Na^+	4140	2997	101.9	1.8	$NaNO_3$
K^+	2000	2462	99.3	1.8	CH_3COOK
Cd^{2+}	25	88.5	101.9	2.3	$Cd(NO_3)_3$
Pb^{2+}	25	16.3	99.4	1.1	$Pb(NO_3)_2$
Ni^{2+}	25	46.2	100.0	2.1	$Ni(OAC)_2$
Co^{2+}	25	46.4	101.0	1.8	$Co(NO_3)_2$
Mn^{2+}	25	43.2	98.0	3.1	$MnSO_4$
Zn^{2+}	25	51.4	100.1	2.2	$ZnSO_4$

Column length, 12 mm; sample volume, 50 ml; sample pH, 6.5; eluent, 5 ml HCl (0.05 mol l^{-1}); other conditions are as in Fig. 1.

[a] The ion concentrations are the maximum concentrations used.

[b] Standard deviation of recovery for three replicated experiments.

slightly higher amount of CTA (say 0.1 mmol) will be desirable, especially when larger sample sizes are applied.

3.7. Analytical performance

The preconcentration procedure for trace metals can be strongly affected by other constituents that are naturally present in a sample. For this reason, the reliability of the proposed method was examined in the presence of possible interfering ions. The interfering elements were added to some model samples as nitrate, chloride, sulfate and acetate salts. Table 5 shows the effect of some interfering ions on the recovery of Cu^{2+} on the column. As the results show, in no case was a significant effect on the recovery observed. It should be mentioned that the ion concentrations in the table are the maximum concentrations tested. Hence, this method may tolerate higher concentrations of the diverse ions.

For a sample volume of 150 ml and a preconcentration factor of 60, a detection limit of 1.0 $\mu g\,l^{-1}$ was obtained for measurement with flame AAS. By the use of more sensitive techniques such as ICP-AES or ET-AAS, much lower detection limits can certainly be obtained. A precision better than 2.5%, expressed as a relative standard deviation, was also achieved for six replicated analyses of a 0.5 $mg\,l^{-1}$ Cu^{2+} sample. A single column could be used in this work for more than 6 months, performing about 400 enrichment-elution-regeneration cycles, without observing significant change in its properties.

3.8. Application for real samples

The proposed method was applied to the determination of copper in tap water of Khorram Abad and two river water samples from Abadan and Sarab Robat (located in southwestern of Iran). A volume of 150 ml of the water samples were enriched on the column at pH 6.5. The results are listed in Table 6. As the table shows, a good agreement exists between the results of the proposed method and those reported by ET-AAS at the Lorestan University, Analytical chemistry laboratory in Khorram Abad, Iran.

Table 6
Application of the modified Q-Sepharose column to the preconcentration of Cu^{2+} in some water samples[a]

Water sample	Measured value ($\mu g\,l^{-1}$ Cu^{2+})	Reference value[b] ($\mu g\,l^{-1}$ Cu^{2+})
Khorram Abad tap water (April 2004)	2.93 ± 0.30	3.36 ± 0.5
Abadan river water (February 2004)	95.3 ± 0.2	98.1 ± 0.7
Sarab Robat river water (May 2004)	22.5 ± 0.7	23.4 ± 0.4

[a] Column length, 12 mm; sample volume, 150 ml; eluent, 5 ml HCl (0.05 mol l^{-1}); other conditions are as in Fig. 1.

[b] Measured directly by ET-AAS.

4. Conclusions

The incomplete factorial method is a very useful tool for experimental design in preconcentration and separation systems. Doing some preliminary experiments is essential for the correct selection of the high and low levels of the studied factors. The design can show the relative importance of the variables and interactions between different factors. The most important factors, and their possible interactions with other factors, should be studied in a wider range and more carefully. The purpose of optimization in such preconcentration systems is usually to find a surface, rather than a top point, of the quantitative recovery. Here, a maximum response (quantitative recovery) may be obtained easily, but the question is the extent of tolerance of changing different variables by the system. The study indicated that in optimized conditions (pH 6.5, column length 12 mm, sample flow rate 2.5 $ml\,min^{-1}$, CTA loading 0.1 mmol) the CTA–Q-Sepharose column can tolerate ionic strengths up to 0.18 $mol\,l^{-1}$, sample volumes up to 150 ml, and relatively high concentrations of matrix ions.

This study also established the applicability of Q-Sepharose in preconcentration systems as a promising support for the fast and reproducible loading of anionic chelating agents. CTA is easily loaded on the column, and the modified column can efficiently and selectively be used for preconcentration of Cu^{2+} and probably some other heavy metals in water. The loaded CTA on the anion exchanger can be washed out by an acid. Hence, the column can be used for other purposes as well.

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