Preconcentration of Copper in Tap and Sea Water by Use of Chromotrope-2R Immobilized on an Anionic Resin

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PRECONCENTRATION OF COPPER IN TAP AND SEA WATER BY USE OF CHROMOTROPE-2R IMMOBILIZED ON AN ANIONIC RESIN

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The retention of copper on a novel chelating ion-exchange resin (Chromotrope—2R immobilized on Amberlite IRA-400 resin) was investigated with a view to its use for the atomic spectrometric determination of the metal ion in tap and sea waters. The resin proved to have good kinetic properties for retention of copper at water flow rates up to 13.5 ml/min. The effect of various ions on the retention of copper was also studied. The chelating resin was used for the quantitative separation of copper from cobalt, nickel, zinc, calcium, magnesium and cadmium. The proposed method allows the determination of copper in tap and sea water at concentration ranges of 2–200 and 2–10 μg/l, respectively.

KEY WORDS: Chelating resin, Chromotrope-2R, copper, tap water, sea water, atomic absorption spectrometry, graphite furnace.

INTRODUCTION

The metal ion contents of natural waters such as sea water vary markedly between those of major ions (Ca, Mg, Na and K) and minor ions such as copper. This, notwithstanding to occur at trace levels and the fact it is essential to mammals, may have toxic effects on mammals at concentrations above 100 μg/ml. On the other hand, a low concentration such as 5 μg/ml is exceedingly toxic for marine ecosystems (biota)[1]. Such a high toxicity and the rather complex matrices where it occurs, make the determination of copper quite delicate at best. One way of determining copper in this context involves using highly sensitive and selective techniques such as electron activation, isotopic dilution mass spectrometry, graphite-furnace atomic absorption spectroscopy, etc.; alternatively, one can use some particular preconcentration, separation and determination procedures.

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Until recently, solvent-extraction techniques were among the most commonly used for the preconcentration of metal ions prior to their determination. However, inasmuch as they are typically used under static conditions, they are of little application when the sample is diluted in rather a large volume. The use of various types of adsorbents for concentration and/or separation of metal ions has gained increasing popularity in the last few years on account of the high concentration factors they provide. The supports used for this purpose include active carbon,[2] alumina,[3] cationic resins,[4–6] complex-forming resins[7–9] and even chelating agents immobilized on various supports such as silica gel,[10–13] cellulose[14] or ion-exchange resins.[15–23] The complex-forming agents used in this context are also quite varied in nature; the more common are organic substances containing aromatic rings, most of which bear ionic functions, particularly sulphonic groups.[17–21]

On the other hand, metal ions preconcentrated in the above-mentioned types of resins can be determined by using a variety of complexometric,[12] densitometric,[24,25] and atomic absorption spectroscopic (either electroatomization[7,20,21] or flame-atomization[7,9,11,14,15,19,21–23]) methods. The last alternative in its flame-atomization variant is the most frequently used.

However, the determination of Cu(II) is very often interfered by the presence of Ni(II) and Co(II), from which it must be separated. In this paper we investigate the retention of copper, cobalt and nickel by Amberlite IRA-400 resin modified with Chromotrope-2R (CTR) and develop a method for the preconcentration of copper and its separation from potentially interfering ions such as Co(II), Ni(II), Zn(II) and Cd(II), as well as from major components of water such as Ca(II) and Mg(II). The proposed method was applied to the determination of Cu(II) in tap and sea water.

EXPERIMENTAL

Reagents

The Chromotrope-2R modified chelating resin used and its synthesis were described elsewhere.[26]

Standard solutions of the metal ions assayed containing *ca.* 1000 mg/l of each were prepared by dissolving the required amounts of their nitrates in de-ionized water and acidifying the solutions with nitric acid. Their concentrations were checked by AAS using certified standard solutions (1000 mg/l, Fisher). Stock solutions were made by dilution of these standards as required.

Buffers encompassing the pH range 4.0–6.5 were prepared from 0.5 M sodium acetate that was adjusted to the required pH with acetic acid. Also, buffers of pH 6.5–7.5 were made from 20% (w/v) hexamethylenetetramine, and others of pH 7.5–9.0 from 1.2% (w/v) tris (hydroxymethyl)aminomethane, all of which were diluted with water and pH-adjusted with 1 M HCl. Extreme pH values were obtained by adding HCl (pH < 3.5) or NaOH (pH > 9).

All other reagents used were of analytical grade.

High-purity water obtained from a Millipore Milli-Q system was used throughout.

Apparatus

The metal ions were quantified by using a Pye Unicam SP1900 and a Perkin-Elmer 3030 spectrophotometer equipped with a deuterium corrector, an HGA 500 graphite furnace and an AS-40 autosampler. pH measurements were made with a Radiometer PHM64 digital pH-meter furnished with a combined glass-calomel electrode. Retention was measured by using a glass column (25 cm × 1 cm ID) furnished with a Rotaflo tap at the bottom.

Procedure

Retention of metal ions   The metal ions studied were retained in a column containing 5 g of the modified resin that was pre-stabilized by passing the eluent to be used in each case. The retention of Cu(II), Co(II) and Ni(II) as a function of pH was studied by passing 100 ml of solutions of different pH values (adjusted with 1 M HCl or NaOH) containing 186.5, 141.7 and 138.7 µg, respectively, of each ion at a flow-rate of 1 ml/min through the column. The effluents were collected in 5-ml fractions that were used to determine the concentration of the metal ion concerned by atomic absorption spectroscopy.[27]

The influence of the solution volume used on the retention of copper was investigated by passing a fixed amount of metal ion (186.5 µg) dissolved in volumes of 0.1 M NaAcO between 100 and 5000 ml at a constant flow-rate of 10 ml/min through the column.

The effect of the flow-rate on the retention of copper was studied over the range 1–21 ml/min by passing 100 ml of 0.1 M NaAcO containing 186.5 µg of the metal ion and subsequently eluting the retained metal with 0.1 HCl.

The breakthrough capacity of the modified resin was measured by passing 100 ml of 0.1 NaAcO containing between 19 and 3730 µg of Cu(II) and then washing the column with 100 ml of NaAcO and eluting retained copper with 0.1 M HCl.

Effect of foreign ions on the retention of Cu(II)

One-litre 0.1 M NaAcO solutions containing 186.5 µg of Cu(II) and variable amounts of foreign ions were passed through the column, which was subsequently washed with 100 ml of 0.1 M NaAcO. Retained copper was then eluted with 0.1 M HCl and measured by AAS. Interferences were quantified as the differences between measured and added Cu(II) in each instance. A given ion was considered to interfere with the determination of copper when such a difference exceeded 5%.

Determination of Cu(II) in mixtures with metal ions

Synthetic mixtures containing 186.5 µg of Cu(II) and different amounts of Ni(II), Co(II), Ca(II), Cd(II), Zn(II) and Mg(II) in metal ion-to-copper ratios from 1 to 15 were buffered appropriately and placed at the column head. Then, 100 ml of 0.1 M NaAcO was passed to

elute all metal ions except Cu(II), which was subsequently removed by passing 100 ml of 0.1 M HCl. The eluates were collected in 5-ml fractions that were used to determine the concentrations of the different ions.

Analysis of reference water samples

A volume of 100 ml of samples was adjusted to pH 8.5 with 5 M NaOH and passed through the modified resin at a rate of 10 ml/min, which was then washed with 25 ml of 0.1 M NaAcO. Retained copper was subsequently eluted by passing 0.1 M HCl through the column at a rate of 1 ml/min and collected in 5-ml fractions that were used to determine copper by AAS.

Analysis of tap water

Volumes of 1–5 l of tap water samples containing 9–190 µg of Cu(II) at pH 8.5 were passed at a constant flow-rate of 10 ml/min through a column containing 5 g of modified resin. Retained copper was then eluted with 100 ml of 0.1 M HCl and the eluate was collected in 25-ml fractions and analyzed by AAS. The results thus obtained are compared with those provided by direct graphite-furnace atomic absorption spectroscopy (GFAAS) under the conditions given in Table 1.

Determination of Cu in sea water

A known amount of Cu(II) was added to synthetic sea water prepared according to Grasshoff[28]. The added amount was compared with that measured by AAS after pre-concentration in the modified resin.

Table 1 Analytical conditions for graphite furnace atomic absorption spectrometry analyses of cooper in Sea and Tap water.

Step	Temperature, °C		Ramp time, s		Hold time, s		Gas flow, ml/min	
	Sea	Tap	Sea	Tap	Sea	Tap	Sea	Tap
Dry	90		10		20		300	
		120		5		10		300
	110		5		60		300	
Char	600		10		40		300	
		900		10		10		300
	1200		10		40		300	
Atomize	2500	2000	0*	0*	3	2	50	0
Clean	2650	2650	1	1	4	3	300	300

Wavelength: 324.4 nm; Lamp current: 15 mA; Spectral band pass: 0.7 nm; Deuterium background correction was on during atomization.
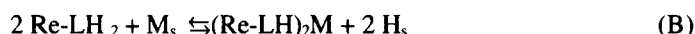* Maximum power heating.

The preconcentration and determination of Cu in sea water were carried out in the same way as for the tap water samples.

RESULTS AND DISCUSSION

In an earlier paper[26] we reported the preparation and features of Amberlite IRA-400 resin modified with Chromotrope-2R, which was found to contain 56.66% of moisture and 0.267 millimoles of CTR per gram of modified resin. We found the modified resin to be stable at any acetate concentration and its stability against other anions studied to decrease in the following order: hydroxide > chloride > nitrate > perchlorate. In any case, the resin remained stable for at least 12 months.

Under static conditions,[26,29] the resin was found to provide retention efficiencies above 98% for Hg(II), Cu(II), Al(III), Fe(III), Pb(II) and Co(II) at different pH values. On the other hand, even though the exact mechanism whereby metal ions are retained in a resin modified with a chelating ligand remains unknown, some authors[30] compare the stability of binding of ions to this type of complex-forming resin to that of the complexes formed between metal ions and chelates in solution. Some have even developed equations for predicting the pH at which retention will be quantitative.

Studies on the solution equilibria of Cu(II), Co(II) and Ni(II) with CTR[31] have shown them to form complexes of 1 : 1 or 1 : 2 stoichiometry according to

$$\text{Re-LH}_2 + M_s \leftrightarrows \text{Re-LHM} + H_s \qquad (A)$$

$$2\,\text{Re-LH}_2 + M_s \leftrightarrows (\text{Re-LH})_2 M + 2\,H_s \qquad (B)$$

The equations relating the stability constant of the dissolved complexes and the partition coefficient of each ion in the resin are

$$\log D = \log \beta_{111} + \log K_{ii} + \log K_a + \log [\text{ReLH}_2] + pH \qquad (1)$$

$$\log D = \log \beta_{122} + \log K_{ii} + 2 \log K_a + 2 \log [\text{ReLH}_2] + 2\,pH \qquad (2)$$

for equilibrium (A) and (B), respectively, where Re-LH_2 denotes resin-bound CTR, M_s and H_s dissolved metal ion and proton, $[\text{Re-LH}_2]$ the reagent concentration in the resin, K_{ii} the ion-exchange constant of the metal, K_a the reagent deprotonation constant, and β_{111} and β_{122} the formation constants of the complexes MLH and $M(LH)_2$, respectively.

The pH values at which log D = 2, obtained by applying the above equations to Cu(II), Co(II) and Ni(II), are listed in Table 2. As can be seen, the experimental values obtained on the assumption of equilibrium (A) are quite consistent with the theoretical predictions.

Figure 1 shows the results obtained for the individual retention of ions in solutions containing 186.5 µg of Cu(II), 141.7 µg of Co(II) and 138.7 µg of Ni(II), respectively, as a function of pH under dynamic conditions. Retention was 100% for Cu(II) and Co(II) above pH 7.5 and 10.5, respectively, and 65% for Ni(II) above pH 10.

Table 2   Comparison of pH values at which log D = 2 obtained experimentally and by applying the equations (1) and (2).

Metal ion	$pH_{cal}(ML)$	$pH_{cal}(ML_2)$	pH_{exp}
Cu(II)	4.09	5.03	4.35
Ni(II)	5.60	9.02	5.70
Co(II)	6.63	10.39	6.60

Based on the results obtained for 100-ml volumes of Co(II) solutions at pH 11, retention of this ion was only quantitative when 10^{-3} M NaOH was used; all other buffer solutions, including NH$_3$, B$_4$O$_7^{2-}$/NaOH and HPO$_4^{2-}$/PO$_4^{3-}$, only provided partial retention. As regards the NaOH solution volume used, retention of this ion was found to decrease with increase in this variable; it amounted to 90% for a volume of 1000 ml, so the resin was inadequate for preconcentration of Co(II).
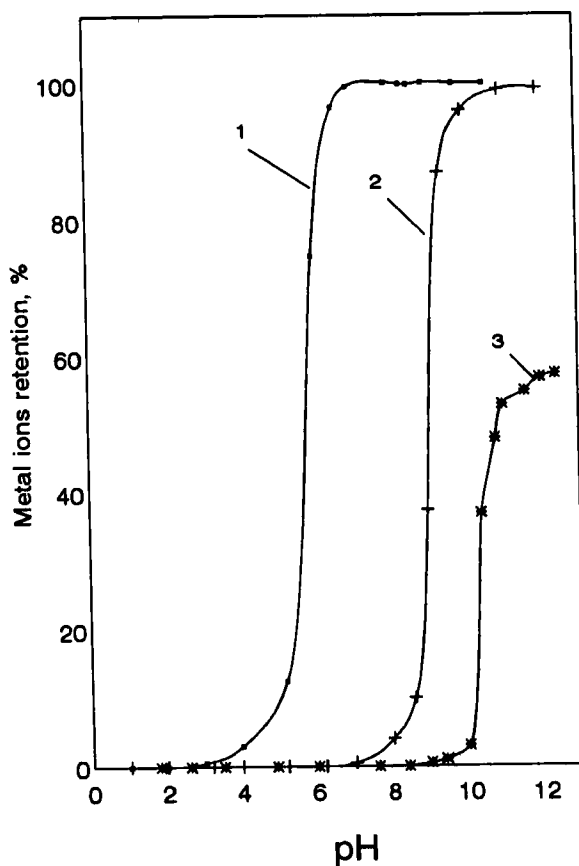

Figure 1   Retention of metal ions on the CTR resin as a function of pH, under dynamic conditions. Flow-rate equal 1 ml/min.: 1) Cu(II) = 186.5 µg; 2) Co(II) = 141.7 µg and 3) Ni(II) = 138.7 µg.

Table 3   Effect of the volume of sample on the retention of Cu(II). (186.5 μg added; rate 10 ml/min).

Volume (ml)	Concentration (μg/l)	Cu adsorbed (μg)	Cu adsorbed (%)
5000	37.3	186.5	100.0
4000	46.6	187.3	100.4
3000	62.2	185.9	99.7
2000	93.2	188.6	101.1
1000	186.5	185.7	99.6
500	373.0	186.9	100.2
250	746.0	187.8	100.7
100	1865.0	186.9	100.2

Retention of Cu(II) in different media (pH > 7.5) was found to be quantitative in acetate, NaOH and $B_4O_7^{2-}$/NaOH, but not in NH_3 (65.30% and 87.40% for 0.2 and 0.04 M NH_3, respectively). Table 3 shows the retentions obtained by using a fixed amount of Cu(II) (186.5 μg) and resin (5 g), and various volumes of 0.1 M NaAcO. The solution volume used did not appreciably affect retention over the studied interval, so Cu(II) can indeed be pre-
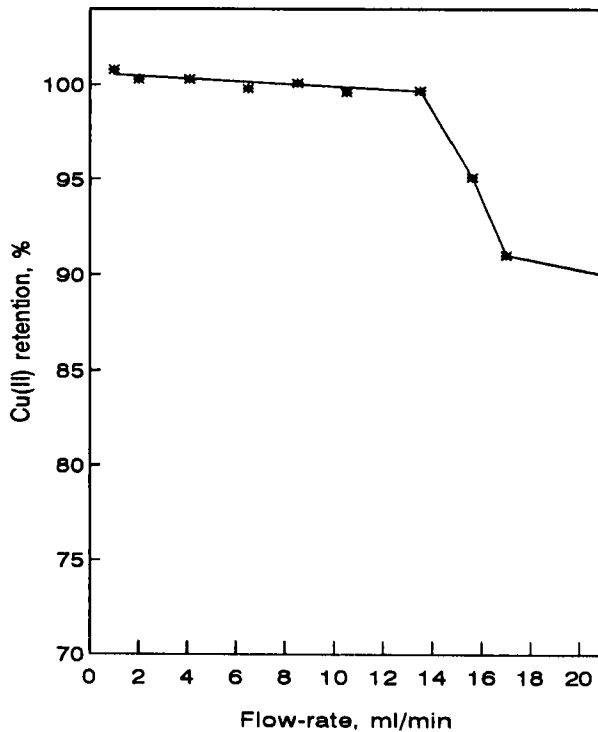
Figure 2   Flow-rate effect on the retention of 186.5 μg of Cu(II) in NaAcO 0.1 M on the CTR resin.

concentrated from dilute solutions by using the modified resin. Of the different eluents assayed (0.5, 0.1, 0.05 and 0.01 M HCl, and 1 M HAcO), a 0.1 M solution of HCl was found to be the most suitable as it provided the sharpest elution peaks and did not elute CTR, so the resin could be reused unaltered.

Figure 2 shows the variation of Cu(II) retention as a function of the flow-rate. The retention was quantitative below 13.5 ml/min, above which it started to decrease (*e.g.*, 90% at 21 ml/min).

Figure 3 shows a plot of the amount of retained Cu(II) (in µg), passed at a rate of 10 ml/min, per gram of resin against the amount of added Cu(II) (also in µg) per gram of resin. The amount retained was equal to that added when the latter was smaller than 200 µg/g modified resin, but was smaller otherwise. The breakthrough capacity of the resin was thus 200 µg/g resin at 10 ml/min.

Table 4 lists the results obtained in the separation of Cu(II) from mixtures containing different amounts of Co(II), Ni(II), Zn(II), Cd(II), Ca(II) and Mg(II). The separation was always quantitative when 100 ml 0.1 M NaAcO was used as first eluent and 0.1 M HCl as second. Recoveries ranged between 96.5% and 102.3 % for all ions and were thus quite acceptable for the technique used.

Table 5 shows the retentions obtained for 186.5 µg of Cu(II) in the presence of various ions, most of such ions did not interfere at all—not even those cations that were retained by
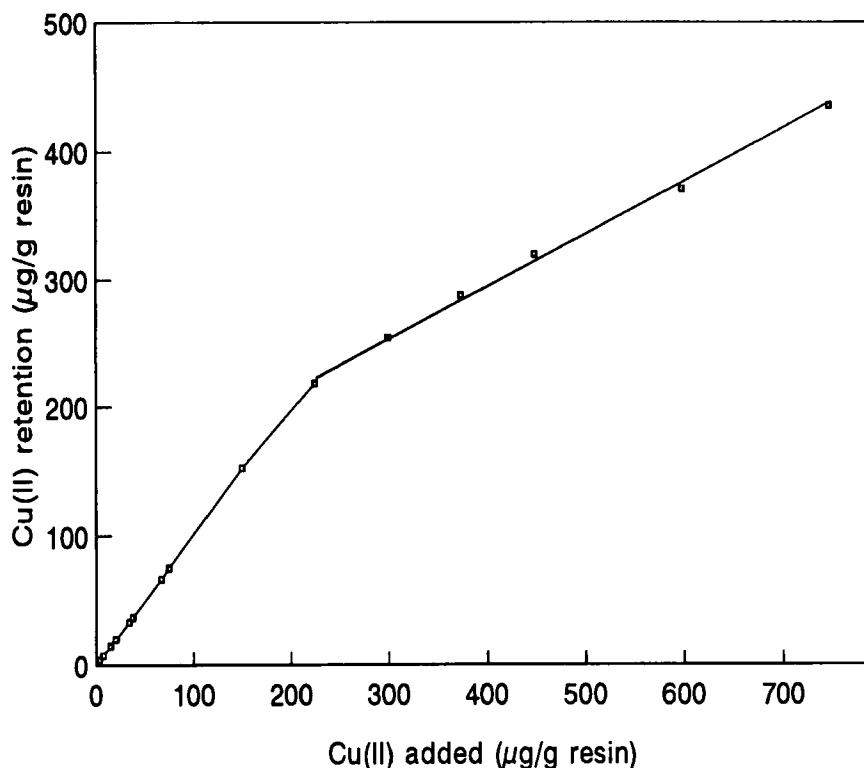

Figure 3   Retention-capacity of CTR resin for Cu(II).

Table 4 Resolution of cooper in mixtures with other metal ions on CTR-loaded Amberlite IRA-400 (186.5 µg of Cu(II) added; average of three measurements).

Cu(II) found/µg	Metal ion	Added/µg	Found/µg
186.8	Co(II)	283.4	283.5
183.6		1417.0	1379.0
183.8	Ni(II)	277.6	279.3
186.4		1388.2	1344.4
190.4	Ca(II)	204.0	202.3
183.6		2040.0	2009.1
187.6	Zn(II)	183.2	181.4
184.1		1832.0	1873.8
184.1	Cd(II)	296.2	292.5
187.0		2962.0	2952.5
186.8	Mg(II)	216.0	214.1
188.6		2700.0	2702.6

Table 5 Effect of foreign ions on determination of 186.5 µg of Cu(II).

Ions	Added, mg	Cu found, µg	Error, %
Sr(II)	218000	187.2	0.3
Ca(II)	216000	181.5	-2.7
Cd(II)	118580	184.5	-1.1
Mn(II)	117850	186.8	0.2
Mg(II)	107850	186.8	0.2
Zn(II)	73760	186.4	-0.1
Pb(II)	21840	182.2	-2.3
Hg(II)	19740	186.7	0.1
Ni(II)	13880	185.9	-0.3
Co(II)	7000	187.3	0.4
Al(III)	2400	185.2	-0.7
Th(IV)	2320	183.8	-1.5
Cr(III)	330	184.1	-1.3
Fe(III)	170	181.8	-2.5
Fe(III)*	1700	187.1	0.3
F	190000	185.6	-0.5
Cl⁻	188500	183.6	-1.5
ClO₄⁻	18650	186.1	-0.2
NO₃⁻	18600	185.4	-0.4
Br⁻	186000	185.5	-0.5
SO₃⁼	186000	188.3	1.0
B₄O₇⁼	186000	184.0	-1.3
SO₄⁼	182400	184.4	-1.1
I⁻	20500	187.1	0.3
Citrate	19000	187.1	0.3
Tartrate	18000	183.8	-1.4
CN⁻	260	123.4	-33.9

* 1700 µg of Fe(III) + 190000 µg of F⁻

the resin [*e.g.* Hg(II)].[26] The most severe interferences were from cations forming copious precipitates at the pH used and those anions that reacted with Cu(II) in some way. Iron(III) interfered in amounts larger than 177 µg; however, such a tolerated limit can be raised tenfold by adding fluoride ion to the solutions.

A statistical study of the results obtained in the AAS determination of 10.064 µg of Cu(II) in 1 l of water after preconcentration in the modified resin revealed that the method was subjected to no systematic errors ($\mu = 10.05 \pm 0.10$, $\sigma = 0.152$, $n = 10$).

The method was validated by analyzing a reference water sample from the National Bureau of Standards (SRM 1643b) with the following trace ion contents (in ng/g): 40 As, 44 Ba, 19 Be, 11 Bi, 94 B, 20 Cd, 18.6 Cr, 26 Co, 99 Fe, 24 Pb, 28 Mn, 85 Mo, 49 Ni, 10 Se, 10 Ag, 227 Sr, 8 Ta, 45 V and 66 Zn. The reference sample also contained 35, 8, 15 and 3 µg/ml Ca, Na, Mg and K, respectively. The Cu content provided by the proposed method, 21.94 $\pm$ 0.3 µg/ml, is quite consistent (within 1.5%) with the certified value (22.27 $\pm$ 0.4 µg/ml at a density of 1.017 µg/ml and 23°C).

Determination of Cu(II) in tap water

The results obtained in the determination of Cu(II) in tap water by AAS after preconcentration in CTR-modified Amberlite IRA-400, as well as by graphite-furnace atomic absorption spectroscopy (GFAAS) with no preconcentration are gathered in Table 6. The two sets of values are quite consistent, so the modified resin is appropriate for the preconcentration of Cu(II) at concentrations between 2 and 200 µg/ml.

Determination of Cu(II) in sea water

This involved a preliminary study of the preconcentration of Cu(II) in synthetic sea water,[28] the results of which are listed in Table 7. The concentrations obtained by AAS following preconcentration coincide with the added concentrations.

Table 6   Determination of Cu(II) in Tap Water by AAS after preconcentration on CTR-loaded Amberlite IRA-400 and GFAAS without preconcentration.

Sample	Volume, l	Cu-concentration (µg/l)[a]	
		Proposed method	*GFAAS*[b]
1	5	1.95±0.01	1.92±0.01
2	5	3.50±0.02	3.41±0.01
3	5	6.00±0.02	5.65±0.02
4	5	17.10±0.03	16.84±0.02
5	1	20.99±0.03	20.57±0.01
6	1	39.20±0.01	39.22±0.03
7	1	77.78±0.04	76.52±0.01
8	1	189.48±0.02	188.42±0.04

[a]Mean values of three determinations.
[b]GFAAS, grafite furnace atomic absorption spectrometry.

Table 7 Determination of Cu(II) in Artificial Seawater by AAS after preconcentration on CTR-loaded Amberlite IRA-400.

Sample	Volume, l	Cu-concentration (µg/l)	
		Proposed method[a]	Added
1	5	2.02±0.05	2.01
2	5	2.70±0.03	2.69
3	5	4.02±0.02	4.03
4	2	5.05±0.07	5.03
5	2	6.72±0.09	6.71
6	2	8.39±0.07	8.39

[a]Mean values of three determinations.

The results obtained by applying the proposed AAS-preconcentration procedure to four samples of sea water were consistent with those directly obtained by graphite-furnace atomic absorption spectroscopy (Table 8), which confirms the suitability of the resin for preconcentrating Cu(II) in sea water and avoiding the matrix effects typically encountered in this type of sample.

CONCLUSIONS

The proposed method offers some advantages over classical liquid-liquid preconcentration methods in those cases where a rather large sample volume is to be concentrated by a given factor. In addition, it is highly selective, which enables application of various analytical techniques for the determination of the metal ion.

Acknowledgements

Table 8 Determination of Cu(II) in Seawater by AAS after preconcentration on CTR-loaded Amberlite IRA-400 and GFAAS without preconcentration.

Sample	Volume, l	Cu-concentration (µg/l)[a]	
		Proposed method	GFAAS[b]
1	5	2.28±0.01	2.33±0.05
2	5	2.96±0.03	3.01±0.06
3	2	6.98±0.03	7.01±0.04
4	2	8.68±0.01	8.73±0.06

[a]Mean values of three determinations
[b]GFAAS, grafite furnace atomic absorption spectrometry.

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