

A Comparative Investigation of Copper and Cobalt Imprinted Polymers: Evidence for Retention of the Chosen Complex Stoichiometry in the Imprinted Cavities

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Supplementary Information

Solid Phase Extraction (SPE) Studies

As the copper imprinted polymer, CuVbMIP, synthesised exhibited high capacity and selectivity for copper in presence of various competitor ions (Table 1), it was investigated for the SPE capabilities for pre-concentration of copper from different matrices.

Table 1. Results of batch sorption studies with the copper imprinted and non-imprinted polymers in acetate buffer (pH 4.8)

Metal ion solution	Capacity ($\mu\text{mol/g}$)	
	Cu-VbMIP	VbNIP
Mixture (2 mM each) of Co^{2+} , Cu^{2+} , Ni^{2+} , and Zn^{2+}	Cu: 191.3 (± 5.9) Other ions: BDL	Cu: 66.2 (± 3.7) Zn: 19.7 (± 1.0) Ni: 11.3 (± 0.9) Co: BDL

The batch mode SPE studies were carried out in two steps. The first step involved stirring a known volume of the copper containing solution of known concentration with known amount of the polymer (CuVbMIP) for a fixed time. The contact time for sorption was 30 min in all the cases except the experiments wherein 1000 ml solutions were used. In the latter case, the contact time was 75 min to aid better mixing of large volume of the solutions used. The second step involved extraction of the sorbed metal ions from the MIP. For extraction, the treated solution along with the polymer was filtered through a Millipore (30 mm dia) filtration assembly under vacuum. The polymer collected was washed with 2 ml methanol and dried under vacuum. The dried polymer was then shaken with 0.3 M HCl in a vial for 30 min and the supernatant collected by centrifugation, which was analysed for copper ions by ICP-AES. Enrichment factor was calculated as ratio of volume of the experimental solution treated over the volume of the acid eluent used.

The copper recovery values achieved are tabulated in Table 2. From a 55 ml of 0.2 ppm copper solution made in Ultrapure water, buffered at pH 4.8 with 20 mM acetate buffer, near complete copper sorption could be achieved by treating it with 10 mg Cu-VbMIP for 30 min. The sorbed copper was quantitatively eluted out using 2 ml 0.3 M HCl leading to an enrichment factor of 27. When 1000 mL of the same solution was treated with 100 mg Cu-VbMIP, similar extraction efficiency could be obtained. An enrichment factor of 500 was obtained in this case as the sorbed copper ions were extracted into 2 ml of 0.3 M HCl.

Table 2. Copper recovery by the imprinted polymer, Cu-VbMIP, from copper solutions (prepared in Ultrapure water)

Volume (ml)	Added Cu (μg)	Cu recovery (%)
55	11	98.4 (± 0.6)
1000	200	97.1 (± 1.1)
1000	100	97.9 (± 1.2)

Presence of interfering metal ions could affect the efficiency of extraction by competitive sorption. Therefore, the extraction studies were also done in presence of other metal ions. The competitive studies were done in binary mixtures as well as in mixture containing multiple interfering ions along with 0.5 ppm copper. The results (Table 3) show that the presence of other ions does not affect the polymer's preconcentration efficiency for copper.

Table 3. Copper recovery by the imprinted polymer, Cu-VbMIP, from solutions (prepared in Ultrapure water) containing 0.1 ppm copper, and various interfering ions

Interfering ion (Concentration)	Cu recovery (%)
Zn ²⁺ (1.0 ppm)	101.3
Ni ²⁺ (1.0 ppm)	98.7
Ca ²⁺ (10 ppm)	100.2
Mg ²⁺ (10 ppm)	99.1
Mixture [Ni ²⁺ (1 ppm) + Zn ²⁺ (1 ppm) + Ca ²⁺ (10 ppm) + Mg ²⁺ (10 ppm)]	97.9

SPE studies have also been done with real water samples such as tap water and seawater. High extraction efficiencies could be obtained for these samples as well (Table 4). The normal level of copper in this region's seawater is known to be around 4 ppb¹. The seawater used in this study was not directly collected but after it was pumped through a copper mesh for an experimental

loop facility maintained for simulation studies. The seawater is contaminated with copper ions during this process and leads to an increased copper concentration in the collected sample as reflected in the concentration value shown in the table.

Table 4. Copper recovery by the imprinted polymer, Cu-VbMIP, from different water samples

Sample	Added Cu (µg/l)	Cu recovery (µg/l)
Seawater	0	29.2
	200	233.0
Tapwater	0	1.39
	200	200.5

1. R. Rajamohan, T.S. Rao, B. Anupkumar, A.C. Sahayam, M. Balarama Krishna, V.P. Venugopalan and S.V. Narasimhan, *Indian J. Mar. Sci.*, 2010, **39**, 182-191.