

Preconcentration of Copper Ion in Aqueous Phase on Methacrylate Polymers

BIRSEN DEMIRATA-ÖZTÜRK, GÜLCİN GÜMÜS, AYSEGÜL ÖNCÜL-KOC, and HUCESTE CATALGIL-GIZ*

I.T.Ü. Fen Edebiyat Fakültesi Kimya bölümü 80626 Maslak, İstanbul, Türkiye

SYNOPSIS

Copper was preconcentrated from aqueous solutions by adsorption on polymethyl methacrylate, polymethacrylonitrile, and their copolymers prepared by group transfer polymerization. Atomic absorption spectrometry was used to determine the metal ion. The copper (II) ion was collected from aqueous solutions starting from pH 2. In both homopolymers and copolymers, an increase of retention starting from pH 2 to 7 was observed. Below pH 2, no retention was observed. The retention of the ion from the aqueous phase on the polymers was above 90% at pH 7. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

With increasing attention to the effect of toxic materials on public health, development of analysis methods capable of determining trace amounts of such materials has become necessary. On the other hand, modern technology requires extremely pure materials, and it is important to determine trace amounts of impurities in any of these processes. For these reasons, determination of trace element concentration is an important subject of chemistry.

Copper is a highly toxic metal. Although an adult human body contains 100–150 mg copper, daily intake exceeding 3.7 mg causes cell poisoning. Its effect is partly as an irritant, causing vomiting, painful diarrhea, and cardiac failure. Accumulation of more than 200 mg of copper in the body is poisonous.

The most common technique for determining trace amounts of metal ions is preconcentrating the element to be determined. This is done on a matrix of polymeric resins, which selectively binds the desired material. After this procedure, the concentrated material can be analyzed by spectrophotometric methods.^{1–10}

In this work, preliminary results on the preconcentration of a toxic ion, copper, on a polymeric matrix is reported.

The polymeric resins used in this work were polymethyl methacrylate (PMMA), polymethacrylonitrile (PMAN), and their copolymers, all synthesized by group transfer polymerization (GTP). GTP is a new polymerization method introduced by the DuPont group in 1983. In GTP, polymeric chains grow from one active end only, resulting in linear unbranched polymers.^{11–14}

In such chains, the N and O groups, which should be mostly responsible for the interaction between metal ions and resins, are not masked. This property is believed to enhance the ability to hold metal ions. Another important property of GTP is to give monodisperse polymers at room temperature; the molecular weights and heterogeneity indexes of the resins used in this work are given in Table I.

Since the pH value of the solution effects the holding ability of the resin, the pH dependence is also studied for a wide pH range.

EXPERIMENTAL

Materials

Methyl methacrylate and methacrylonitrile (Aldrich Co.) were freed from inhibitor by treating with 5% aqueous sodium hydroxide solution, washed with distilled water several times, then dried over calcium hydride. The monomers were obtained by fractional distillation. Tetrahydrofuran (THF) (Aldrich Co.)

* To whom correspondence should be addressed.

Table I The Molecular Weights and the Heterogeneity Indexes for Polymers and Copolymers Used in Preconcentration Studies

Polymer and Copolymer Systems	$M_n \times 10^{-4}$	M_w/M_n
PMMA	2.45	1.15
PMAN	2.30	1.05
Cop I ^a	2.40	1.10
Cop II ^b	2.45	1.05

^a Cop I = 1 MMA + 4 MAN.^b Cop II = 4 MMA + 1 MAN.

was refluxed over Na/benzophenone (Aldrich Co.) until dry, then distilled into the reaction flask prior to use. Methyl trimethyl silyl dimethylketene acetal (1-methoxy 2-methyl-1-trimethylsilyl-1-propene) (MTS) (Aldrich Co.), tris(dimethyl amino)sulfonium difluoride (TASHF₂) (Aldrich Co.), and other chemically pure materials were used without further purification.

A WTW 8120 pH meter was used to measure the pH of solutions. To prepare the CuCl₂ solutions and to wash the resins and for pH adjustments, HCl and NaOH were used. Pure CuCl₂ (7 g) was dissolved in water and diluted up to 500 mL. The concentration of the solutions was checked by AAS and diluted to the necessary concentration.¹¹⁻¹⁴

Polymerization

The monomer mixture (5.0 ml), the initiator MTS (0.10 ml), and THF as solvent (50 ml) were mixed under an atmosphere of dry nitrogen. The catalyst, TASHF₂, was then added as a solution (0.10M) in

Table II The Amount of Copper Adsorbed Per Grams of Homopolymers and Copolymers at Different pH Values

pH	Amount Adsorbed (mg Cu/g Resin) ^a			
	PMMA	PMAN	Cop I ^b	Cop II ^c
2.71	1.05	1.18	1.28	1.35
3.95	1.58	1.73	1.88	2.01
4.47	1.91	1.86	2.14	2.35
5.42	3.09	3.00	3.93	3.79
6.15	3.57	3.38	4.26	4.16
7.18	4.53	4.54	4.80	4.60

^a Cu concentration, 5 mg/g resin; pH = 7; particle size, 841-500 μm.^b Cop I = 1 MMA + 4 MAN.^c Cop II = 4 MMA + 1 MAN.

acetonitrile. The mixture immediately warmed; after cooling, the polymer was precipitated in petroleum ether (b.p. 30-40). It was redissolved and reprecipitated, then dried *in vacuo* at room temperature overnight.¹²

Preconcentration was performed by batch and column techniques.

Batch Technique

The exchange capacity for copper ion is as follows. 50 ml of 15 ppm copper solution (pH 7) and 0.1 g resin were stirred vigorously at a rate 350 for 2 h. After filtering the resins, copper was determined in the filtrate by the AAS method. Copper analysis was also carried out on the eluate, which was obtained by the treatment of the resin with 1 mol/l HCl.

The effect of particle size and time of mixing on adsorption were studied in similar experiments.

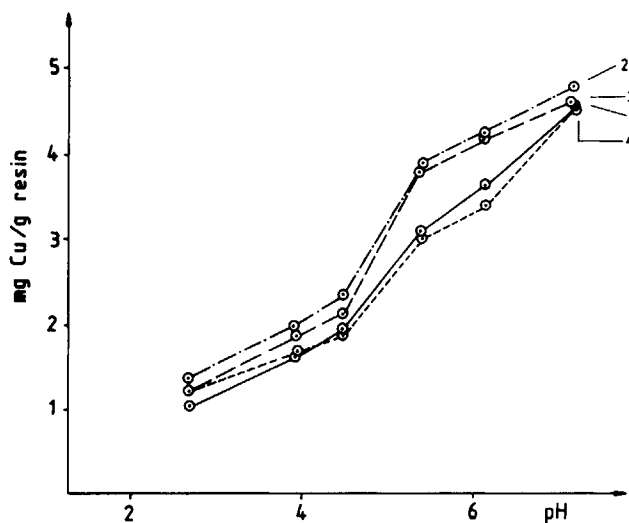
**Figure 1** Amount copper adsorbed versus pH for all polymers studied: 1, PMMA, 2, 1MAN + 4MMA, 3, 4MAN + 1MMA, and 4, PMAN.

Table III Preconcentration of Copper Ions from Dilute Solutions

Polymer	Cu Concentration (mg/mL)	Sample Volume (mL)	%Retention
PMMA	0.25	1000	97
PMAN	0.25	1000	99
4 MN + 1 MMA	0.25	1000	100
1 MN + 4 MMA	0.25	1000	99

Effect of pH

50 ml solutions of 10 ppm Cu(II), with varying pH from 2.71 to 7.18, were mixed with 0.1 g of resin and stirred vigorously for 30 min. At the end of this period, the amount of copper adsorbed on the resin was determined by AAS. After each experiment, homopolymers and copolymers were washed first with HCl and then with distilled water. Eluent water was tested by AgNO₃ to check the removal of acid.

Column Technique

Resins (1.5 g of each) were left in distilled water for 24 h and were filled into 0.5 cm diameter columns by a compression pump. Columns were washed with 0.1M of HCl solution for 24 h and then washed with distilled water until they gave no chlorine reaction. Dilute copper solution (pH 7) was passed through the columns at a flow rate of 3 ml/min; the adsorbed copper, which was eluted with 1M HCl, was analyzed with AAS.

Table IV The Effect of Mixing Time on Retention

Time (min)	Amount Adsorbed (mg Cu/g Resin) ^a			
	PMMA	PMAN	Cop I ^b	Cop II ^c
5	4.47	4.50	4.73	4.54
10	4.47	4.49	4.75	4.57
15	4.51	4.53	4.78	4.59
20	4.52	4.55	4.81	4.60
25	4.53	4.56	4.79	4.61
30	4.50	4.54	4.80	4.60
40	4.53	4.56	4.82	4.59

^a Cu concentration, 5 mg/g resin; pH = 7; particle size, 841–500 μm.

^b Cop I = 1 MMA + 4 MN.

^c Cop II = 4 MMA + 1 MN.

Copper Analysis

The amount of copper in the solvent left after the removal of the resin, and the recovered copper from the solvent obtained by washing off the resin, were analyzed by atomic absorption spectrometry (Shimadzu AA 670).

The working conditions were as follows: wavelength, 324.75 nm; cavity cathode lamp, Cu; and slit width, 0.27 nm.

RESULTS AND DISCUSSION

Retention ratios versus pH values obtained from the batch technique for 0.5 ppm Cu solution are given in Table II and plotted in Figure 1. For all polymers, the retention increases rapidly and steadily as the pH of solution is increased, with no retention below pH 2 and almost complete (>90%) retention at pH 7. Results obtained from the column technique at pH 7 are also similar, with 97–100% retention with the polymers studied (Table III).

At low pH values, the high H⁺ ion concentration at the interface electrostatically repels positively charged metal ions, preventing their approach to the polymer surface. For this reason, low retention values at low pH values observed are in line with expectations. The rate of adsorp-

Table V Preconcentration Capacity Determination in Polymers

Polymer	Capacity (mg Cu/g Resin)
PMMA	6.10
PMAN	6.50
Cop I ^a	6.17
Cop II ^b	6.10

^a Cop I = 1 MMA + 4 MN.

^b Cop II = 4 MMA + 1 MN.

Table VI The Effect of Particle Size on Preconcentration

Particle Size (μm)	Amount Adsorbed (mg Cu/g Resin) ^a			
	PMMA	PMAN	Cop I ^b	Cop II ^d
> 841	4.35	4.62	4.48	4.37
841-500	4.45	4.80	4.60	4.50
500-350	4.65	4.87	4.65	4.61

^a Cu concentration, 5 mg/g resin; pH = 7; mixing time = 30 min.

^b Cop I = 1 MMA + 4 MN.

^c Cop II = 4 MMA + 1 MN.

tion has been found to be very high. More than 95% of the retention occurred in the first 5 min (Table IV).

Although the capacities of the resins given in Table V (pH 7) are not high, this should not affect their usefulness for preconcentration of trace amounts. The results given in Table VI show that retention does not depend on particle size.

Retention percentages and capacities of both homopolymers and their copolymers were comparable. This indicates that the effectiveness of O groups of PMMA and N groups of PMAN are similar.

We could not find any value in the literature for the retention of copper by PMAN and for its copolymers with methyl methacrylate. In studies on Co, Mn, Ni, and Fe ions on polyacrylonitrile (PAN) resin, a maximum retention of 85% has been observed at pH 6. The resin used in that study was synthesized by free radical polymerization.⁹⁻¹⁰

In conclusion, we can state that the almost complete retention in a neutral environment indicates that PMMA, PMAN, and their copolymers synthesized by GTP should be very useful in preconcentration of copper. Further work is in progress on the retention of Cu on PMMA and PMAN synthesized by free radical polymerization. It is hoped that the results will clarify the relationship between retention and polymerization mechanism.

REFERENCES

1. B. M. Vanderborght and R. E. Van Grieken, *Anal. Chem.*, **49**, 311 (1977).
2. H. Ince, S. Akman, and U. Koklu, *Fresenius J. Anal. Chem.*, **342**, 560-562 (1992).
3. K. Terada, A. Inoue, J. Inamura, and T. Kiba, *Bull. Chem. Soc. Jpn.*, **50**, 1060-1065 (1977).
4. B. Evtimova and V. Michaylova, *Anal. Chim. Acta*, **232**, 393-395 (1990).
5. L. Elci, M. Soylak, and M. Dogan, *Fresenius J. Anal. Chem.*, **342**, 175-178 (1992).
6. A. Denizli, M. Olcay, A. Tuncel, E. Piskin, and T. Doga, *J. Chem.*, **16**, 135-143 (1992).
7. A. Corsini, S. Chiang, and R. DiFrancia, *Anal. Chem.*, **54**, 1435-1437 (1982).
8. C-C. Wan, S. Chiang, and A. Corsini, *Anal. Chem.*, **57**, 719-723 (1985).
9. N. Arik and A. R. Türker, *Fresenius J. Anal. Chem.*, **339**, 874-876 (1991).
10. A. R. Türker, N. Arik, and O. Sanli, *Ondokuzmayis Univ. Sci. J.*, **2**, 179-185 (1990).
11. O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham, and T. V. RajanBabu, *J. Am. Chem. Soc.*, **105**, 5706 (1983).
12. H. Catalgil and A. D. Jenkins, *Eur. Polym. J.*, **27**, 651 (1991).
13. P. M. Mai and A. H. E. Muller, *Macromol. Chem. Rapid. Comm.*, **8**, 99-107 (1987).
14. P. M. Mai and A. H. E. Muller, *Macromol. Chem. Rapid. Comm.*, **8**, 247-253 (1987).

Received January 19, 1996

Accepted February 1, 1996