

Synthesis and Application of Spherical Macroporous Epoxy–Polyamide Chelating Resin for Preconcentration and Separation of Trace Ga(III), In(III), Bi(III), V(V), Cr(III), and Ti(IV) from Solution Samples

Dong Yang, Xijun Chang, Yongwen Liu, Sui Wang

Department of Chemistry, Lanzhou University, Lanzhou, China

Received 24 November 2003; accepted 27 July 2004

DOI 10.1002/app.21321

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: An ICP-AES method using a new spherical macroporous epoxy–polyamide chelating resin to enrich and separate trace Ga(III), In(III), Bi(III), V(V), Cr(III), and Ti(IV) ions from solution samples is established. The results show that the analyzed ions can be enriched quantitatively by 0.1 g of the resin at pH 4, with recoveries > 98%. The ions can be desorbed quantitatively with 10 mL of 2M HCl from the resin column with recoveries > 96%, and 100–1000-fold excesses of Ca(II), Mg(II), Fe(III), Cu(II), Zn(II), Al(III), Ni(II), and Mn(II) cause little interference in the determination of these ions by ICP-AES. The chelating resin is reused for ten times; the recoveries of these ions are still over 95%. The

relative standard deviations for enrichment and determination of 100 ng ml⁻¹ Ga(III), In(III), and Bi(III), 10 ng ml⁻¹ V(V), Cr(III), and Ti(IV) are in the range 0.6–2.3%. The concentration of each ion found in the real wastewater sample and alloy sample is in good agreement with the values provided by the plant. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2330–2334, 2005

Key words: macroporous epoxy–polyamide chelating resin; preconcentration; separation; gallium; indium; bismuth; vanadium; chromium; titanium

INTRODUCTION

The preconcentration and separation of trace elements by using chelating resins^{1–6} or chelating fibers^{7–10} have been reported widely. However, the synthesis of the resins or the fibers usually takes a long time and a complex synthetic process. Accordingly, epoxy-urea,¹¹ epoxy-imidazole,¹² and epoxy-dicyandiamide¹³ chelating resin were synthesized rapidly by Chang et al. and used for preconcentration and separation of trace elements. In this article, a new spherical macroporous epoxy–polyamide chelating resin is synthesized rapidly by one step reaction and applied to the enrichment of trace metal ions in solution samples. The resin shows better acid and alkali resistance and its synthesis is more simple and rapid than that of the above adsorbents.^{11–13} The structure of the chelating resin is analyzed by using Fourier transform infrared spectroscopy (FT-IR). The properties of the macroporous chelating resin for the preconcentration and separation of trace of Ga(III), In(III), Bi(III), V(V), Cr(III), and Ti(IV) from solution samples, as measured by inductively-coupled plasma atomic emission spectrometry (ICP-AES), are studied in detail. The precision and the

accuracy of the proposed method are achieved by analysis of a real wastewater sample and an alloy solution sample with satisfactory results.

EXPERIMENTAL PROCEDURES

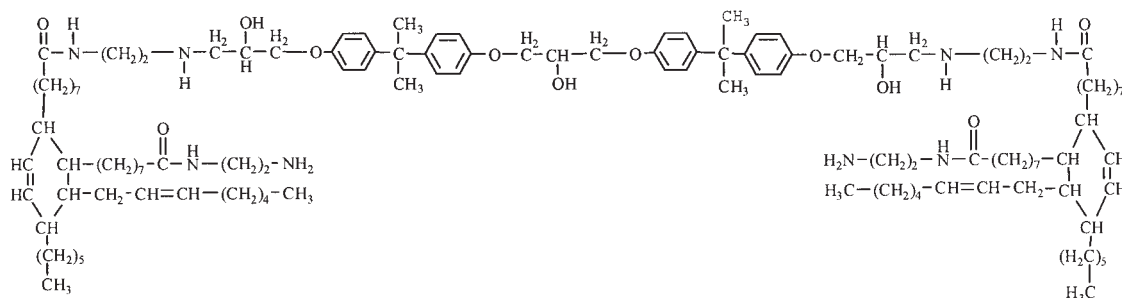
Instruments and apparatus

An ICP/6500 inductively coupled plasma atom emission spectrometer (Perkin–Elmer), a Nicolet NEXUS 670 FTIR (America), a Pore Sizer 9320 (Micromeritics Instrument Corp.), an Analysensysteme GmbH VarioEL element analyzer (Germany), and a PHS-10c digital pH meter (Xiaoshan, China) are used. The adsorption column is a glass tube (12 × 0.5 cm i.d.; 0.15cm i.d. at the lower end) containing 0.1g of resin in high-purity water overnight. It is held in place by cotton-wool.

Reagents and standards

Reagents of high or analytical purity are used for all experiments. Stock solutions of 1mg ml⁻¹ Ga(III), In(III), Bi(III), V(V), Cr(III), and Ti(IV) are prepared by dissolving spectroscopically pure Ga₂O₃, In₂O₃, Bi₂O₃, V₂O₅, Cr(NO₃)₃, and TiO₂, respectively, in dilute HNO₃. They are diluted and mixed to give stock standard solutions of 100 μg ml⁻¹ of Ga, In, and Bi, and 10 μg ml⁻¹ of V, Cr, and Ti in 1M HNO₃, and the standard solutions are used for all experiments.

Correspondence to: X. Chang (chemwangsui@sina.com.cn).



Scheme 1 Possible structure of the resin.

Synthesis and characterization of the chelating resin

A 10 g amount of epoxy resin, 10 g of polyamide resin, and 200 mL of distilled water were mixed in a three-necked flask. After 30 min reaction with stirring at 85–95°C, the cooled product was washed with distilled water until it became neutral and dried under IR irradiation. The resin was passed through a 35-mesh sieve, and a spherical macroporous chelating resin of 35–55 mesh (pores in⁻²) particle size is obtained with the possible structure given in Scheme 1. Two measurements of the nitrogen content of the resin gave 3.54% and 3.53%. The porosity of the resin determined by the mercury intrusion method was: average pore diameter: 21.9 nm, total pore area: 15.0 m² g⁻¹, median pore diameter: 17.5 nm. The resin was, therefore, macroporous.¹⁴

The IR spectrum of the macroporous epoxy-polyamide chelating resin is shown in Figure 1. According to references,^{15,16} the peaks in Figure 1 can be assigned as follow: 3335.80 cm⁻¹ (γ O-H and N-H), 2925.57 and 2854.96 cm⁻¹ (γ C-H of CH₂ and CH), 1645.98 cm⁻¹

(γ C = O of $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—N—}$), 1608.38 and 1509.24 cm⁻¹ (γ C = C of Ar), 1460.45 cm⁻¹ (δ_s CH₂), 1380.43 and 1361.34 cm⁻¹ (δ CH₃ of C(CH₃)₂), 1295.85 cm⁻¹ (γ C-N), 1246.85 cm⁻¹ (γ_{as} C-O-C of O-Ar), 1181.76 and 1036.48 cm⁻¹ (γ_{as} C-O of O-CH₂), 828.87 cm⁻¹ (δ Ar of 1.4 substituted), 765.73 cm⁻¹ (δ_p CH₂). (γ , stretching vibration; δ , bending vibration; γ_{as} , antisymmetric stretching vibration; δ_s , scissor vibration; δ_p , rocking vibration; Ar, benzene). Based on the above identified

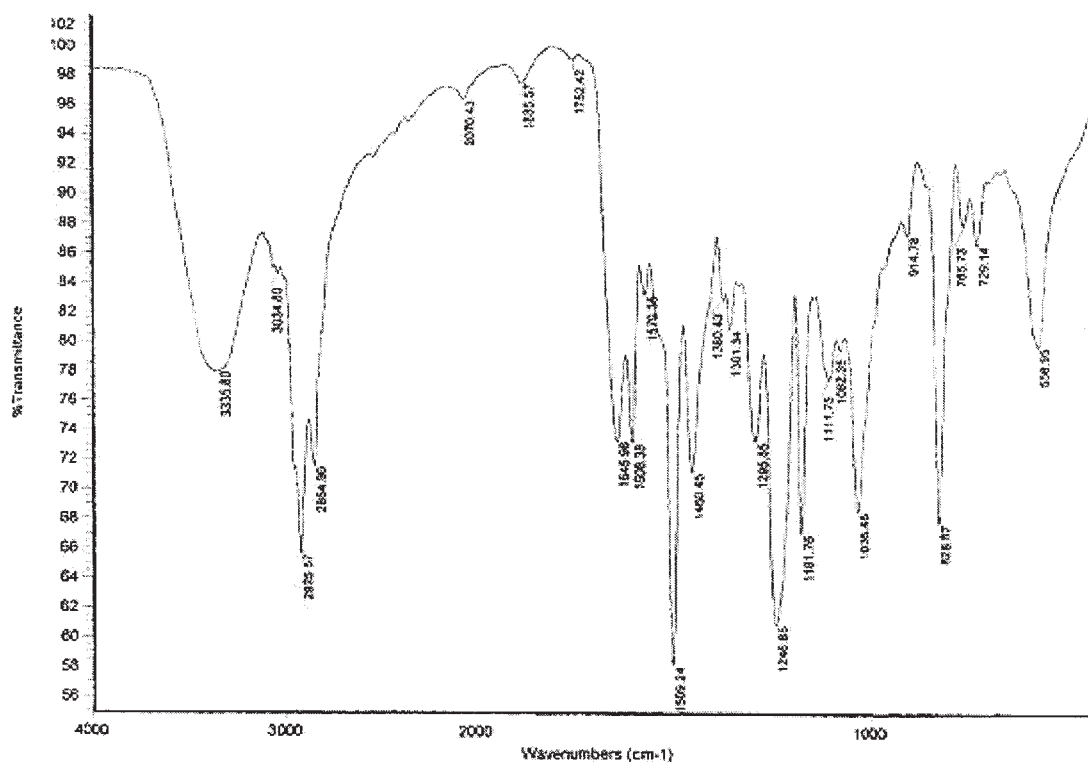


Figure 1 Infrared spectrum of the spherical macroporous epoxy-polyamide chelating resin.

TABLE I
Effect of pH on Enrichment Recovery

Element	Recovery %					
	1	2	3	4	5	6
Ga	0	10	92	100	99	97
In	0	0	56	98	100	100
Bi	41	94	100	100	99	100
V	17	45	100	100	100	100
Cr	0	0	57	99	100	100
Ti	38	72	95	100	100	97

peaks, comparing the IR spectrum of chelating resin with that of epoxy resin, the 750 cm^{-1} of the epoxy group band disappears. These observations demonstrate that the analytical functional groups have been attached to the resin.

Analytical procedure

The mixed standard solutions of Ga, In, Bi, V, Cr, and Ti or real sample solutions are pipetted into beakers (100–500 mL). The solutions are adjusted to pH 4 with aqueous ammonia and dilute HNO_3 and pass through the adsorbing columns at a flow rate of 3 mL min^{-1} . The analytes are desorbed from each column with 10 mL of 2M HCl solution at a flow rate of 1.0 mL min^{-1} . Subsequently, the ions in the 10 mL of eluate are determined by the ICP spectrometer. The conditions for analysis by ICP-AES are: forward power 1100 W, viewing height 10 mm, argon plasma gas flow rate 14 L min^{-1} , argon nebulizer gas flow rate 1.0 L min^{-1} , argon intermediate gas flow rate 0.6 L min^{-1} ; wavelengths: Ga 294.364 nm, In 230.606 nm, Bi 223.061 nm, V 292.402 nm, Cr 205.552 nm, Ti 334.941 nm.

RESULTS AND DISCUSSION

Effect of acidity on enrichment

Equal concentrations of mixed standards are diluted to equal volumes and enriched through the columns in the pH range 1–6 as described above. The results (Table I) show that trace Bi at pH 2–6, Ga, V, and Ti at

TABLE II
Effect of Flow Rate (ml min^{-1}) on Enrichment Recovery

Element	Recovery %						
	1.0	2.0	3.0	4.0	5.0	6.0	7.0
Ga	99	100	100	98	100	83	69
In	100	100	98	100	89	62	42
Bi	98	100	98	90	86	78	52
V	100	99	100	100	100	96	88
Cr	100	99	99	100	92	79	69
Ti	100	100	100	98	98	89	48

TABLE III
Influence of Desorption Acidity (10 ml HCl) on Recovery

Element	Recovery %					
	1M	2M	3M	4M	5M	6M
Ga	71	100	100	93	93	78
In	70	97	98	92	85	89
Bi	51	96	96	94	91	82
V	71	99	93	88	82	70
Cr	60	100	100	92	94	87
Ti	58	100	100	100	97	86

pH 3–6, In and Cr at pH 4–6 can be enriched quantitatively by the resin with recoveries of 92–100%. To determine these elements simultaneously, pH 4 is selected as the enrichment pH. Meanwhile, at pH 1–6, the chelating resin hardly enriched such metal ions as K, Na, Ca, Mg, Zn(II), Co(II), Cd(II), Ni(II), Tl(I), Y(III), La(III), Nd(III), Sm(III), Eu(III), Gd(III), Dy(III), Ho(III), Er(III), and Tm(III), and enriched only slightly Yb(III), Sc(III), Cu(II), and Pb(II).

Effect of flow rate on enrichment

When using the recommended procedure, the flow rate for preconcentration of the analytes on the resin columns at pH 4.0 is varied between 1.0 and 7.0 mL min^{-1} . The results, given in Table II, show that Ga, In, Bi, V, Cr, and Ti ions can be enriched quantitatively at flow rates below 4.0 mL min^{-1} . A 3.0 mL min^{-1} flow rate is selected for further study.

Influence of desorption acidity

After traces of Ga, In, Bi, V, Cr, and Ti ions are enriched on the resin columns following the above procedure, each column is eluted with 10 mL of 1–6M HCl. The results in Table III show that these elements can be quantitatively desorbed with 10 mL of 2M HCl from the columns with recoveries of 96–100%.

TABLE IV
Influence of Desorption Flow Rate (ml min^{-1}) on Recovery

Element	Recovery %					
	0.5	1.0	1.5	2.0	2.5	3.0
Ga	100	100	91	87	85	78
In	100	98	99	92	84	79
Bi	97	96	82	81	77	60
V	100	100	97	91	86	76
Cr	100	100	100	94	81	75
Ti	100	99	96	93	78	70

TABLE V
Interference of Other Ions on Analyte Recoveries

Interfering ions conc ($\mu\text{g ml}^{-1}$)	Ca(II) 10	Mg (II) 10	Fe (III) 10	Cu (II) 10	Ni (II) 10	Al(III) ^a 10	Zn(II) 0	Mn(II) 10
Recovery ^b %	Ga	100	96	100	100	92	96	100
	In	100	100	100	100	93	95	100
	Bi	99	100	96	92	93	94	97
	V	100	100	97	100	100	99	100
	Cr	100	98	100	100	94	98	95
	Ti	97	99	95	98	97	97	100

^a Al is masked with 0.1g citric acid.

^b The concentration of Ga, In, and Bi is 100 ng ml⁻¹ each. The concentration of V, Cr, and Ti is 10 ng ml⁻¹ each.

Influence of desorption flow rate

Using the column procedure, the influence of the flow rate (0.5–3.0 mL min⁻¹) on desorption of the analytes from the columns with 10 mL of 2M HCl is investigated. Table IV shows that the analytes can be desorbed quantitatively from the resin columns at 1.0 mL min⁻¹ with recoveries > 96%.

Stability, reuse, and capacity of resin

After the chelating resin is treated with strong acids or concentrated bases, the resin is washed to neutrality with distilled water and used for enrichment of analyte ions. The results show that the recoveries of trace Ga, In, Bi, V, Cr, and Ti are > 96%. There is no obvious swelling effect on the resin.

When the resin is used repeatedly (up to 10 times) as described for enrichment and determination of Ga, In, Bi, V, Cr, and Ti ions (after these ions are desorbed from the resin each time with 2M HCl, the resin column is washed to neutrality with distilled water), the adsorption efficiency is still > 95%

A 0.05 g portion of the resin is placed in each of the six conical flasks. A stock solution of Ga, In, Bi, V, Cr, and Ti is added to each flask and diluted to an equal volume. The acidity of each solution is adjusted to pH 4, and the vessels are shaken in a mechanical vibrator. The concentrations of the above ions in solution are measured by ICP-AES until equilibrium is reached. Thus, the saturated adsorption capacity of the resin is calculated to be 233 mg g⁻¹ for Ga, 134 mg g⁻¹ for In, 266 mg g⁻¹ for Bi, 110 mg g⁻¹ for V, 114 mg g⁻¹ for Cr, and 35 mg g⁻¹ for Ti.

Interference

Different potential interfering ions are added to dilute analytes standards. The analytes are preconcentrated and determined as described above. The results, summarized in Table V, show that hundred-fold or thousand-fold excesses of these other ions caused little interference on the recoveries of Ga, In, Bi, V, Cr, and Ti ions.

TABLE VI
Analytical Results for Two Samples from a Metal Smelter

Sample	Concentration (ng ml ⁻¹)				Recovery %	Error
	Given	Found \pm S.D.	Added	Sum \pm S.D.		
Wastewater						
Ga	7.2	7.0 \pm 0.3	100	103.3 \pm 0.5	96.3	2.8
In	42.6	42.1 \pm 0.6	100	142.1 \pm 0.4	100	1.2
Bi	196.7	193.9 \pm 1.0	100	292.4 \pm 1.2	98.5	1.4
V	13.5	13.4 \pm 0.1	10	23.4 \pm 0.4	100	0.7
Cr	—	—	10	9.9 \pm 0.2	99	—
Ti	—	—	10	10 \pm 0.1	100	—
Alloy solution						
Ga	65.0	62.4 \pm 0.7	100	158.2 \pm 0.6	95.8	4.0
In	53.4	52.8 \pm 0.8	100	151.0 \pm 0.9	98.2	1.1
Bi	52.0	51.0 \pm 0.9	100	147.7 \pm 1.6	96.7	1.9
V	30.5	30.5 \pm 0.2	10	40.5 \pm 0.4	100	0
Cr	4.8	4.7 \pm 0.1	10	14.7 \pm 0.3	100	2.1
Ti	3.6	3.5 \pm 0.1	10	13.4 \pm 0.1	99.0	2.7

Analytical precision and accuracy

Under the select conditions, the recoveries of 100 ng ml⁻¹ of Ga, In, and Bi, and 10 ng ml⁻¹ of V, Cr, and Ti ions in 500 mL of solutions, enriched and determined simultaneously seven times, are in the range of 96–100%. The relative standard deviation (RSD) is between 0.6% and 2.3%.

The accuracy of the proposed method is checked by analyzing 500 mL of real wastewater (from a metal smelter) and real solution samples (dissolving alloy sample from a metal smelter), using the standard addition method. The results, listed in Table VI, show > 95.8% recoveries for trace Ga, In, Bi, V, Cr, and Ti ions and are in agreement with the analytical values provided by the smelter operator with an average error < 4.0%. So, the proposed method is reliable, feasible, and accurate.

CONCLUSIONS

The proposed method is quick, convenient, precise, and accurate, and its application is reliable and satisfactory. The synthesis of the spherical macroporous resin is simpler, quicker, and more economic than that of those already available.^{1–13}

References

1. Brajter, K.; Slonawska, K. *Talanta* 1983, 30, 7.
2. Prakash, N.; Casanady, G.; Michaelis, M. R. A. *Mikrochim Acta* 1989, 3, 257.
3. Rivas, B. L.; Maturana, H. A.; Peric, I. M.; Pereira, E. *Bol Soc Chil Quim* 1994, 39, 211.
4. Kantipuly, C.; Katragadda, S.; Chow, A.; Gesser, H. V. *Talanta* 1990, 37, 491.
5. Touorova, V.; Ivanova, E.; Terebenina, A.; Jordanvo, N.; Dimitrova, K.; Borisov, G. *Talanta* 1989, 36, 817.
6. Chang, X. J.; Luo, X. Y.; Zhan, G. Y.; Su, Z. X. *Talanta* 1992, 39, 937.
7. Luo, X. Y.; Su, Z. X.; Chang, X. J.; Zhan, G. Y.; Chao, X. H. *Analyst* 1991, 116, 965.
8. Chang, X. J.; Luo, X. Y.; Su, Z. X.; Zhan, G. Y.; Gao, W. Y. *Fresenius J Anal Chem* 1994, 349, 438.
9. Chang, X. J.; Li, Y. F.; Zhan, G. Y.; Luo, X. Y.; Gao, W. Y. *Talanta* 1996, 43, 407.
10. Chang, X. J.; Su, Z. X.; Li, Y. F.; Zhan, G. Y.; Luo, X. Y. *Mikrochim Acta* 1997, 126, 137.
11. Chang, X. J.; Su, Z. X.; Yang, D.; Luo, X. Y.; Gong, B. L. *Anal Lett* 1997, 30, 2611.
12. Chang, X. J.; Su, Z. X.; Yang, D.; Gong, B. L.; Pu, Q. S.; Li, S. K. *Anal. Chim Acta* 1997, 354, 143.
13. Gong, B. L.; Li, X. Q.; Wang, F. G.; Chang, X. J. *Talanta* 2000, 52, 217.
14. He, B. L.; Huang, W. Q. *Ions Exchanger and Adsorption Resins*; Publishing House of Shanghai Science and Education: Shanghai, 1995; pp 93–129.
15. Dong, Q. N. *IR Spectra Methods*; Publishing House of the Chem Industry: Beijing, 1979; pp 99–179.
16. Cheng, Y. Q. *IR Spectra Methods and Use*; Publishing House of Shanghai: Shanghai, 1993; pp 89–112.