

## Solid phase extraction of cerium(IV) with crosslinked poly(acrylic acid) coated on silica gel

Pranesh Chowdhury\*, Susanta K Pandit & Bhabatosh Mandal\*

Analytical Laboratory, Department of Chemistry, Visva-Bharati, Santiniketan 731 235, India

Email: pranesh\_02@yahoo.co.in

Received 5 October 2007; revised 22 August 2008

A selective method has been developed for extraction and separation of Ce(IV) with the high molecular mass crosslinked poly(acrylic acid), coated on silanized silica gel. The coated materials act as stationary phase for the extraction. The structure and thermal stability of crosslinked poly(acrylic acid) has been elucidated with the help of FTIR and TGA. Ion exchange and breakthrough capacity of the exchanger have been measured. Surface morphology of the exchanger has been studied by SEM. Ce(IV) has been separated quantitatively from various synthetic mixtures containing metal ions commonly present in thorium and uranium ores, minerals and fission products. The developed method has been tested for some real samples. A plausible mechanism for Ce(IV) extraction and elution has been suggested.

**IPC Code:** Int. Cl.<sup>8</sup> B01D53/81

Recently, the solid phase extraction<sup>1</sup> (SPE) technique has gained importance since the technique is fast, simple and cost effective. SPE is based on the utilization of a solid support, coated or immobilized with different materials<sup>1</sup> such as polyelectrolyte, high molecular mass carboxylic acid, chelating agent, surfactant, quaternary ammonium salt, etc. Silica gel is found to act as a successful support since it does not swell or strain, has good mechanical strength and can undergo heat treatment<sup>1</sup>. There are several reports in literature dealing with polymer on silica support for selective separation of metal ions<sup>2</sup>. Pure ceric salts are now widely used in analytical chemistry<sup>3</sup>, organic synthesis<sup>4</sup>, polymer preparation<sup>4</sup>, ceramic industry and petroleum cracking<sup>5</sup>. Highly pure Ce(IV) is also required as catalysts in various reactions<sup>6</sup>. Studies on nuclear fission require the complete separation of Ce(IV) from uranium and thorium ores, minerals and fission products<sup>5</sup>. There are several reports in the literature on extraction of Ce(IV) by liquid cation exchanger<sup>7</sup> (Versatic-10) and by solvent extraction<sup>8</sup> with Versatic-911. Extraction chromatographic studies of Ce(IV) with high molecular mass

carboxylic acids such as SRS-100 and *n*-capric acid have also been reported<sup>9-11</sup>. However, the selectivity and exchange capacity of the reported materials are relatively poor. The crosslinked poly(acrylic acid) is widely used in the retention and recovery of heavy metals ions<sup>12-16</sup>. However, crosslinked poly(acrylic acid), coated on silanized silica gel has not yet been reported.

We report herein the systematic studies on solid phase extraction of Ce(IV) and its separation from synthetic mixtures containing metal ions commonly present in thorium and uranium ores with the help of crosslinked poly(acrylic acid) (coated on silanized silica gel).

### Experimental

Acrylic acid (Qualigens Fine Chemicals, Mumbai, India), sodium lauryl sulphate (Glaxo, Mumbai, India), N,N'-methylene bisacrylamide (Fluka, Buchs, Switzerland), ammonium persulphate (SD Fine Chem. Ltd, Boisar, India), ammonium ceric sulphate (Merck, Mumbai, India), dimethyl dichlorosilane (Merck, Mumbai, India), and ascorbic acid (BDH, Mumbai, India) were used as received.

Fourier transform infrared (FTIR) spectra of the polymer were recorded on Shimadzu FTIR (model No. 8400 S) in the range 4000-400 cm<sup>-1</sup> using KBr pellet. An Elico LI-120 pH meter, thermostat and chromatographic column (i.d. 0.8 cm) were used. Ion exchange and breakthrough capacity of the prepared exchanger were determined<sup>10</sup>. Scanning electron micrograph (SEM) was taken with a camera (Hitachi S-570, Japan). Thermal analysis was done by Perkin Elmer thermal analyser in nitrogen atmosphere at temperature rise of 10°C/min.

### Preparation of crosslinked poly(acrylic acid) and ion-exchanger material

Acrylic acid (1 mL), distilled water (10 mL) and sodium lauryl sulphate (1 g) were taken in a three-necked round bottom flask, kept in a constant temperature (70°C) water bath and mixed well by a magnetic stirrer. Pure nitrogen gas was passed through the solution at least for 30 min to create an inert atmosphere. N, N'-methylene-bis-acrylamide (0.5 g) and ammonium persulphate (1 g) were then added and stirred. After two hours, the precipitated white polymer was filtered, washed with distilled

water and dried under vacuum until constant weight. Silica gel (25 g) was rendered hydrophobic by exposing it to vapours of dimethyl dichlorosilane (2.5 mL) in nitrogen atmosphere to make it an inert support<sup>10</sup>. The dimethyl dichlorosilane treated (silanized) silica gel was then washed with anhydrous methanol and dried at 100°C. It was then impregnated with 18% (w/v) polymer solution in benzene and dried in a rotary vacuum evaporator to achieve uniform coating. The exchanger was washed with distilled water and dried. Ion exchange bed was prepared by usual method<sup>10</sup>.

#### Physico-chemical characteristics of the exchanger

The ion exchange capacity of the prepared exchanger was determined at 25°C and found to be 2.52 meq H<sup>+</sup> per gram. The value is superior to the literature value<sup>8-11</sup> of SRS-100, Versatic-10 and *n*-capric acid. The breakthrough capacity of the material with respect to Ce(IV) is 15.93 and 17.62 mg per gram of dry exchanger at pH 5 and 5.5 respectively. The exchanger is thermally stable up to 150 °C and chemically unaffected with different dilute acids. Density of the material was found 1.2 g.cm<sup>-3</sup>. SEM photograph confirms that the material is porous in nature (Fig. 1).

The FTIR spectrum shows several characteristic peaks at 1220, 1640, 1700, 2800, 2900 and 3360 cm<sup>-1</sup> which correspond to stretching of C-C (long skeleton), C=O (secondary amide), C=O (carboxylic acid), C-H (alkane), O-H (carboxylic acid) and N-H (amide) bonds<sup>17</sup> respectively. These are the characteristic spectral feature of bisacrylamide crosslinked poly (acrylic acid)<sup>13-15</sup> (I).

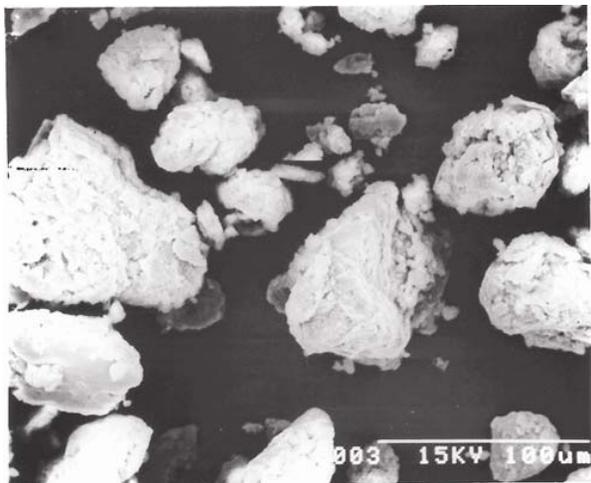
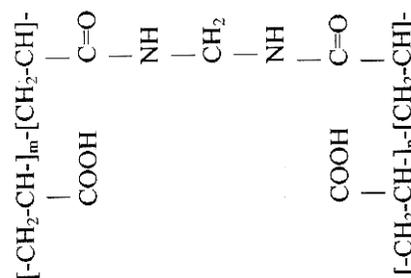


Fig. 1 — SEM photograph of developed ion exchanger resin.



Structure of crosslinked poly (acrylic acid)  
(I)

The presence of cross-linking in the polymer was also verified by the solubility and hardness test. Poly(acrylic acid), [-CH<sub>2</sub>-CH(COOH)-]<sub>n</sub> is highly soluble in aqueous medium<sup>18</sup>. However, the synthesized polymer is completely insoluble in water but soluble in benzene. The insolubility may be attributed to the presence of cross-linking in the poly(acrylic acid). The hardness of the polymer is increased with the increase of cross-linker (N, N'-methylene bis acrylamide).

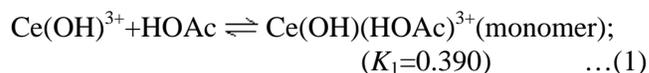
#### General extraction procedure

Ion exchanger was loaded in a chromatographic column (i.d. 0.8 cm) to achieve a bed height of 8 cm and washed with 2M HCl to remove excess organic solvent. An aliquot of Ce(IV) in acetate buffer (10 mL) was passed through the column (pre-adjusted to pH = 5.0) at a flow rate of 1.0 mL min<sup>-1</sup>. After extraction, Ce(IV) was eluted with suitable eluents and the amount of Ce(IV) in each fraction was determined complexometrically.

## Results and discussion

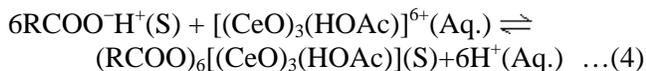
#### Effect of pH on cerium(IV) extraction

The extraction of Ce(IV) was studied within the pH range 2.5-6.5 in presence of 0.1M acetate buffer. Quantitative extraction of Ce(IV) was observed at pH 4 - 6. Common anions like Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> do not have any interference upon the extraction. In acetate buffer (pH: 4 - 6), the ceric ion remains mainly as trimeric species<sup>19</sup> (Eqs. 1-3).





Being of suitable size and charge (+6) the trimeric species goes to the exchange site as per the suggested path (Eq. 4):



The absence of sharp peak at  $1700 \text{ cm}^{-1}$  and appearance of a new peak at  $1595 \text{ cm}^{-1}$  in the FTIR spectrum of cerium adsorbed exchanger (spectrum not shown), clearly indicates the presence of carboxylate anion<sup>17</sup> in the metal loaded sample. At low  $p\text{H}$  ( $<4.0$ ), the equilibrium (Eq. 4) shifts towards left, while ceric remains as monomeric species having lower charge (+3). As a result, quantitative extraction of Ce(IV) does not take place at low  $p\text{H}$  and the ion passes through with the mobile phase smoothly at  $p\text{H} \leq 2.5$ . At higher  $p\text{H}$  ( $>6.0$ ), the ceric salt undergone hydrolysis and does not participate in the exchange process.

#### Selection of eluent for Ce(IV) and diverse metal ions

Systematic studies on stripping gives the quantitative elution of Ce(IV) with  $\text{HNO}_3$  ( $\geq 0.005\text{M}$ ),  $\text{H}_2\text{SO}_4$  ( $\geq 0.003\text{M}$ ),  $\text{HCl}$  ( $\geq 0.003\text{M}$ ) and  $\text{CH}_3\text{COOH}$  ( $\geq 0.05\text{M}$ ). The stripping (elution) follows the reverse path of extraction (Eq. 4). Thus, organic acid ( $\text{CH}_3\text{COOH}$ ), being weak electrolyte is less efficient than that of inorganic acids used. Among inorganic acids,  $\text{HNO}_3$  is less active as compared to both  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ , due to its lower complex formation ability. The complex formation ability of different anions with Ce(IV) follows the order<sup>19</sup>:  $\text{Cl}^- \approx \text{SO}_4^{2-} > \text{NO}_3^- > \text{CH}_3\text{COO}^-$ . The elution of diverse metal ions has been carried out with different acids. It was found that Al(III) and Cd(II) were stripped quantitatively with  $0.02$  and  $0.1\text{M}$   $\text{H}_2\text{SO}_4$  respectively, and Pb(II) and Zr(IV) with  $0.01$  and  $8.5\text{M}$   $\text{HNO}_3$  respectively. Similarly, quantitative elution of U(VI) with  $0.5\text{M}$   $\text{CH}_3\text{COOH}$ , Hg(II) with  $0.1\text{M}$   $\text{HNO}_3$  and  $0.05\text{M}$   $\text{H}_2\text{SO}_4$ , V(IV) with  $0.1\text{M}$   $\text{CH}_3\text{COOH}$ , Th(IV) with  $0.5\text{M}$   $\text{HNO}_3$  and  $3.0\text{M}$   $\text{CH}_3\text{COOH}$ , Ga(III) with  $0.5\text{M}$   $\text{HNO}_3$ , and Fe(III) with  $0.5\text{M}$   $\text{HNO}_3$  and  $0.05\text{M}$   $\text{H}_2\text{SO}_4$  were observed. These eluents were used throughout the experiments. The requirement of different acids for stripping various diverse metal ions may be attributed to the differences in interaction between metal ion and exchanger. Stronger

interaction requires higher acid concentration for qualitative elution of that metal ion.

#### Method of Ce(IV) separation from binary mixtures

It was possible to separate Ce(IV) from several metal ions present in binary mixture by exploiting the differences in  $p\text{H}$  for extraction and by using selective stripping agents. Each binary mixture was prepared by mixing an aliquot of standard solution of Ce(IV) ( $3.39 \text{ mg mL}^{-1}$ ) and one of the diverse metal ions in acetate buffer at desired  $p\text{H}$  (Table 1). When the binary mixture ( $\text{Ce}^{\text{IV}} + \text{Fe}^{\text{III}}$ ) or ( $\text{Ce}^{\text{IV}} + \text{Zr}^{\text{IV}}$ ) was passed through the column at  $p\text{H}$  2.5, both Fe(III) and Zr(IV) were extracted into the bed and Ce(IV) passed through with the mobile phase. The retention of zirconium(IV) and iron (III), and exclusion of cerium(IV) at  $p\text{H}$  2.5 may be due to difference in charge of the hydrated metal ions. The effective charge of the hydrated metal ions at  $p\text{H}$  2.5 follows the order<sup>19</sup>:  $\text{Zr}(\text{IV}) (+8) > \text{Fe}(\text{III}) (+4) > \text{Ce}(\text{IV}) (+3)$ . The lower charge leads to exclusion of cerium(IV). Extracted Fe(III) and Zr(IV) were eluted quantitatively with  $0.5\text{M}$   $\text{HNO}_3$  and  $8.5\text{M}$   $\text{HNO}_3$  respectively. At  $p\text{H}$  5.0, Th(IV), Hg(II), Cd(II), Pb(II), Ga(III), U(VI), Al(III) and V(IV) were extracted quantitatively along with Ce(IV) from their respective binary mixtures except La(III), which passed with the mobile phase. Ce(IV) was eluted first from the column with the help of its selective eluents i.e.,  $0.02\text{M}$   $\text{HNO}_3$  for the systems  $\text{Ce}^{\text{IV}}/\text{Th}^{\text{IV}}$ ,  $\text{Ce}^{\text{IV}}/\text{Ga}^{\text{III}}$  and  $\text{Ce}^{\text{IV}}/\text{La}^{\text{III}}$ ;  $0.005\text{M}$   $\text{H}_2\text{SO}_4$  for  $\text{Ce}^{\text{IV}}/\text{Hg}^{\text{II}}$ ,  $\text{Ce}^{\text{IV}}/\text{Cd}^{\text{II}}$ ,  $\text{Ce}^{\text{IV}}/\text{Pb}^{\text{II}}$  and  $\text{Ce}^{\text{IV}}/\text{Al}^{\text{III}}$ ;  $0.1\text{M}$   $\text{CH}_3\text{COOH}$  for  $\text{Ce}^{\text{IV}}/\text{U}^{\text{VI}}$  and  $0.05\text{M}$   $\text{CH}_3\text{COOH}$  for  $\text{Ce}^{\text{IV}}/\text{V}^{\text{IV}}$ . Diverse metal ion Hg(II) was eluted with  $0.05\text{M}$   $\text{H}_2\text{SO}_4$ . Similarly, Pb(II), Th(IV) and Ga(III) ions were eluted with  $0.01$ ,  $0.5$  and  $0.5\text{M}$   $\text{HNO}_3$ , and Al(III) and Cd(II) with  $0.02\text{M}$  and  $0.1\text{M}$   $\text{H}_2\text{SO}_4$  respectively. V(IV) and U(VI) were eluted with  $0.1\text{M}$   $\text{CH}_3\text{COOH}$  and  $0.5\text{M}$   $\text{CH}_3\text{COOH}$  respectively. Required volume of each eluents is given in Table 1. After recovery, metal ions were determined complexometrically.

#### Application of the developed method

In order to assess the possible analytical applications the proposed method was applied for separation of Ce(IV) from multi-component synthetic mixtures containing cerium with different metal ions commonly associated with ores, alloys and industrial samples (Table 1). A clean separation of cerium(IV) from ternary synthetic mixture is exhibited by a representative elution curve (Fig. 2). The effectiveness of the proposed method was judged

Table 1 — Separations of Ce(IV) from metal ion mixtures. [Ce(IV) taken = 3.39 mg; Flow rate = 1.0 mL min<sup>-1</sup>; pH = 5.0; Temp. = 25 °C]

Sample	Added (mg)	Recovered <sup>a</sup> (mg)	Recovery (%)	Eluent (M) (mL)	Sample	Added (mg)	Recovered <sup>a</sup> (mg)	Recovery (%)	Eluent (M) (mL)
Ce(IV)	3.39	3.41	100.58	0.02 HNO <sub>3</sub> , (70)	Ce(IV)	3.39	3.41	100.58	0.05 CH <sub>3</sub> COOH, (85)
Th(IV)	3.77	3.75	99.46	0.5 HNO <sub>3</sub> , (50)	V(IV)	2.06	2.08	100.97	0.1 CH <sub>3</sub> COOH, (80)
Ce(IV)	3.39	3.37	99.41	0.005 H <sub>2</sub> SO <sub>4</sub> , (40)	Ce(IV)	3.39	3.40	100.29	0.02 HNO <sub>3</sub> , (70)
Hg(II)	3.95	3.99	101.01	0.05 H <sub>2</sub> SO <sub>4</sub> , (70)	La(III)	3.60	3.57	99.16	-----, (---)
Ce(IV)	3.39	3.41	100.58	0.05 H <sub>2</sub> SO <sub>4</sub> , (40)	Ce(IV)	3.39	3.42	100.88	0.02 HNO <sub>3</sub> , (70)
Cd(II)	3.50	3.52	100.57	0.1 H <sub>2</sub> SO <sub>4</sub> , (30)	Th(IV)	3.77	3.73	98.93	0.5 HNO <sub>3</sub> , (50)
Ce(IV)	3.39	3.38	99.70	0.005 H <sub>2</sub> SO <sub>4</sub> , (40)	Zr(IV) <sup>b</sup>	2.49	2.51	100.80	8.5 HNO <sub>3</sub> , (80)
Pb(II)	3.10	3.13	100.96	0.01 HNO <sub>3</sub> , (50)	Ce(IV)	3.39	3.38	99.70	0.1 CH <sub>3</sub> COOH, (75)
Ce(IV)	3.39	3.37	99.41	-----, (---)	U(VI)	2.76	2.73	98.91	0.5 CH <sub>3</sub> COOH, (60)
Fe(III) <sup>b</sup>	3.40	3.43	100.88	0.50 HNO <sub>3</sub> , (40)	Hg(II)	3.95	3.97	100.50	0.1 HNO <sub>3</sub> , (60)
Ce(IV)	3.39	3.42	100.88	0.02 HNO <sub>3</sub> , (70)	Ce(IV)	3.39	3.42	100.88	0.05CH <sub>3</sub> COOH, (85)
Ga(III)	2.63	2.61	99.23	0.5 HNO <sub>3</sub> , (40)	V(IV)	2.06	2.04	99.02	0.1 CH <sub>3</sub> COOH, (80)
Ce(IV)	3.39	3.37	99.41	0.1 CH <sub>3</sub> COOH, (75)	Th(IV)	3.77	3.79	100.53	3.0 CH <sub>3</sub> COOH, (80)
U(VI)	2.76	2.78	100.72	0.5 CH <sub>3</sub> COOH, (60)	Ce(IV)	3.39	3.41	100.58	0.005 H <sub>2</sub> SO <sub>4</sub> , (40)
Ce(IV)	3.39	3.41	100.58	-----, (---)	Cd(II)	3.50	3.48	99.42	0.1H <sub>2</sub> SO <sub>4</sub> , (30)
Zr(IV) <sup>b</sup>	2.49	2.46	98.79	8.5 HNO <sub>3</sub> , (80)	Fe(III) <sup>b</sup>	3.40	3.38	99.41	0.05 H <sub>2</sub> SO <sub>4</sub> , (40)
Ce(IV)	3.39	3.40	100.29	0.005 H <sub>2</sub> SO <sub>4</sub> , (40)	Ce(IV)	3.39	3.36	99.11	0.02 HNO <sub>3</sub> , (70)
Al(III)	3.22	3.19	99.06	0.02 H <sub>2</sub> SO <sub>4</sub> , (50)	Hg(II)	3.95	3.92	99.24	0.1 HNO <sub>3</sub> , (60)
					Th(IV)	3.77	3.74	99.20	0.5 HNO <sub>3</sub> , (50)
					Ce(IV)	3.39	3.42	100.88	0.02 HNO <sub>3</sub> , (70)
					Ga(III)	2.63	2.61	99.23	0.5 HNO <sub>3</sub> , (40)
					Fe(III) <sup>b</sup>	3.41	3.38	99.12	0.5 HNO <sub>3</sub> , (40)
					Zr(IV) <sup>b</sup>	2.49	2.47	99.19	8.5 HNO <sub>3</sub> , (80)
					Ce(IV)	3.39	3.42	100.88	0.1 CH <sub>3</sub> COOH, (75)
					U(VI)	2.76	2.73	98.91	0.5 CH <sub>3</sub> COOH, (60)
					Th(IV)	3.77	3.80	100.79	3.0 CH <sub>3</sub> COOH, (80)
					Fe(III) <sup>b</sup>	3.40	3.43	100.88	0.5 HNO <sub>3</sub> , (40)

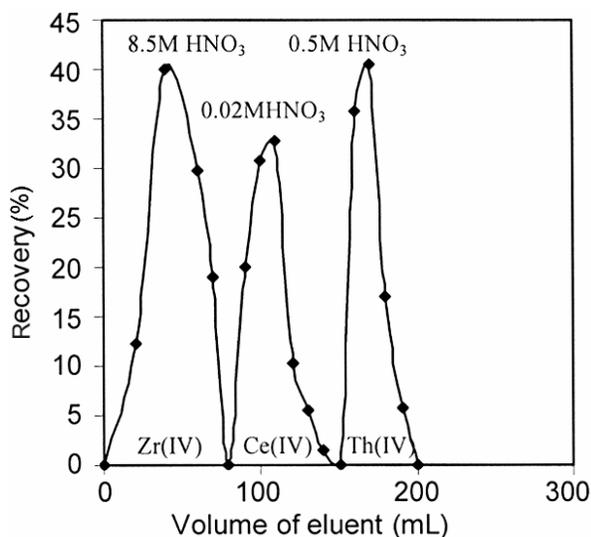
<sup>a</sup>Average of three determinations<sup>b</sup>pH = 2.5

Fig. 2 — Elution profile of Ce(IV), Th(IV) and Zr(IV) mixture.

using several minerals, digested by standard procedure<sup>19</sup> (Table 2). Results show high degree of effectiveness and utility of the proposed method.

Table 2 — Separation of Ce(IV) from real samples

Samples	Found <sup>a</sup> (%)	Cert. comp. (%)	Rel. error (%)
Monazite (71 bG)	CeO <sub>2</sub> : 20.50 Ce: 62.41	CeO <sub>2</sub> : 21.40; ThO <sub>2</sub> : 06.20	-4.21 (s.d. = 0.32)
Bastnasite (JBFM)	Ce: 09.60	Ce: 63.94; La: 10.15	-2.40 (s.d. = 0.26)
Al-Ce alloy (MM 10)		Ce: 10.00; Al: 90.00	-4.00 (s.d. = 0.31)

<sup>a</sup>Average of three determinations

The proposed method is simple, rapid, selective and economic. It needs only 2.5 hours for complete separation and estimation. It was found that exchanger bed could be used more than 40 cycles with its full exchange capacity. The exchange and break-through capacity of the prepared cation exchanger are considerably higher than the commercially available Versatic-10, SRS-100 and *n*-capric acid. The developed exchanger functions well in the temperature range 20-40 °C and pH range 4.0-6.0 with respect to Ce(IV). Clear separation of

Ce(IV) have been achieved from several toxic and heavy metal ions (Fe(III), Zr(IV), U(VI), Th(IV), V(IV), Hg(II), Pb(II), Cd(II), Ga(III) and Al(III)). Results achieved are satisfactory and recovery of Fe(III), Zr(IV), U(VI), Th(IV), V(IV), Hg(II), Pb(II), Cd(II), Ga(III) and Al(III) were quantitative.

### References

- 1 Sarkar M, Das M & Datta P K, *Atom Spectrosc*, 26 (2005) 221.
- 2 Sarkar M, Das M & Datta P K, *J Coll Interf Sci*, 246 (2002) 263.
- 3 Vogel A I, *Quantitative Inorganic Analysis*, 3<sup>rd</sup> Edn, (Longmans, London) 1961, p. 341.
- 4 Chowdhury P, Ali A, Kundu T & Ghosh A, *J Indian Chem Soc*, 84 (2007) 88.
- 5 Greenwood N N & Earnshaw A, *Chemistry of the Elements*, 2<sup>nd</sup> Edn. (Butterworth-Heineman, Oxford), 2005, p. 1232.
- 6 Wright C S, Fisher J, Thomsett D & Walton R I, *Angew Chem*, 118 (2005) 2502.
- 7 Roy U S & Modak S C, *J Indian Chem Soc*, LIX (1982) 392.
- 8 Datta K K & Roy U S, *J Indian Chem Soc*, 81 (2004) 898.
- 9 Ghosh K & Roy U S, *J Indian Chem Soc*, 28 (1989) 1125.
- 10 Mandal B & Roy U S, *J Indian Chem Soc*, 76 (1999) 304.
- 11 Mitra K & Roy U S, *J Indian Chem Soc*, 69 (1992) 563.
- 12 Kavlak S, Kaplam H & Guner A, *J Appl Polym Sci*, 92 (2004) 2698.
- 13 Rivas B L, Quilodran B & Quiroz E, *J Appl Polym Sci*, 99 (2006) 697.
- 14 Chowdhury P & Ali A, *J Polym Mater*, 22 (2005) 277.
- 15 Shukla S & Baja A K, *J Appl Polym Sci*, 102 (2006) 84.
- 16 Huang J, Huang Z M, Bao Y Z, & Weng Z X, *J Appl Polym Sci*, 100 (2006) 1594.
- 17 Dyer J H, *Applications of Absorption Spectroscopy of Organic Compounds*, 8<sup>th</sup> Indian Printing, (Prentice Hall, New Delhi) 1991, p. 33.
- 18 Billmeyer F W, Jr, *Text Book of Polymer Science*, 3<sup>rd</sup> Edn, (John Wiley and Sons, New York), 1984, p. 387.
- 19 Sarkar R, *General and Inorganic Chemistry, Part II*, 1<sup>st</sup> Edn, (New Central Book Agency, Kolkata), 2003, p. 1102.