Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.808468

52 (2014) 452–458
January

Taylor & Francis
Taylor & Francis Group

Amberlite XAD-2 impregnated with Cyanex272 for zirconium(IV) enrichment followed by spectrophotometric determination

Manjusha Karve*, Jayram V. Gholave

Department of Chemistry, University of Mumbai, Vidyanagari, Mumbai 400098, India
Tel. +91 22 26543569; Fax: +91 22 26528547; email: manjusha@chem.mu.ac.in

Received 16 April 2012; Accepted 29 April 2013

ABSTRACT

A solid-phase extraction method for zirconium(IV) enrichment in nitric acid media using a column packed with Amberlite XAD-2 impregnated with Cyanex272 is proposed. The optimum conditions for quantitative sorption and desorption of zirconium(IV) were investigated. The method developed was applied for the isolation of zirconium(IV) from complex synthetic mixtures and an electronic scrap sample. A USGS standard soil sample (GXR-2) was validated for the separation and recovery of zirconium(IV). The limit of detection for zirconium(IV) was $3.2\,\mu g\,dm^{-3}$ and reusability for more than 27 cycles was observed with a relative standard deviation of 0.8%.

Keywords: Amberlite XAD-2; Cyanex272; Zirconium(IV); Electronic scrap

1. Introduction

Zirconium is an industrially important element used as a getter in vacuum tubes, in surgical appliances, photoflash bulbs, explosive primers, rayon spinnerets, lamp filaments and as an alloying agent in steel. In chemical industries, its extensive usage is on account of its corrosion resistance to common acids, alkalis and sea water. Zirconium has a low absorption cross-section for neutrons, and is therefore used for cladding fuel elements in the nuclear energy applications. Nuclear power generation utilizes more than 90% of zirconium metal [1], necessitating its isolation for reuse. Although solvent extraction has been extensively studied for separation and determination of zirconium [2], systematic studies for its solid-phase extraction are few.

A solid-phase extraction method using 1-(2-pyridylazo)-2-naphthol [PAN] impregnated on clinoptilite [3] for preconcentration of traces of zirconium(IV) was devised while zirconium was determined from tap, waste water and alloy sample using zirconium(IV)-imprinted silica [4]. Amberchrom CG-71 resin was modified with TODGA [N,N,N′N′-tetraoctyldiglycolamide] and TEHDGA [N,N,N′N′tetrakis-2-ethyhexyldiglycolamide] [5] and impregnated with N–benzoyl-N-phenylhydroxylamine for zirconium(IV) [6,7], while CMPO [octyl(phenyl)-N,N-diisobutylcabamoylmethylphosphine oxide] was impregnated on silica [8]. Duolite 101 and green algae modified with Alizarin Red S reagent had a sorption capacity of $0.55\,mmol\,g^{-1}$ and $0.26\,mmol\,g^{-1}$ for zirconium(IV), respectively [9]. The sorbent α-ben-

---

*Corresponding author.

Presented at the DAE—BRNS Biennial Symposium on Emerging Trends in Separation Science and Technology (SESTEC 2012) Mumbai, India, 27 February–1 March 2012

zoin oxime was impregnated on Amberlite XAD-2000 for solid-phase extraction of zirconium(IV) [10]. A liquid cation exchanger impregnated sorbent for solid-phase extraction and determination of zirconium(IV) was lacking. Our earlier work on an impregnated resin was encouraging [11]. Hence in the present work we prepared a sorbent using Amberlite XAD-2 immobilized with Cyanex272 [bis(2,4,4-trimethylpentyl)phosphinic acid]. The solid phase was used to preconcentrate zirconium(IV) and applied for its determination from electronic scrap sample and multicomponent mixtures. The method developed for separation of zirconium(IV) was validated using a USGS standard soil sample GXR-2.

2. Experimental

2.1. Instrumentation

A glass column of 150 mm length and 10 mm internal diameter was used for the packing of the solid phase. A digital balance (Mettler Toledo, Model-AB204) was used for weighing. Digispec-110D visible spectrophotometer was used for metal detection. A flame atomic absorption spectrophotometer (FAAS), AAnalyst200 (Perkin Elmer) and an inductively coupled plasma atomic emission spectrometer (ICP-AES), JY JOBIN YVON HORIBA ULTIMA 2 were also used.

2.2. Chemicals and reagents

A stock solution containing 1.0 mg mL^{-1} zirconium (IV) was prepared from zirconyl nitrate monohydrate $ZrO(NO_3)_2.H_2O$ (Loba Chemie). It was standardized complexometrically [12] and a working solution containing 20 μg mL^{-1} of zirconium(IV) was prepared by appropriate dilution. An aqueous solution of arsenazo(III) (0.1% w/v) (S.d. Fine Chemicals) was used for spectrophotometric determination of zirconium(IV). Amberlite XAD-2 (20–60 mesh size, 0.41 mL pore/mL, 90 Å mean pore diameter and 330 m^2 g $^{-1}$ average surface area) obtained from Supelco, Sigma Aldrich Co. was pretreated by washing with 2 M HNO_3, 2 M HCl, distilled water and acetone to remove the impurities and air-dried prior to use [13]. Cyanex272 was obtained as a gift sample from Cytec Canada. All chemicals and reagents used were of AR grade.

2.3. Preparation of Cyanex272-impregnated Amberlite XAD-2 resin

To prepare the impregnated resin, Amberlite XAD-2 resin (100 mg) and Cyanex272 (100 mg) in methanol were mixed together till it resulted in almost complete evaporation of methanol. The XAD-2-impregnated Cyanex272 resin was then kept overnight at room temperature and uniformly packed in a glass column (150 mm length and 10 mm internal diameter) with glass wool as support. The amount of Cyanex272 sorbed on the resin was evaluated by washing the resin with a known volume of methanol to completely elute the extractant and which was subsequently titrated with sodium hydroxide.

2.4. General procedure for sorption of zirconium(IV)

The column containing the sorbent was preconditioned with 10 bed volumes of 0.01 M HNO_3. A 10.0 mL sample solution containing 2.0 μg mL^{-1} zirconium(IV) in 0.01 M HNO_3 was passed through the column at a flow rate of 1.0 mL min^{-1}. Zirconium(IV) was then recovered with 10.0 mL of 1.5 M H_2SO_4 at a flow rate of 0.2 mL min^{-1} and determined spectrophotometrically using 0.1% arsenazo(III) at 670 nm [14].

2.5. Procedure for the analysis of USGS standard soil GXR-2 and electronic scrap sample

A 1.0 g of USGS standard soil sample, GXR-2 was treated with HF and HNO_3 in 1:5 ratio in a Teflon beaker at 150°C [15]. After complete digestion, the residue was extracted with double distilled water. An aliquot from this diluted solution was used to extract iron(III) with diethyl ether to eliminate its interference [16] during zirconium(IV) sorption. The aqueous phase was used for the determination of zirconium (IV) using the general procedure.

A 0.1 g sample of scrap material obtained from electronic wastes was fused with sodium peroxide at 550°C [17] and was repeatedly extracted and digested with 1:1 HNO_3 and finally made to a suitable volume with double distilled water. A known aliquot of sample containing zirconium(IV) was then passed through the column under its optimum sorption conditions and determined as mentioned above.

3. Results and discussion

3.1. Influence of amount of Cyanex272

Amberlite XAD-2 (100 mg) was impregnated with varying amounts of Cyanex272 (25–100 mg) in order to understand its influence on sorption of zirconium (IV). Each sorbent prepared was packed in a column and 20 μg zirconium(IV) in 0.01 M HNO_3 solution was passed at a flow rate of 1.0 mL min^{-1} and determined as per the general procedure. These studies indicated that 100 mg of Cyanex272 was sufficient for impregnating 100 mg of Amberlite XAD-2 to achieve quantitative sorption (99.2 ± 0.7)% of zirconium(IV) (Fig. 1). The amounts lower than 100 mg of Cyanex272 might be inadequate for complete pore filling of the resin, thus reducing the accessibility for complexation of zirconium(IV). Further studies were carried out using 100 mg Cyanex272 impregnated on 100 mg Amberlite XAD-2 resin.

3.2. Effect of aqueous phase acidity

The influence of aqueous-phase acidity on the sorption of zirconium(IV) was systematically studied using (0.0001–1.0) M of different mineral acids. The results presented in Fig. 2 indicate that zirconium(IV) was quantitatively sorbed from 0.01 M HNO_3 and 0.01 M HCl. However, further studies were carried out using 0.01 M HNO_3 as the aqueous phase.

3.3. Influence of aqueous phase flow rate

A sample solution (10.0 mL) containing 2.0 μg mL^{-1} zirconium(IV) in 0.01 M HNO_3 was passed through the column at (0.5–5.0) mL min^{-1} aqueous-phase flow rate. Sorption of zirconium(IV) was quantitative with a flow rate of 1.0 mL min^{-1}. Zirconium(IV) sorption was (94.2 ± 0.8)% at 2.0 mL min^{-1} while, at a sample flow rate of 5.0 mL min^{-1} it was (77.7 ± 1.6)%. The observed decrease in sorption of zirconium(IV) may be due to its insufficient contact with the impregnated resin. Hence, an optimum sample flow rate of 1.0 mL min^{-1} was maintained throughout the studies.

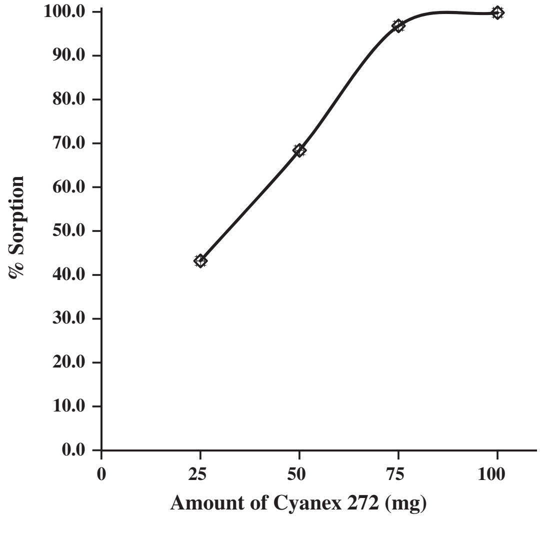

Fig. 1. Effect of amount of Cyanex272 on sorption of zirconium(IV).
Experimental condition: column packed with 100 mg Amberlite XAD-2 impregnated with different amount of Cyanex272. Aqueous phase condition = 20 μg zirconium(IV) in 10.0 mL 0.01 M HNO_3, 1.0 mL min^{-1} flow rate ($N = 3$).

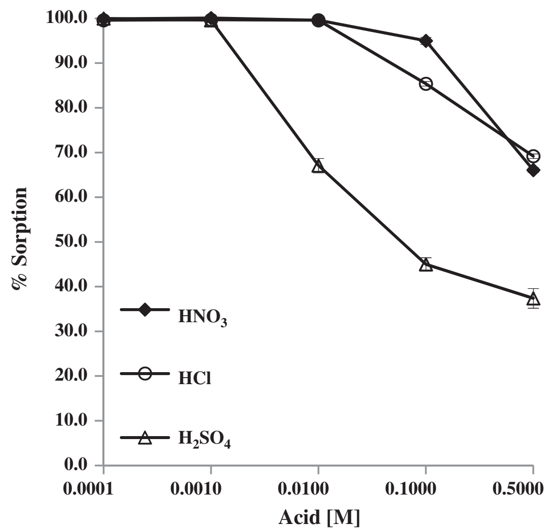

Fig. 2. Effect of aqueous phase acidity on sorption of zirconium(IV).
Experimental condition: column packed with 100 mg Amberlite XAD-2 impregnated with 100 mg Cyanex272. Aqueous phase condition = 20 μg zirconium(IV) in 10.0 mL, 1.0 mL min^{-1} flow rate ($N = 3$).

3.4. Breakthrough volume

Sample volumes (10–100) mL containing 20 μg zirconium(IV) were passed through the column packed with the impregnated resin at the optimum flow rate. Using these sample solutions, not more than (0.01 ± 0.007) μg mL^{-1} zirconium(IV) was detected in the aqueous solution. A plot of sample volume vs. percent sorption of zirconium(IV) (Fig. 3) indicated that the breakthrough volume for zirconium(IV) was greater than 100 mL.

3.5. Influence of various eluting agents on desorption of zirconium(IV)

Various eluents were systematically studied to understand the desorption of zirconium(IV) from the column (Table 1). Higher concentrations of HNO_3 and H_2SO_4 were not studied as preliminary experiments indicated leaching of the extractant from the impregnated resin. Recovery of zirconium(IV) was quantitative (98.6 ± 0.9)% with 1.5 M H_2SO_4 and (97.3 ± 0.3)% with 0.1 M $H_2C_2O_4$. Preliminary studies with 0.1 M $H_2C_2O_4$ showed possible leaching of Cyanex272 from impregnated resin Hence, we selected 1.5 M H_2SO_4 to optimize the elution conditions. Different volumes (5.0–20.0) mL and flow rates (0.2–1.0) mL min^{-1} of

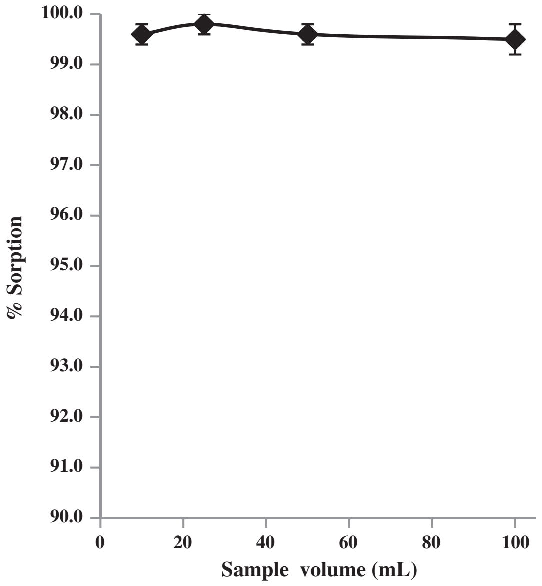

Fig. 3. Breakthrough volume.
Experimental condition: column packed with 100 mg Amberlite XAD-2 impregnated with 100 mg Cyanex272. Aqueous phase condition = 20 µg zirconium(IV) in 0.01 M HNO_3, 1.0 mL min^{-1} flow rate ($N = 3$).

1.5 M H_2SO_4 were studied. 5.0 mL of 1.5 M H_2SO_4 could recover only (90.9 ± 0.5)% of zirconium(IV) at a flow rate 0.2 mL min^{-1}, while (96.3 ± 0.8)% zirconium (IV) was recovered with 10.0 mL of 1.5 M H_2SO_4 at a flow rate of 0.4 mL min^{-1}. Hence, the eluent used for zirconium(IV) throughout the studies was 10.0 mL, 1.5 M H_2SO_4 at 0.2 mL min^{-1} flow rate.

3.6. Preconcentration factor

Sorption of zirconium(IV) was quantitative even from 100 mL of aqueous phase, while quantitative recovery was achieved using 10.0 mL of 1.5 M H_2SO_4, resulting in a preconcentration factor of 10 for zirconium(IV).

3.7. Column bed reusability

The stability and potential reusability of the column was assessed by monitoring the change in sorption of zirconium(IV) through a number of sorption – desorption cycles under the optimum conditions using the same column. The eluent used was 1.5 M H_2SO_4 at 0.2 mL min^{-1} flow rate. The sorption of zirconium(IV) was (98.1 ± 0.8)% and it remained unchanged even after continuous usage up-to 27

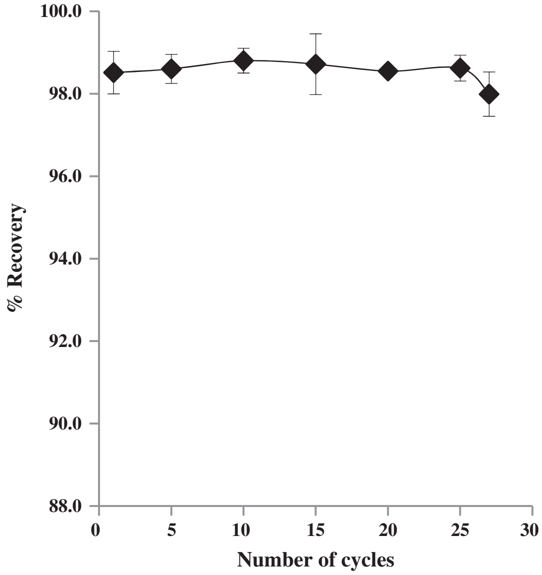

Fig. 4. Column bed reusability.
Experimental condition: column packed with 100 mg Amberlite XAD-2 impregnated with 100 mg Cyanex272. Aqueous phase condition = 20 µg zirconium(IV) in 10.0 mL 0.01 M HNO_3, 1.0 mL min^{-1} flow rate; Elution condition = 10.0 mL of 1.5 M H_2SO_4, 0.2 mL min^{-1} flow rate ($N = 3$).

Table 1
Influence of eluting agents Aqueous phase condition = 20 µg zirconium(IV) in 10.0 mL 0.01 M HNO_3, 1.0 mL min^{-1} flow rate; elution condition = 10.0 mL at 0.2 mL min^{-1} flow rate

% Recovery ± *s*								
Conc. [M] →Eluents ↓	0.01	0.1	0.5	1.0	1.5	2.0	3.0	4.0
HCl	0.5 ± 0.5	3.9 ± 3.9	13.1 ± 0.9	25.0 ± 1.0	22.3 ± 0.4	19.7 ± 1.5	14.7 ± 1.1	0.2 ± 0.2
HNO_3	1.6 ± 0.7	11.7 ± 1.2	35.4 ± 1.1	44.9 ± 0.8	–	–	–	–
H_2SO_4	39.4 ± 3.2	68.1 ± 0.7	81.4 ± 0.9	93.7 ± 0.7	98.6 ± 0.9	98.2 ± 0.8	–	–
$HClO_4$	0.3 ± 0.3	3.9 ± 0.2	0.2 ± 0.3	0.2 ± 0.3	0.1 ± 0.5	0.0 ± 0.0	0.2 ± 0.2	0.3 ± 0.3
CH_3COOH	0.6 ± 0.5	7.0 ± 7.0	13.9 ± 1.0	28.6 ± 0.5	21.8 ± 0.6	15.1 ± 1.2	11.7 ± 0.7	10.7 ± 1.2
$H_2C_2O_4$	71.2 ± 1.8	97.3 ± 0.3	95.8 ± 0.7	92.8 ± 1.1	–	–	–	–

Note: *s* = S. D. ($N = 3$).

cycles (Fig. 4) indicating a good reusability and reliability of the resin.

3.8. Effect of diverse ions on sorption of zirconium(IV)

The influence of alkali, alkaline earths, transition metals and rare earth elements on the sorption of zirconium(IV) was studied under its optimum conditions. The tolerance limit was set as the amount of foreign ion required to cause ± 2.0% change in the recovery of zirconium(IV). Cations like sodium(I) and potassium(I) were tolerated in 1:250 and 1:125 ratios, respectively. Barium(II) and strontium(II) were tolerated in 1:25 ratio, while nickel(II) and lead(II) were tolerated in 1:12.5 ratio. Calcium(II), cobalt(II), manganese(II) and all the rare earth elements were tolerated in 1:5 ratio. The tolerance limit ratios for scandium(III), magnesium(II), zinc(II), cadmium(II) and copper(II) was 1:2.5. Iron(III) was tolerated in a 1:1.5 ratio only, owing to interference due to co-extraction. The anion F^- was tolerated in 1:50 ratio and Cl^- in 1:250 ratio, while NO_3^- and PO_4^{3-} were tolerated in 1:125 ratio. The tolerance limit ratio for SO_4^{2-} was 1:25. Citrate, tartarate and ascorbate were tolerated in 1:5 ratio.

3.9. Separation of zirconium(IV) in binary mixtures

Zirconium(IV) was separated from binary mixtures. The distribution ratio was calculated from the ratio of concentration of metal in solid phase to its concentration in the aqueous phase (D = [M]Org.:[M] Aq.). These results indicated that zirconium(IV) was almost completely retained by the column, while the sorption of the diverse ions was negligible under the optimum conditions resulting in very high separation factors ($\beta = D_{Zr}:D_M$) (Table 2).

3.10. Precision and detection limit

Precision of the method developed was investigated using optimum conditions for sorption and desorption of zirconium(IV) on column and expressed in terms of the relative standard deviation (RSD). Determination of the zirconium(IV) as per general procedure in six replicate experiments had a RSD of 0.8%. The limit of detection (LOD) evaluated, as three

Table 2
Separation of zirconium(IV) from binary mixtures Aqueous phase condition = 10.0 mL of 0.01 M HNO_3 containing 2.0 μg mL^{-1} zirconium(IV) + other metal ion, 1.0 mL min^{-1} flow rate; elution condition = 10.0 mL of 1.5 M H_2SO_4, 0.2 mL min^{-1} flow rate

Metal ion added	Concentration of metal (μg mL^{-1})	Metal ion unextracted (%) ± a	Recovery of zirconium(IV) (%) ± a	Separation factor (β) $\beta = D_{Zr}:D_M$
Na^+	500	99.3 ± 1.2	98.8 ± 0.6	1.168×10^4
K^+	250	99.0 ± 1.7	99.0 ± 0.5	1.014×10^4
Ca^{2+}	10	99.4 ± 0.2	98.8 ± 0.6	1.445×10^4
Mg^{2+}	5	98.4 ± 1.2	98.7 ± 0.6	4.572×10^3
Ba^2	50	97.2 ± 0.4	98.7 ± 0.2	2.706×10^3
Sr^{2+}	50	98.4 ± 0.2	98.8 ± 0.3	5.063×10^3
Pb^{2+}	25	99.2 ± 0.6	98.8 ± 0.6	8.733×10^3
Mn^{2+}	10	98.3 ± 0.5	98.6 ± 0.5	4.858×10^3
Co^{2+}	10	98.9 ± 0.1	98.8 ± 0.3	7.007×10^3
Ni^{2+}	25	98.6 ± 0.7	98.8 ± 0.5	5.662×10^3
Cu^{2+}	5	99.2 ± 0.2	99.0 ± 0.3	1.14×10^4
Zn^{2+}	5	98.9 ± 0.2	98.7 ± 0.4	6.864×10^3
Cd^2	5	98.6 ± 0.2	99.0 ± 0.2	7.145×10^3
Sc^{3+}	5	84.8 ± 3.9	98.8 ± 0.3	4.58×10^2
Y^{3+}	10	98.4 ± 0.6	98.8 ± 0.2	5.173×10^3
La^{3+}	10	98.8 ± 0.2	99.1 ± 0.3	9.328×10^3
Ce^{4+}	10	99.2 ± 0.3	98.9 ± 0.4	1.07×10^4
Pr^{3+}	10	97.7 ± 0.2	98.9 ± 0.2	3.999×10^3
Nd^{3+}	10	98.5 ± 0.3	98.8 ± 0.3	5.287×10^3
Dy^{3+}	10	99.3 ± 0.1	99.0 ± 0.2	1.453×10^3

Note: a = % RSD (N = 3).

Table 3
Separation of zirconium(IV) from synthetic mixtures Aqueous phase condition = 10.0 mL of 0.01 M HNO_3 containing 2.0 µg mL^{-1} zirconium(IV) + other metal ion, 1.0 mL min^{-1} flow rate; elution condition = 10.0 mL of 1.5 M H_2SO_4, 0.2 mL min^{-1} flow rate

Composition of mixture	Recovery of zirconium(IV) (%) ± *a*
Na(I);10 µg, K(I);5 µg, Zr(IV);20 µg	98.8 ± 0.3
Na(I);50 µg, Y(III);20 µg, Zr(IV);20 µg	98.8 ± 0.6
Sr(II);5 µg, Ca(II);20 µg, K(I);10 µg, Na(I);10 µg, Zr(IV);20 µg	98.7 ± 0.5
Ce(IV);15 µg, Fe(III);5 µg, Y(III);5 µg, Ca(II);15 µg, Na(I);20 µg, Zr(IV);20 µg	99.1 ± 0.3

Note: *a* = % RSD (*N* = 3).

times the standard deviation of the blank signal [18] was 3.2 µg L^{-1}.

4. Analytical applications

4.1. Separation of zirconium(IV) from synthetic mixtures

The method developed was applied to separate and recover zirconium(IV) from synthetic mixtures containing elements commonly associated with it. These elements were not sorbed under the optimum conditions for sorption of zirconium(IV) and were quantitatively determined in the aqueous phase by FAAS or ICP-AES. While the recovery of zirconium (IV) was quantitative with an RSD of not more than 0.8% (Table 3).

4.2. Recovery of zirconium(IV) from electronic scrap

The applicability of the method developed was checked using an aliquot of sample prepared as described in experimental Section 2.5. The amount of zirconium(IV) detected in electronic scrap was (604.3 ± 0.49) mg g^{-1} as against 612.5 mg present in it (Table 4). This result using sample solution was cross-checked by ICP-AES analysis and corresponded to a (98.6 ± 0.8)% recovery for zirconium(IV) and had RSD within 0.8%.

Table 4
Aqueous phase condition = an aliquot of sample in 0.01 M HNO_3, 1.0 mL min^{-1} flow rate; elution condition = 10.0 mL of 1.5 M H_2SO_4, 0.2 mL min^{-1} flow rate

Sample	Concentration of zirconum(IV) ± s (mg g^{-1}) (proposed method)	Concentration of zirconum(IV) (mg g^{-1}) (ICP-AES)	Recovery (%) ± a zirconum(IV) (proposed method)
Electronic scrap sample	604.3 ± 0.49	612.5	98.6 ± 0.8
GXR-2	0.259 ± 0.001	0.263	98.8 ± 0.4

Note: *s* = Standard deviation *a* = % RSD (*N* = 3).

Table 5
Summary of solid phase extraction methodologies developed for zirconium(IV)

Solid support/ligand	P. F.	Reusability (No. of cycles)	LOD (µg L^{-1})	Breakthrough volume (mL)/Sample flow rate (mL min^{-1})	Ref.
Clinoptilite/PAN	130	15	0.1	650/2	(3)
Silica/zirconium imprinted	200	–	0.14	400/1	(4)
Duolite 101, Green Algae/alizarin Red S	–	15	0.2	500/1, 2	(9)
XAD-2000/α-benzoin oxime	100	–	0.48	1,000/10	(10)
XAD-2/Cyanex272	10	27	3.2	100/1	Present work

4.3. Method validation using USGS standard soil sample (GXR-2)

The method developed for separation and recovery of zirconium(IV) was validated using USGS standard soil sample (GXR-2) as mentioned in the experimental Section 2.5. The recovery of zirconium(IV) was (98.8 ± 0.4)% using the proposed method, indicating the suitability of the method developed for separation of zirconium(IV) from complex matrices like soil.

5. Conclusion

The method developed for sorption of zirconium (IV) using Amberlite XAD-2 resin impregnated with Cyanex272 is simple, selective and specific for isolation of traces of zirconium(IV). The solid-phase extraction methods for zirconium(IV) were compared (Table 5). The reusability of the column for several runs minimized the wastes. The method has a potential to separate zirconium(IV) from a host of associated elements with high separation factors. The method was successfully applied for the separation and determination of zirconium(IV) from real samples.

References

[1] David R. Lide, CRC Handbook of Chemistry and Physics, 89th ed., Taylor & Francis group, Boca Raton, FL, 2008.

[2] Y.K. Agrawal, S. Sudhakar, Extraction, separation and preconcentration of zirconium, Sep. Purif. Technol. 27 (2002) 111–119.

[3] H. Faghihian, M. Kabiri-Tadi, A novel solid-phase extraction method for separation and preconcentration of zirconium, Microchim. Acta 168 (2010) 147–152.

[4] X. Chang, X. Wang, N. Jiang, Q. He, Y. Zhai, X. Zhu, Z. Hu, Silica gel surface-imprinted solid-phase extraction of Zr(IV) from aqueous solutions, Microchim. Acta 162 (2008) 113–119.

[5] E.P. Horwitz, D.R. McAlister, A.H. Bond, R.E. Barrans, Novel extraction of chromatographic resins based on tetraalkyldiglycolamides: Characterization and potential applications, Solvent Extr. Ion Exch. 23 (2005) 319–344.

[6] X.J. Yang, C. Pin, Determination of niobium, tantalum, zirconium and hafnium in geological materials by extraction chromatography and inductively coupled plasma mass spectrometry, Anal. Chim. Acta 458 (2002) 375–386.

[7] X.J. Yang, C. Pin, A novel solid-phase extraction scheme for the group separation of high field strength elements (Nb, Ta, Zr, Hf) from Al-, Ti-, and Fe-rich geological materials, Sep. Sci. Technol. 36 (2001) 571–585.

[8] A. Zhang, Q. Hu, W. Wang, E. Kuraoka, Application of a macroporous silica-based CMPO-impregnated polymeric composite in group partitioning of long-lived minor actinides from highly active liquid by extraction chromatography, Ind. Eng. Chem. Res. 47 (2008) 6158–6165.

[9] M.M. Hassanien, Separation and preconcentration of zirconium and/or hafnium using alizarin Red S immobilized on natural or polymeric support, Sep. Sci. Technol. 40 (2005) 1621–1634.

[10] J.B. Ghasemi, E. Zolfonoun, Simultaneous spectrophotometric determination of trace amounts of uranium, thorium, and zirconium using the partial least squares method after their preconcentration by α-benzoin oxime modified Amberlite XAD-2000 resin, Talanta, 80 (2010) 1191–1197.

[11] M. Karve, R.V. Rajgor, Amberlite XAD-2 impregnated organophosphinic acid extractant for separation of Uranium (VI) from rare earth elements, Desalination 232 (2008) 191–197.

[12] F.J. Welcher, The Analytical Uses of Ethylenediaminetetraacetic Acid, D. Van Nostrand, New Jersey, NJ, 1978.

[13] H. Matsunaga, A.A. Ismail, Y. Wakui, T. Yokoyama, Extraction of rare earth elements with 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate impregnated resins having different morphology and reagent content, React. Funct. Polym. 49 (2001) 189–195.

[14] F.D. Snell, Photometric and Fluorometric Methods of Analysis of Metals, Part-2, John Wiley and Sons, New York, NY, 1978.

[15] K. Prasad, P. Gopikrishna, R. Kala, T. Prasada Rao, G.R.K. Naidu, Solid phase extraction vis-a-vis coprecipitation preconcentration of cadmium and lead from soils onto 5,7-dibromoquinoline-8-ol embedded benzophenone and determination by FAAS, Talanta, 69 (2006) 938–945.

[16] A.K. De, S.M. Khopkar, R.A. Chalmers, Solvent Extraction of Metals, Van Nostrand: Reinhold, London, 1970.

[17] W.F. Hillebrand, G.E.F. Lundell, Applied Inorganic Analysis of Metal, Minerals and Rocks, John Wiley and Sons, New York, 1953.

[18] D.A. Skoog, F.J. Holler, T.A. Nieman, Principles of Instrumental Analysis, 5th ed., Harcourt Brace and Company, Philadelphia, 1998.