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Separation and Preconcentration of Zirconium and/or Hafnium Using Alizarine Red S Immobilized on Natural or Polymeric Support

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Separation and Preconcentration of Zirconium and/or Hafnium Using Alizarine Red S Immobilized on Natural or Polymeric Support

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Abstract: Alizarine red S (ARS) is one of the most sensitive reagents used for the spectrophotometric determination of Zr/Hf (IV). Duolite 101 A as anion exchanger or green algae (Mougeatia species) were used for loading ARS as modified chelating agent. Selective enrichment of both Zr and Hf using the modified substrate under batch and column conditions were studied and discussed at different pH values as well as salinity (ionic strength), sorption kinetics, resin capacity, type of eluent, fluoride effect, breakthrough curves, and durability. Both the modified substrate sorbs Zr and/or Hf over a wide range of pH (2.5–8). The maximum sorption capacity for Zr/Hf were 0.26/0.27 mmol g^{-1} on modified algae and 0.55/0.57 mmol g^{-1} on Duolite resin at pH 3.5, respectively. The lowest detection limits of preconcentration ≈0.2 μgL^{-1} with a preconcentration factor for Zr or Hf were 200 fold. Iron (III), Cu(II), Th(IV), UO_2(II), and Ce(IV) are also sorbed with different extents, but Ba(II), Sr(II), Ca(II), Mg(II), Mn(II), Ni(II), Al(III), and Cr(III) are not sorbed at pH 3.5. Tolerance limits of NaF, NaCl, Na_2SO_4, Na_2HPO_4, and $NaNO_3$ on the sorption are reported. The use of fluoride ion and EDTA as masking agent and a citric-HCl mixtures as an eluent can overcome the metals interferences, leading to 99–100% recovery and selective enrichment of Zr or Hf. The relative standard deviation (RSD) of the separation and preconcentration of Zr and/or Hf on the two supports are in the range ≈1.7–2.4, respectively. Zirconium and Hafnium have been

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separated and preconcentrated from synthetic samples containing UO_2(II), Th(IV), and Ce(IV) ions and certified ores.

Keywords: Alizarine red S, zirconium, hafnium, Duolite 101 A, Mougeatia algae

1. INTRODUCTION

Solid-phase extraction (SPE) on the base of modified sorbents is found to be a simple and cost-effective tool for separation and preconcentration, enhancing detection and sensitivity of various compounds in complicated objects (1–3). The attraction of the SPE technique is to reduce solvent usage and exposure, disposal costs, and extraction time for sample preparation. Development for a more cost-effective remediation system is necessary. There has been a tremendous amount of attention given to the use of biological systems for removal of heavy metal ions from contaminated areas (4–8). Interest in using plants for environmental remediation is increasing due to their natural capacity by accumulating heavy metal ions and degrading organic compounds. Biological organisms such as algae, fungus erythrocytes, and bacteria are characterized by surface-rich functionality ranging from weak to strong anionic and cationic groups, and can be used to accumulate or preconcentrate heavy metal ions from aqueous solutions. This so-called biosorption process occurs when ions are adsorbed on the surface of the organism through interactions with some function groups such as carboxylate, hydroxyl, sulphate, phosphate, and amine. Both living and nonliving organisms as free cells or immobilized on a substrate can be used for biosorption. The lyophilized (dead) procedure is based on the fact that chemical species are retained on the external membrane of the cells (9). Application of chelating resins can be easily applied for separation and preconcentration of metal ions. Therefore, there is a continued interest in the synthesis of insoluble functionalized polymers that can provide good stability and selectivity, high sorption capacity for metal ions, and good flexibility in working conditions. Designing of the chelating resins for selective enrichment of some metal ions can be done by two methodologies: a) covalent coupling of a functionalized compound with a polymer through $-CH_2-$ or $-N{=}N-$ groups (10–17); b) sorption of chelating ligand onto neutral or anionic resins (18–23). The first one renders leaching out of the ligand and has a moderate capacity, but the second one has a high capacity and does not result in leaching.

Alizarine red S (ARS) has extractive properties and has frequently been used as a reagent for spectrophotometric determination of some metal ions (24–27).

The aim of this work is to develop an efficient, rapid, and low-cost method for selective solid phase extraction (SPE) and enrichment for both Zr and/or Hf ions from UO_2^{2+}, Th(IV), and Ce(IV) over Duolite 101 A anion exchanger or green algae (*Mougeatia* species) after modification with Alizarine red

S (ARS) through the reaction between anionic bond for Duolite 101 A and carboxylate, chloride, or phosphate groups on the surface of the green algae.

2. EXPERIMENTAL

2.1. Chemicals and Reagents

All reagents were of analytical grade. The stock solution (1 mg/mL) of Zr was prepared by dissolving 3.531 g of $ZrCl_4 \cdot 8H_2O$ in 0.1 M HCl (1 L) to prevent metal hydrolysis. The stock solution of Hf (1 mg/mL) was prepared by dissolving the product of fusing 1.17 g of HfO_2 with 1 g of $K_2S_2O_7$ at $\approx$1000°C in 0.1 M HCl (1 L). A 2% solution of Alizarine red S (ARS) was prepared in 10% ethanol-water mixture. Arsinazo III stock solution was prepared by dissolving 0.5 g in 100 mL of doubly distilled water. Buffer solutions (pH 3–8) were prepared by mixing 0.5 mol l^{-1} acetic acid and 0.1 mol l^{-1} NaOH, whereas pH values <3 were adjusted by using chloroacetic acid + HCl mixtures. A 0.5 mol l^{-1} citric acid was prepared by dissolving 10.5 g in 1 L doubly distilled water. Solutions of alkali metal salts (4%), sodium fluoride, sodium salt of EDTA, and various metal salts (0.1%) were used to study the interferences of anions and cations. The real samples of zirconium and hafnium ores were obtained from the National Institute of Metallurgy, South Africa.

2.2. Materials for Solid Supports

Anion exchanger beads Duolite A 101, particle size $\leq$1 mm, were purchased from Rohm and Haas. To attain its complete reactivity before interaction with ARS, the resin was washed with 0.05 mol l^{-1} HCl, distilled water, 0.05 mol l^{-1} NaOH solution, and doubly distilled water until obtaining pH 7. This was then filtered off and dried at 60°C for 12 hours. Green algae was kindly supplied by the Department of Botany, Faculty of Science, Mansoura University, Egypt. Algae was washed by water, twice by 0.01 mol l^{-1} HCl to remove any debris or soluble biomolecules that might interact with metal ions, then washed with 0.1% EDTA solution to remove any adsorbed metal ions, and finally with plenty of water. This was then filtered and oven-dried at 60°C for 1 day. Dried samples were grinded and sieved to give particle size $\leq$0.17 mm.

2.3. Preparation of ARS Modified Support

The resin or green algae was saturated with ARS chelating compound by mechanical shaking of 10 g resin or green algae preconditioned with buffer solution (pH 5), soaked for 6 hours, and washed with water. A volume of

100 mL of ARS (2%) was mechanically shacked with the conditioned solid substrates. The fading of the red color of ARS solution and coloration of the solid supports with intense red color were shaken as an indication to the progress of the reaction. The solid supports were centrifuged, decanted, filtered off, thoroughly washed with doubly distilled water, and finally dried.

2.4. Stability of the Modified Supports in Mineral Acids and NaCl Media

The modified supports (500 mg) loaded with ARS were packed in a column, and 50 mL of mineral acids (HCl, HNO_3, and $HClO_4$) or NaCl solution of known concentrations (Table 1) were passed through it with a flow rate of 1.5 mL/min^{-1}. The leached out amount of ARS appearing in the effluent was spectrophotometrically determined at 470 nm (28).

2.5. Recommended Procedure for Preconcentration of Zr and/or Hf

Both batch and column methods were used to concentrate trace of Zr and/or Hf ions.

2.5.1. Batch Method

The sample solution (200 mL of 10 μg/mL) of Zr and/or Hf was introduced in a glass-stoppered bottle (500 mL) after adjusting its pH to 3.5 in the presence

Table 1. Effect of acid concentration and ionic strength using NaCl solution on the ARS modified supports

Eluent	Concentration (mol l^{-1})	Release (ARS) %	
		Resin exchange	Algae
HCl	0.05	—	—
	0.1	2	0.3
	0.5	5	0.7
HNO_3	0.05	—	—
	0.1	1.5	0.4
	0.5	4.5	0.9
$HClO_4$	0.05	—	—
	0.1	1.2	0.6
	0.5	3.5	1.2
NaCl	0.1	—	—
	0.5	2	—
	1.0	4	—

of NaF and EDTA (2 mL of 0.01% each). The modified Duolite 101 A or algae (100 mg) was added to the bottle and the mixtures were shaken for 30 min. The solid phases were either filtered off, washed with water, dried and used for metal complex characterization, or eluted with a mixture of equivalent volume of 2.5 mL HCl (0.05 mol l^{-1}) + 2.5 mL citric acid (0.5 mol l^{-1}). The concentration of Zr and/or Hf in the eluate was determined spectrophotometrically by using ARS (28) or Arsenazo(III) (29).

2.5.2. Column Method

By a slurry method, a minicolumn of 0.5-cm diameter and 7-cm length was packed with 1.4 g of modified resin beads or 0.5 g of modified green algae, which was refreshed by washing with 0.05 mol l^{-1} HCl, then by distilled water, and finally with a mixture of NaF (2.5 mL of 0.001%), EDTA (2.5 mL of 0.001%), and 5 mL buffer (pH 3.5). Under the optimum conditions, 200 mL solution of Zr and/or Hf (0.5 μg mL^{-1}, each) were passed through the column with a flow rate of 2 mL/min^{-1}. The column was washed with water. A mixture of 2.5 mL HCl (0.05 mol l^{-1}) + 2.5 mL citric acid (0.5 mol l^{-1}) was used for stripping Zr and/or Hf with a flow rate of 1 mL/min^{-1} and the metal ions in the effluent were determined as explained above.

2.6. Apparatus

Spectrophotometric measurements were carried out on a Unicam UV2 spectrometer in the range 200–900 nm using 1 cm matched quartz cells. The concentration of the metal ion was determined with a Perkin-Elmer 2380 atomic absorption spectrometer. The infrared spectra were obtained using a Mattson 5000 FTIR spectrometer as KBr discs. The pH measurements were carried out with a Hanna Instrument 8519 pH-meter with a combined glass electrode. In column operation, a funnel-tipped glass column with a length of 10 cm and 0.5 cm diameter was used. A mechanical shaker having a speed control facility was used for batch equilibration.

3. RESULTS AND DISCUSSION

3.1. Characterization of Solid Supports with ARS and with Metal Ions

Qualitative analysis using FTIR was used to compare between the starting solid supports and those after loading with ARS and with the metal ions. The presence of characteristic bands of ARS at 1640 [ν(C=O)], 1332 [δ(OH)], 1304, 1215, 1192 [$\nu(SO_3^{2-})$], and 890 cm^{-1} [ν(C=S)] (30) vibrations indicate the chemical loading of ARS moiety. Also, the absorption spectra of the solid supports prepared at pH 3.5, in Nujol (mull), show an absorption band at 470 nm assigned to ARS moiety (28). This confirms the immobilization of ARS moiety on Duolite 101 A or green algae. The IR spectra of loaded solid supports with metal ions and those of free supports were compared and indicate no change in SO_3^{2-} bands, but both of the C=O and OH bands have a shift (10 cm^{-1}) to lower wavenumbers, indicating that the sorption mechanism is mainly through the chelation of metal ions via phenolic OH and keto groups.

Moreover, the electronic spectra of the metal loaded on solid supports in Nujol mull showed a blue shift in the absorption band of the free supports to 520 nm, confirming the IR data.

3.2. Effect of pH and Flow Rate

The influence of pH on the separation and preconcentration of both Zr and Hf was studied in the range of 1.5–8.0 using NaOH and HCl (0.1 mol l^{-1}) and sodium acetate (0.2 mol l^{-1}) for the pH adjustment taking into consideration that the zirconyl and hafnyl ions were hydrolyzed in the pH ca. 2.0. NaF was added to prevent the hydrolysis. Figure 1 shows that the modified supports were reached to maximum capacity in the pH range 2.5–8.0. The pH 3.5 is suitable for these studies to avoid hydrolysis and to obtain selective separation and preconcentration for the two ions from different media.

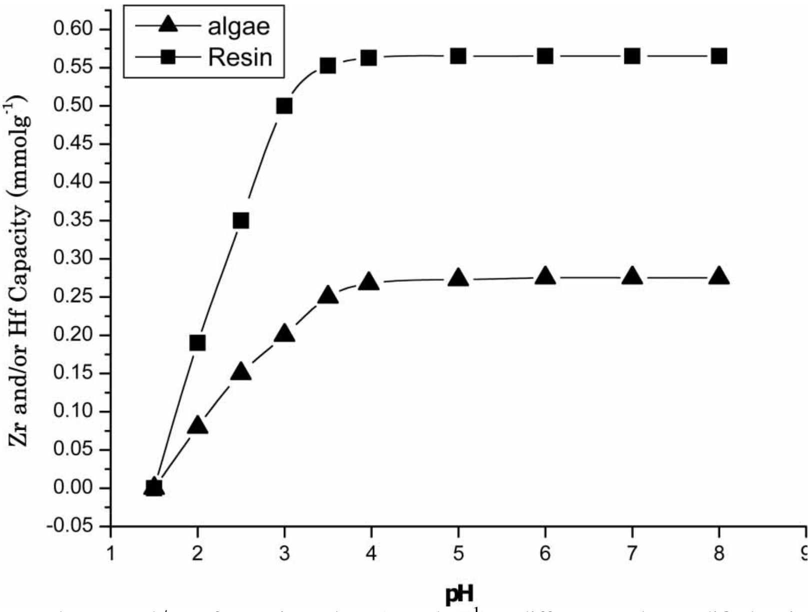

Figure 1. Zr and/or Hf capacity values (mmol g^{-1}) at different pH by modified resin and algae.

The effect of flow rate of samples and stripping solutions from the solid supports, i.e., retention and recovery in a minicolumn technique (0.4 mm and 7.00 cm length packed with modified resin or algae) was investigated. It is interesting to note that the adsorption of the metal ions was found quantitatively and reproducible in the range 1–5 mL min^{-1}. The flow rate was found to be 1.5 and 2 mL/min^{-1} for both Duolite exchanger and alga, respectively. On the other hand, quantitative stripping of the two ions achieves at 1.0 mL/min^{-1} flow rate by using 2.5 mL of both HCl (0.05 mol l^{-1}) and citric (0.5 mol l^{-1}).

3.3. Kinetics of Zr and/or Hf Sorption

The rate of sorption of both Zr and Hf on the solid supports was determined by batch experiments. A 100 mg of modified resin or algae was stirred with 100 mL solution containing 10 μg mL^{-1} of Zr and/or Hf at room temperature for time intervals 5, 10, 20, 30, 45 min. at pH 3.5 in the presence of NaF and EDTA. The data represented in Fig. 2, show complete loading in a time less than 15 min for each metal ion with relatively rapid sorption of the loaded algae than Duolite resin. The rapid uptake of metal ions in green algae compared with modified resin may be due to the small size particles (high surface area) and the hydrophilic character of green algae as well as the high metal accessibility of its chelating sites.

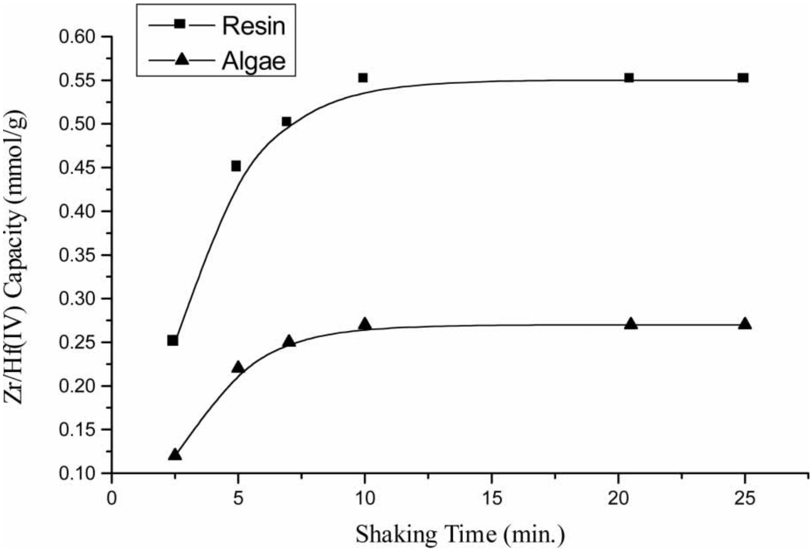

Figure 2. Zr and/or Hf capacity values (mmol g^{-1}) at different shaking times (min.) by modified resin and algae.

3.4. Total Sorption Capacity

A 0.5 g of resin beads or green algae was stirred for 12 hours in 100 mL solution containing 50 μg mL^{-1} of Zr and/or Hf at pH 3.5 in presence of NaF and EDTA. The metal ion concentration in the supernatant liquid was determined as mentioned. The sorption capacity of the resin for the two metal ions was ascertained from the difference between the metal ion concentration in the solution before and after sorption. The capacity of the modified supports was also determined by desorbing the metal ions with a mixture of HCl/citric acid. The values obtained from the two methods are similar for the two metal ions and are in the range 0.26 ± 0.01 and 0.55 ± 0.02 mmole g^{-1} for green algae and Duolite, respectively. The capacity of the two modified solid supports was also found to vary within 1.7–2.4% (RSD) for different batches of ARS/Duolite 101 A or ARS/algae. These values relatively indicate for the formation of 1:1 stoichiometric ratio of ARS:Zr and/or ARS:Hf, which is in good agreement with the capacity determined for ARS (0.55 and 0.27 mmol g^{-1}) loaded on both Duolite 101 A and green algae, respectively.

3.5. Stability and Reusability of the Modified Solid Supports

The resulting data in Table 1 show that 0.05 mol l^{-1} of all mineral acids are not sensitive to release any quantity of ARS, while 0.1–0.5 mol l^{-1} released ARS in a range of 1.2–4.5% for the modified support resin. The releasing amount decreases in the case of algae to the range 0.3–1.2%. Also, sodium chloride solution has no effect on the modified algae in the concentration range 0.1–1.0 mol l^{-1}, while in concentration greater than 0.1 mol l^{-1}, NaCl released ARS from the modified resin.

Zirconium and/or Hf ions were sorbed and desorbed several times in a batch technique by using powder algae or bead granular resin. It was found that the sorption capacity of both modifiers after 15 cycles of its equilibration with the two metal ions changes less than 1.0%. The modified resin is better than algae because its decay time is ca. 1 year, while algae must be used within 2 days. Its Low cost and safety make resin superior to algae. The modified supports can be regenerated by HCl/citric acid (0.05 and 0.5 mol l^{-1}).

3.6. Choice of Eluent

In order to choose a proper eluent for retained Zr and/or Hf ions, after extraction of 5 μg from 500 mL water by the proposed modified supports, the Zr and/or Hf were stripped with varying volumes of HCl, HNO_3, and H_2SO_4 (0.05 mol l^{-1}). The results show that all of the above acids are not stripped of any quantity of the retained Zr and/or Hf. The increase in acidity led to the increase in leaching out of the stripping of ARS from solid supports. Mixture of citric acid (0.5 mol l^{-1}) and HCl or H_2SO_4 or HNO_3 (0.05 mol l^{-1}) could afford the quantitative elution for both Zr and/or Hf from the modifiers. The results obtained show high similarity for the three acids, so Fig. 3 is taken as a representative example for the data of HCl only. The obtained data confirm that previously mentioned in literature (28), which shows that ARS reacts with Zr and Hf in the pH range 1–2 indicating that all acids in this pH have no effect on the stripping of metal ions. A mixture of citric/HCl is capable of stripping Zr and Hf due to the complex formation between citric and Zr and/or Hf in the recommended acidity.

The quantitative stripping of the retained Zr and Hf ions by modified supports was then studied by using various concentrations of citric and 0.05 mol l^{-1} HCl. Figure 3 shows that elution of Zr and Hf was quantitatively stripped with 2.5 mL HCl (0.05 mol l^{-1}) and 2.5 mL citric acid (0.5 mol l^{-1}).

3.7. Interferences

In order to investigate the selective separation and determination of Zr and/or Hf ions from its mixtures with diverse metal ions, an aliquot of aqueous

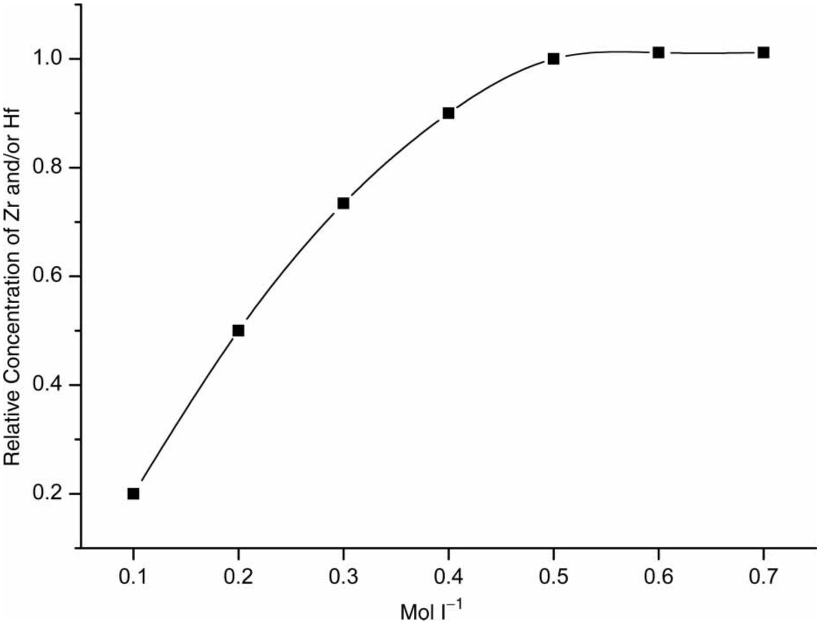

Figure 3. Elution of Zr and/or Hf as a function of concentration of citric acid (2.5 mL) at constant HCl concentration 0.05 mol l^{-1} (2.5 mL) of modified supports.

solution (100 mL) containing 10 μg Zr and/or Hf and interfering cations or anions in different concentrations was taken and the recommended procedure was followed. The results are summarized in Table 2. The results show that ($\leq$500 mgL^{-1}) Ca^{2+}, Mg^{2+}, or Sr^{2+} and ($<$50 mgL^{-1}) Ni^{2+}, Co^{2+}, Cd^{2+}, or Zn^{2+} do not interfere in the Zr/Hf separation by this procedure. Also, chloride, SO_4^-, NO_3^-, $H_2PO_4^-$, F$^-$, and Br$^-$ salts can be used without interference in the range 1%. However, Fe^{3+}, Al^{3+}, Ce^{4+}, UO_2^{2+}, and Th^{4+} interfere in the separation and selectivity of both Zr and Hf. The interference from Fe^{3+} and Al^{3+} can be eliminated using F$^-$ as masking agent. EDTA (0.01 mol l^{-1}) can overcome the interference of Cu^{2+}, In^{3+}, and Ga^{3+} where Ce^{4+} can be reduced to Ce^{3+} (nonleachable form) by using oxalate salt. The use of 0.05 mol l^{-1} HCl as eluent can selectively UO_2^{2+} and Th^{4+}, which cosorbed with Zr and Hf.

3.8. Analytical Performance and Application

In the utilization of a column, the breakthrough capacity is an important parameter that depends mainly on the Zr and/or Hf concentration. In order to obtain the breakthrough curve, the column was packed with solid supports while 0.05 mmol Zr and/or Hf solution buffered in pH 3.5 was passed at a flow rate of 1.5 mL/min^{-1}. The effluent received after time elapse of 10 min was fractionized in 5 mL portions and Zr and/or Hf was determined. The breakthrough curve Fig. 4 indicated that the column was exhausted with 500 and 700 mL of 0.05 mmol l^{-1} Zr and/or Hf for modified resin and green algae, respectively. To evaluate the feasibility of the separation procedures under investigation, the separation of Zr and/or Hf from two monazite ores, synthetic and spiked water samples, was carried out. The results are given in Table 3. For the determination of Zr and/or Hf

Table 2. Tolerance ratios of the foreign ions on the separation of 5 μg of Zr and/or Hf in 20 mL water at optimum conditions

Tolerance of foreign ions (Zr and/or Hf) ratio (W/W)	Ions
1000	Br$^-$, Cl$^-$, NO_2^-, NO_3^-, SO_4^{2-}, ClO_4^-, $H_2PO_4^-$, SO_3^{2-}, IO_3^-, Acetate
500	Mg(II), Sr(II), Ca(II), Co(II), Ni(II), Zn(II), Pb(II), Hg(II)
100	Al(III)^b, Mo(VI)^a, Ti(II)^a, Cu(II)^a, Fe(III)^b
0.5	UO_2(II), Ce(IV)^c, Th(IV)^a, In(III)^a, Ga(III)^a

[a] In the presence of 0.01 % EDTA.

[b] In presence of 0.01% of F$^-$.

[c] In presence of 0.01% $C_2O_4^-$.

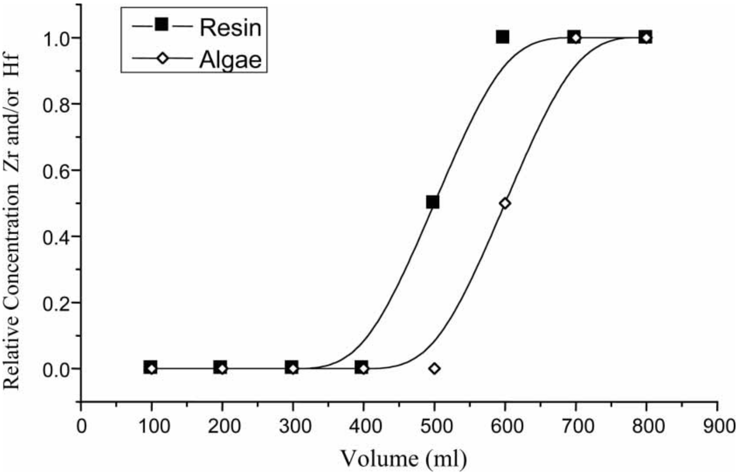

Figure 4. Breakthrough curves for $0.05\,\mathrm{mmol\,l^{-1}}$ Zr and/or Hf, flow rate $1.5\,\mathrm{mL\,min^{-1}}$, whose relative concentration is the fraction of Zr and/or Hf detected in the effluent to the total amount loaded on the two modified supports.

Table 3. Results of preconcentration and determination of Zr and/or Hf in some ores and synthetic mixtures by the proposed method using ARS modified resin or algae[a]

Ore name	Composition Zr and Hf (ppm)	Found	S	RSD	$\lvert t_1 \rvert$-test
202.83 Maltnim-G granite	312	311 (312)	5.60 (7.13)	1.8 (2.3)	0.40 (0.62)
Stream sediment sarm 52	250	250 (249)	4.25 (4.71)	1.7 (1.9)	0.20 (0.94)
Synthetic mixture 50 ppm of interfering ions spiked with 5 ppm Zr and/or Hf each:					
Th(IV), UO$_2$(II), Fe(III), Cu(II)	10	9.95 (9.96)	0.19 (0.17)	1.9 (1.7)	0.59 (0.52)
Cd(II), Zn(II), Mg(II), Ce(IV)	10	9.89 (9.90)	0.25 (0.20)	2.5 (2.1)	0.99 (1.02)
Ce(IV), Th(IV), UO$_2$(II), La(III)	10	9.91 (9.95)	0.29 (0.20)	2.4 (1.5)	0.85 (2.40)
Ca(II), Mg(II), Cu(II), UO$_2$(II)	10	9.93 (9.87)	0.20 (0.13)	2.0 (1.5)	0.79 (1.15)
Sr(II), Ba(II), Pb(II), Th(IV)	10	9.85 (9.90)	0.18 (0.25)	1.8 (2.5)	1.89 (1.18)
Tap water	10	9.90 (9.88)	0.17 (0.20)	1.7 (2.0)	1.33 (1.34)
Sea water	10	— (9.90)	— (0.21)	— (2.4)	— (1.20)

Note: The values given as average of five replicates n = 5.

[a]The data between brackets.

in synthetic and water samples, 5 μg of both ions were spiked to 500 mL prefiltered water and recovered by the two modified supports under the optimum conditions for the two ions. From statistical calculations by standard deviation(s), relative standard deviation (RSD) and T-test at confidence limit 95%, it is clear that the proposed procedure can be applied to samples with different compositions containing Zr and/or Hf with high precision and accuracy.

4. CONCLUSION

The sorbents, ARS immobilized on algae and Duolite 101 A anion exchanger, can be easily prepared. The immobilized Duolite 101 A exhibits high stability and can be used for at least 1 year, and algae for 2 days. The sorbents offer the possibility for preconcentration and selective separation of both Zr and/or Hf in the pH 2.5–8.0 range free from interferences in different natural samples. Zirconium and/or Hf can be easily stripped with HCl/citric mixture. The main advantages of this procedure are i) the extractor system is simple, fast, and low cost, especially in green chemistry (the green algae), ii) the organic solvents are excluded in elution as required in the other procedures, and iii) the high enrichment factor (200) enables one to preconcentrate and separate Zr and/or Hf from natural media. Finally, the remaining ARS in the solid supports after desorption allows one to use the column several times. The high recovery showed that the proposed procedure has good accuracy.

REFERENCES

1. Abou-El-Sherbini, Kh. and Hassanien, M.M. (2004) Synthesis of controlled-pore silica glass functionalized with quercetin and its application for the separation and preconcentration of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II). *Sep. Sci. and Tech.*, 39 (5): 1177–1201.
2. Wang, Z., Shi, L., Chen, G., and Cheng, K.L. (2000) Multivariate spectrofluorimetry of ultra trace zirconium(IV) and hafnium(IV) assisted by several chemometrics methods. *Talanta*, 51 (2): 315–326.
3. Goswami, A. and Singh, A.K. (2002) Silica gel functionalized with resacetophenone: synthesis of a new chelating matrix and its application as metal ion collector for their flame atomic absorption spectrometric determination. *Analytica Chim. Acta*, 454: 229–340.
4. Wilde, E.W. and Benemann, J.R. (1993) Bioremoval of heavy metals by the use of microalgae. *Biothech. Adv.*, 11 (4): 781–812.
5. Wilkinson, S.C., Goulding, K.H., and Ribnson, P.K.J. (1990) Mercury removal by immobilized algae in batch culture system. *Applied Phycology*, 2: 223–230.
6. Yu, Q. and Kaewsarn, P. (1999) Fixed-bed study for Cu(II) removal from aqueous solutions by marine algae *Durvillaea potatorum*. *Environm. Tech.*, 20: 1005–1008.
7. Yu, Q., Malheichal, J.T., Yin, P., and Kaewsarn, P. (1999) Heavy metal uptake capacities of common marine macroalgal biomass. *Water Res.*, 33 (6): 1534–37.

8. Scott, C.D. (1992) Removal of dissolved metal by plant tissue. *Biotechnol. and Bioeng.*, 39: 1064–1068.
9. Bağ, H., Türker, A.R., and Lale, M. (2000) Determination of Cu, Zn, Fe, Ni and Cd by flame atomic absorption spectrophotometry after preconcentration by *Escherichia coli* immobilized on sepiolite. *Talanta*, 51 (5): 1035–1043.
10. Kumar, M., Rathore, D.P.S., and Singh, A.K. (2000) Amberlite XAD-2 functionalized with *o*-aminophenol: synthesis and applications as extractant for copper(II), cobalt(II), cadmium(II), nickel(II), zinc(II) and lead(II). *Talanta*, 51 (6): 1187–1196.
11. Saxena, R., Singh, A.K., and Rathore, D.P.S. (1995) Salicylic acid functionalized polystyrene sorbent amberlite XAD-2. Synthesis and applications as a preconcentrator in the determination of zinc(II) and lead(II) by using atomic absorption spectrometry. *Analyst*, 120: 403–406.
12. Tewari, P.K. and Singh, A.K. (2002) Preconcentration of lead with amberlite XAD-2 and amberlite XAD-7 based chelating resins for its determination by flame atomic absorption spectrometry. *Talanta*, 56 (4): 735–744.
13. Saxena, R., Singh, A.K., and Sambi, S.S. (1994) Synthesis of a chelating polymer matrix by immobilizing alizarin red-S on amberlite XAD-2 and its application to the preconcentration of lead(II), cadmium(II), zinc(II) and nickel(II). *Analytica Chimica Acta*, 295 (1–2): 199–204.
14. Tewari, P.K. and Singh, A.K. (1999) Amberlite XAD-2 functionalized with chromotropic acid: synthesis of a new polymer matrix and its applications in metal ion enrichment for their determination by flame atomic absorption spectrometry. *Analyst*, 124: 1847–1852.
15. Kumar, M., Rathore, D.P.S., and Singh, A.K. (2000) Metal ion enrichment with Amberlite XAD-2 functionalized with Tiron: analytical applications. *Analyst*, 125: 1221–1226.
16. Companó, R., Ferrer, R., Guiteras, J., and Prat, M.D. (1994) Spectrofluorimetric detection of zinc and cadmium with 8-(benzenesulfonamido)-quinoline immobilized on a polymeric matrix. *Analyst*, 119: 1225–1228.
17. Dev, K. and Rao, G.N. (1996) Synthesis and analytical properties of a chelating resin functionalised with bis-(N,N′-salicylidene)1,3-propanediamine ligands. *Talanta*, 43 (3): 451–456.
18. Tewari, P.K. and Singh, A.K. (2000) Amberlite XAD-7 impregnated with xylenol orange: a chelating collector for preconcentration of Cd(II), Co(II), Cu(II), Ni(II), Zn(II) and Fe(III) ions prior to their determination by flame AAS. *Anal. and Bioanal. Chem.*, 367 (6): 562–567.
19. Ferreira, S.L.C., Ferreira, I.R., Dantas, A.F., Lemos, V.A., Araujo, N.M.L., and Costa, A.C.S. (2000) Copper determination in natural water samples by using FAAS after preconcentration onto amberlite XAD-2 loaded with calmagite. *Talanta*, 50 (6): 1253–1259.
20. Ferreira, S.L.C., de Brito, C.F., Dantas, A.F., de Araújo, N.M.L., and Costa, A.C.S. (1997) Nickel determination in saline matrices by ICP-AES after sorption on amberlite XAD-2 loaded with PAN. *Talanta*, 48 (5): 1173–1177.
21. Lee, C.H., Suh, M.Y., Kim, J.S., Kim, D.Y., Kim, W.H., and Eom, T.Y. (1999) Separation and preconcentration of uranium from geological materials with chelating resin containing 4-(2-thiazolylazo)resorcinol functional groups. *Anal. Chim. Acta*, 382: 199–203.
22. Brajter, K. and Zlotorzynska, E.D. (1986) Selective separation of metal ions by use of chelate-forming resins prepared by modification of conventional anion-exchangers with spadns and orange II. *Talanta*, 33 (2): 149–154.

23. Korn, M.G.A., Santos, A.F., Jr., Jaeger, H.V., Silva, N.M.S., and Costa, A.C.S. (2004) Copper, zinc and manganese determination in saline employing FAAS after separation and preconcentration on amberlite XAD-7 and Dewex 1X-8 loaded with alizarine red S. *J. Braz. Chem. Soc.*, 15 (2): 212–218.
24. Naghiro, T., Wang, G.F., and Satake, M. (1995) Column preconcentration of aluminum and copper (II) in alloys, biological samples, and environmental samples with Alizarin Red S and cetyltrimethylammonium-perchlorate adsorbent supported on naphthalene using spectrometry. *Microchem. J.*, 53 (3): 247–256.
25. Khalifa, M.E. (1995) Spectrophotometric determination of copper with alizarine red S (ARS) sensitized by borate. *Chem. Anal. (Warsaw)*, 40: 797–803.
26. Mendez, J.H., Martinez, R.C., Cordero, B.M., and Davila, L.G. (1983) Spectrophotometric determination of aluminium with alizarin red S sensitized with polyvinylpyrrolidone. *Anal. Chim. Acta*, 149: 379–383.
27. Mendez, J.H., Cordero, B.M., and Davila, L.G. (1985) Spectrophotometric determination of zirconium with alizarin red S in the presence of polyvinylpyrrolidone. *Anal. Chim. Acta*, 175: 345–348.
28. Marczenko, Z. (1986) *Separation and Spectrophotometric Determination of Elements*, 2nd Ed.; West Sussex, UK: Harwood Lim.
29. Pakalns, S.P. (1969) Depolymerisation of zirconium in spectrophotometry with arsenazo III. *Anal. Chem. Acta*, 44: 73–83.
30. Nakamoto, K. (1970) *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley Interscience: New York.