



Determination of rare earth elements in seawater by inductively coupled plasma mass spectrometry with off-line column preconcentration using 2,6-diacetylpyridine functionalized Amberlite XAD-4

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ABSTRACT

An off-line column preconcentration technique using a micro-column of 2,6 diacetylpyridine functionalized Amberlite XAD-4 with inductively coupled plasma mass spectrometry (ICP-MS) as a means of detection has been developed. The aim of the method was to determine rare earth elements (REEs) (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) in seawater. Sample solutions (2–10 mL) were passed through the column which was then washed with ultra-pure water to remove residual matrix. The adsorbed cations on the resin were eluted by using 2 mL of 0.1 mol L⁻¹ HNO₃ containing 10 ng mL⁻¹ indium as an internal standard. The eluent was analyzed for the metal concentrations using ICP-MS. Sample pH as well as the sample and eluent flow rates were optimized. The sorption capacity of resin was determined by the batch process, by equilibrating 0.05 g of the resin with solutions of 50 mL of 25 mg L⁻¹ of individual metal ions for 4 h at pH 6.0 at 26 °C. The sorption capacities for the resin were found to range between 47.3 μmol g⁻¹ (for Lu) and 136.7 μmol g⁻¹ (for Gd). Limits of detection (3σ), without any preconcentration, ranged from 2 ng L⁻¹ to 10.3 ng L⁻¹ (for Tm and Lu respectively). The proposed method was applied to the determination of REEs in seawater and tap water samples.

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1. Introduction

Rare earth elements (REEs) are attracting increasingly more attention because of their uses such as in the production of superconductors and super-magnets. Their distribution and concentration relative to each other in nature may also yield important geochemical information and assists in the understanding of the processes occurring in seawater [1,2]. Since the REEs are normally present at the ng L⁻¹ level or below in seawater, advanced analytical techniques are required for their detection; often in conjunction with preconcentration techniques [3]. Neutron activation analysis [4] and isotope dilution mass spectroscopy [5–8] were early choices for the determination of ultra-trace REEs in seawater. However, for over 20 years, inductively coupled plasma mass spectrometry (ICP-MS) has increasingly been used for the determination of REEs because it has the attributes of providing excellent multi-element detection capability with high sensitivity whilst also possessing a wide dynamic range. This has allowed direct determination of trace REEs. Although ICP-MS has the detection power to determine trace elements at sub ng mL⁻¹ levels, it suffers from

problems of ionization suppression by matrix elements [9] as well as isobaric and polyatomic interferences. In particular, the matrix elements in the sample can combine with carbon in the atmosphere and/or argon in the plasma and result in the formation of polyatomic species which may interfere with the determination of numerous analytes including transition metals and REEs [10]. In addition, when the sample contains a very high concentration of dissolved salts, e.g. seawater; clogging of the sample introduction system or of the injector tube of the torch may occur. To overcome these problems, various batch methods have been developed. These include the use of ion exchange pretreatments [11], solvent extraction [12–14] and co-precipitation using iron hydroxide [6,15]. Batch pre-treatment methods have disadvantages, which include often being time-consuming, the potential for contamination and the possibility of errors arising through mis-labelling of samples and other operator-induced problems. Pre-treatments for the separation and pre-concentration of trace elements in flow system have also been developed and possess some advantages. These include the requirement of only small volumes of samples and reagents, and a decrease in the likelihood of contamination from airborne material. The separation of ultra-trace analytes from matrix elements and the preconcentration of the said analytes are required prior to their determination in seawater using ICP-MS. Therefore, various adsorbent materials

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Table 1
ICP-MS and ICP-OES operating conditions.

	ICP-MS conditions	ICP-OES conditions
RF power (W)	1350	1400
Plasma Ar gas flow rate (L min ⁻¹)	13	15
Auxiliary Ar gas flow rate (L min ⁻¹)	1	1.5
Nebulizer gas flow rate	0.8 L min ⁻¹	0.68
Collision cell gas	7% H ₂ in He at 3.5 mL min ⁻¹	
Spray chamber type	PC ³	Sturman-Masters
Nebuliser type	Concentric glass	V-groove
Lens voltages	Optimized daily	
Data Acquisition mode	Peak jump	
Dwell time (ms)	80	
Monitored isotopes	¹³⁹ La; ¹⁴⁰ Ce; ¹⁴¹ Pr; ¹⁴⁶ Nd; ¹⁴⁷ Sm; ¹⁵³ Eu; ¹⁵⁷ Gd; ¹⁵⁹ Tb; ¹⁶³ Dy; ¹⁶⁵ Ho; ¹⁶⁶ Er; ¹⁶⁹ Tm; ¹⁷² Yb; ¹⁷⁵ Lu	
Wavelengths monitored (nm)		La = 333.749; Ce = 418.659; Pr = 417.939; Nd = 401.224; Sm = 359.259; Eu = 420.504; Gd = 342.246; Tb = 350.914; Dy = 353.171; Ho = 345.600; Er = 349.910; Tm = 313.125; Yb = 328.937; Lu = 261.541.
Replicate read time (s)		4
Viewing height (mm)		8

have been developed that have been used for the preconcentration of REEs from seawater. These materials are very diverse and include Muromac A-1 [16,17], iminodiacetate-based resins [18], 8-quinolinol-immobilized fluorinated metal alkoxide glass [MAF-8HQ] [19], poly(acrylamino phosphonic dithiocarbamate) chelating fiber [20], Chelex-100 [12,21,22], activated alumina [23,24], activated carbon [25], HDEHP/H2MEHP adsorbed C18 cartridge [14], inorganic chemically active beads [26], aminocarboxylic sorbents [27], 1-phenyl-3-methyl-4-benzoylpyrazol-5-one coated on the inner walls of a PTFE mini-column [13], nanometer-sized titanium dioxide [28], octadecylsilica [29], maleic acid grafted PTFE fibres [30], Amberlite XAD-7+8HQ [31], alkyl phosphonic acid (APAR) resin [32], C18-cartridge modified with 1-(2-pyridylazo) 2-naphthol (PAN) [33], chitosan resin functionalized with 2-amino-5-hydroxy benzoic acid [34], chitosan resin functionalized with N-(2-hydroxyethyl) glycine [35], chitosan resin functionalized with serine diacetic acid [36], ethylenediamine-*N,N,N'*-triacetate-type chitosan [37] and modified carbon nanofibers [38]. It should be emphasised though that not all of these publications reported the determination of all of the REE [31]. Other papers report extremely impressive limits of detection because of the large preconcentration factors involved. However, this comes at the cost of time, with only 5 samples per hour being analyzed [18,31]. Other resins, e.g. Chelex, are renowned for being susceptible to swelling and shrinking depending on the pH of the sample; which can cause problems with on-line work.

Recently, several chelating matrices have been developed using modified Amberlite XAD series. These XAD resins have good physical properties such as porosity, uniform pore size distribution, high surface area as well as chemical homogeneity and non-ionic structure. They have also been shown to be good adsorbents for large amounts of uncharged compounds [39]. The most widely used support materials in the Amberlite XAD series for this sort of purpose are XAD-2 and XAD-4 [40–43].

The aim of this study was to investigate the optimal sample pH for the adsorption of trace levels of REEs on 2,6-diacetylpyridine functionalized Amberlite XAD-4 resin. Once the optimal adsorption and elution characteristics had been identified, a reliable method for the determination of REEs using an off-line column preconcentration/ICP-MS detection was developed. The method was then applied to the determination of the REEs in seawater samples, a notoriously difficult to analyse sample because it contains high concentrations of dissolved salts and low concentrations of analytes (ng L⁻¹). The use of 2,6-diacetylpyridine functionalized Amberlite XAD-4 resin for the retention of REE has been reported for the first time.

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical reagent grade. Ultra-pure water (18.2 MΩ cm) was obtained from a combined Prima and Maxima water unit (Elga). Nitric acid, ammonia solution and acetic acid were purchased from VWR International. The chelating reagent, 2,6-diacetylpyridine and Amberlite XAD-4 was purchased from Fluka (Gillingham, Dorset, UK).

Working standard solutions of REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) were prepared on a daily basis by stepwise dilution of the multi-element stock standard solution (100 mg L⁻¹, CPI International). Ammonium acetate buffer solution (0.1 M, pH 6.0) was prepared using pure acetic acid and ammonia solution. A seawater sample was collected from Plymouth Sound, UK and a tap water sample was collected from a laboratory at Plymouth University. The seawater was filtered through a 0.45 μm filter before use.

2.2. Instruments

An ICP-MS instrument (X Series 2, Thermo Scientific, Hemel Hempstead, UK) was used for the analyses. It should be noted that Ba and low mass REE can form oxides which can present themselves as polyatomic interferences during the determination of higher mass REE. The instrument used has the option to introduce a reactive gas (7% hydrogen in helium) into a collision cell to help overcome these interferences. The optimisation process for the instrumental detection was therefore a compromise between obtaining maximum sensitivity whilst decreasing the CeO/Ce ratio to a minimum. The operating conditions are shown in Table 1. An ICP-OES instrument (Varian 725-ES, Melbourne, Australia) was used for the preliminary experiments in which the optimal experimental conditions for analyte retention on the resin were identified. Operating conditions for the ICP-OES instrument are also given in Table 1.

2.3. Synthesis of the 2,6-diacetylpyridine functionalized Amberlite XAD-4

The 2,6-diacetylpyridine functionalized Amberlite XAD-4 resin was synthesized according to the procedure given in the literature [44].

2.4. Procedures

2.4.1. Off-line preconcentration and elution procedure

A glass micro-column (5 cm × 3 mm, Omnifit, Cambridge, UK) was packed with 2,6-diacetylpyridine functionalized Amberlite XAD-4. The resin bed was first washed with distilled water and then pre-conditioned by passing 0.5 mL of pH 6.0 ammonium acetate buffer solutions at a rate of 1 mL min⁻¹. The sample solution buffered at the optimum pH using acetic acid/ammonia solution was pumped through the column at a flow rate of 1 mL min⁻¹ by means of a peristaltic pump. After the column loading period, water was pumped through the column at a rate of 1 mL min⁻¹ for 30 s to ensure that any un-retained matrix was removed from the system. The metal ions retained on the resin were eluted by using 2 mL of 0.1 mol L⁻¹ HNO₃ containing 10 ng mL⁻¹ of the internal standards indium and iridium at a flow rate of 1 mL min⁻¹. The eluent was collected and then the analyte concentrations determined using ICP-MS.

2.4.2. Maximum retention capacity of the 2,6-diacetylpyridine functionalized Amberlite XAD-4 resin

The sorption capacity of the chelating resin was determined using a batch method. Resin (0.05 g) was mixed with 50 mL of standards at optimum pH containing 25 mg L⁻¹ of individual analytes. The resins were allowed to equilibrate with these standards at room temperature (26 °C) for a period of 4 h. The resin was then filtered from the standard and the analyte remaining in solution was determined using ICP-MS. If all detectable amounts of an analyte had been removed from a standard, the same batch of resin was equilibrated with a second aliquot (50 mL) of standard. This process continued until there was a measurable level of analyte left in the standard, i.e. the resin had become saturated. The sorption capacity of the resin was then calculated for each analyte from the difference between analyte concentration in the standards before and after sorption.

2.4.3. Analysis of water samples

A seawater sample was collected from Plymouth Sound, UK and a tap water sample was collected from a tap in one of the laboratories at Plymouth University. Before the analysis of water samples, the samples were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size. The pH of the samples was adjusted to 6 using acetic acid/ammonia solution. The resin was pre-conditioned by passing pH 6.0 ammonium acetate buffer solution through the column at a flow rate of 1 mL min⁻¹ for 30 s. After the pre-conditioning, 10 mL of the seawater sample was passed through the column at a flow rate of 1 mL min⁻¹ by means of a peristaltic pump. After the sample had been passed through the column it was washed for 30 s with ultra-pure water to remove residual matrix. The metal ions retained on the resin were eluted by using 2 mL of 0.1 mol L⁻¹ HNO₃ containing 10 μg L⁻¹ In and Ir internal standards at a flow rate of 1 mL min⁻¹. Preconcentration by a factor of 5 was therefore achieved. Finally, the eluent was analyzed for the content of REEs concentrations using ICP-MS. The column was then re-conditioned ready for the next sample by passing through deionised water and buffer solution in succession, both at a flow rate of 1 mL min⁻¹ for 30 s. For validation purposes, a recovery test was undertaken in which REE (50 ng L⁻¹ each) were spiked into the seawater sample. This spiked sample was then analyzed in the same manner as described previously. The same procedure was used for tap water samples, except that 2 mL of tap water samples were passed through the column and REE (0.1 and 1.0 μg L⁻¹) were spiked into the tap water sample.

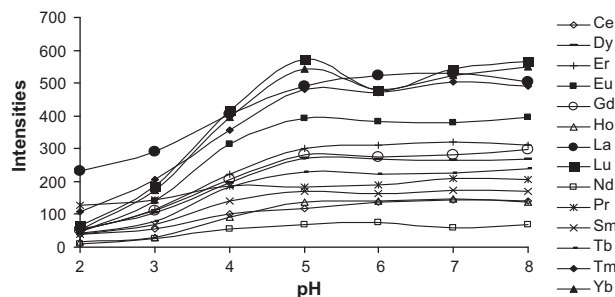


Fig. 1. Influence of pH on the retention of rare earth elements (the intensities were obtained using ICP-OES).

3. Results and discussion

3.1. Optimization

Various chemical variables with the potential to affect the determination and preconcentration of REEs using the resin were studied. Of them, the pH was the most important. The influence of pH on the retention of REEs on the 2,6-diacetylpyridine functionalized Amberlite XAD-4 resin was investigated over the pH range of 2–8. The concentration of REE solutions used was 100 μg L⁻¹. The pH effect was studied using the ICP-OES detection system and the results are shown in Fig. 1. These results showed that emission signals for the metal ions do not change between pH values of 5 and 8 indicating that maximum metal retention occurred. The optimum pH value was selected as 6.0 for use with this resin.

The optimization of the sample flow rate is very important for this type of experiment. Higher sample flow rate and higher adsorption yield are desirable because they will give the highest sample throughput and the greatest sensitivity. Similarly, for preconcentration-based experiments, they will enable the greatest preconcentration factor to be obtained in the shortest time period. However, if the kinetics of the retention is slow, this may limit the rate at which the sample can be pumped through the resin; since at elevated pumping speeds, the analytes may not be retained. The sample flow was changed at rates of between 0.5 and 3.0 mL min⁻¹ and the signal was recorded using the ICP-MS detection system at pH 6.0 without any preconcentration step. The concentration of REE solutions used was 1.0 μg L⁻¹. The intensities were found to decrease very little (by a total of 0.18–3.92%) over this flow rate range, indicating that the kinetics of the retention were very rapid. A sample flow rate of 1.0 mL min⁻¹ was selected as optimum since this was a compromise between optimal sensitivity (found at 0.5 mL min⁻¹) and optimal sample throughput (3.0 mL min⁻¹). The influence of eluent solution (0.1 M HNO₃) flow rate was examined over the range 0.5 to 3.0 mL min⁻¹. The maximum intensities of REEs were obtained at a flow rate of 1.0 mL min⁻¹. At higher elution rates, the intensities were found to gradually decrease, but only by a factor of approximately 6.6–9.6% over the measured range. Hence the eluting flow rate was selected to be 1.0 mL min⁻¹. It was concluded therefore that for only a very marginal drop in sensitivity, the speed of both the retention and elution could be increased significantly. Hence, lower LOD and higher preconcentration factors could be obtained at the expense of only a small decrease in sensitivity.

The optimum values for other, less important, experimental factors are given in Table 2.

3.2. Method validation

In order to evaluate the performance of the method, the linearity and the detection limits were determined. This was

Table 2
Experimental parameters.

Buffer flow time	30 s
Buffer flow rate	1.0 mL min ⁻¹
Sample flow rate	1.0 mL min ⁻¹
Washing time	1 min
Washing rate	1.0 mL min ⁻¹
Elution solution	0.1 M HNO ₃ containing 10 mg L ⁻¹ In
Elution flow rate	1.0 mL min ⁻¹

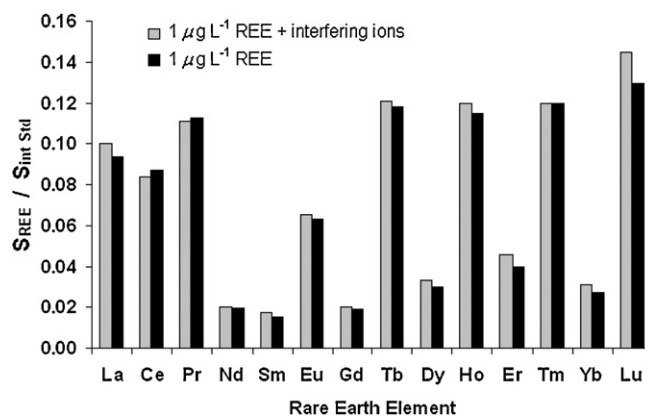
Table 3
Calibration equations and limits of detection obtained by ICP-MS when no preconcentration was used.

Element	LOD (ng L ⁻¹)	Calibration equations	R ²
La	4.0	$y = 0.0937x + 0.0017$	0.9996
Ce	8.7	$y = 0.091x + 0.0018$	0.9831
Pr	7.6	$y = 0.13x + 0.002$	0.9996
Nd	7.4	$y = 0.0243x + 0.0006$	0.9991
Sm	9.2	$y = 0.0216x + 0.0005$	0.9991
Eu	7.0	$y = 0.0842x + 0.0018$	0.9989
Gd	5.6	$y = 0.027x + 0.0005$	0.999
Tb	5.6	$y = 0.1727x + 0.0032$	0.9989
Dy	4.2	$y = 0.0439x + 0.0009$	0.9988
Ho	7.3	$y = 0.1815x + 0.0029$	0.9995
Er	6.4	$y = 0.0613x + 0.0011$	0.9987
Tm	2.0	$y = 0.1911x + 0.0043$	0.9988
Yb	3.2	$y = 0.0439x + 0.0009$	0.9986
Lu	10.3	$y = 0.1888x + 0.0016$	0.9996

followed by an assessment of the accuracy and repeatability.

Standards and blanks were prepared using ultra-pure water. Linearity was demonstrated for all elements over the range 0.10 to at least 2.00 µg L⁻¹. Detection limits were determined by analysing 20 replicate blanks. Limits of detection (3σ) and calibration equations are given in Table 3. The LODs were found to be independent of the sample matrix.

An investigation into the effect of typical seawater composition, i.e. 1270 mg L⁻¹ Mg²⁺, 400 mg L⁻¹ Ca²⁺, 10800 mg L⁻¹ Na⁺, 400 mg L⁻¹ K⁺, 5100 mg L⁻¹ SO₄²⁻, 600 mg L⁻¹ CO₃²⁻, 16600 mg L⁻¹ Cl⁻, and 620 mg L⁻¹ NO₃⁻ on the signal of 1 µg L⁻¹ of each analyte was undertaken. This is because the elevated levels of these species in seawater can cause a variety of problems and make the direct determination of trace metals in this matrix using a standard quadrupole ICP-MS instrument difficult. After passing the sample through the mini-column, the resin was washed with water for 30 s at a flow rate of 1.0 mL min⁻¹ to remove the sample matrix from the column. The results are shown graphically in Fig. 2. It was observed that for 12 of the 14 REE, there is a subtle enhancement in recovery in the presence of interfering ions. This was attributed to the presence of the REE at ultra-trace levels in

**Fig. 2.** The effect of interfering ions (1270 mg L⁻¹ Mg²⁺, 400 mg L⁻¹ Ca²⁺, 10,800 mg L⁻¹ Na⁺, 400 mg L⁻¹ K⁺, 5100 mg L⁻¹ SO₄²⁻, 600 mg L⁻¹ CO₃²⁻, 16,600 mg L⁻¹ Cl⁻, 620 mg L⁻¹ NO₃⁻) on the signal of 1 µg L⁻¹ metal ions (n = 3).

the salts used during the interference study. The enhancement in recovery did not exceed 15% for any of the analytes determined at the 1 µg L⁻¹ level. The enhancement was confirmed to arise from contaminants of the salts by analysis of the matrix in the absence of any added REE. This demonstrates that the column was efficient at retaining the analytes, effectively separating them from matrix constituents that may either occupy the active sites on the resin, hence causing the analytes to break through, or form polyatomic interferences which would lead to a positive interference effect.

3.3. Application of the method to water samples

The proposed method, after being optimised in terms of the parameters described above, was applied to the determination of REEs in spiked tap water and seawater samples. Unfortunately, certified reference materials of this type where the REE concentrations are known, were not available. Consequently, other method validation approaches had to be performed. Tap water and seawater samples were spiked with several concentrations of rare earth metal ions; the spiked concentrations were as close as possible to the concentrations found, and the recovery tests were examined. The results are given in Tables 4 and 5. Recoveries (R) of spike additions to tap water and sea water samples were quantitative. These results demonstrate the applicability of the procedure for REEs determination in natural water samples. The results shown in Table 4 indicate that the REEs were present at such low concentration in the tap water that they were below the LOD of the technique. Therefore, recovery experiments alone were done for Tap water samples. No extra preconcentration procedures were

Table 4
Recovery values by ICP-MS for tap water samples spiked with 0.1 and 1.0 µg L⁻¹ (n = 4).

Element	Tap water	0.1 µg L ⁻¹ added tap water	Recovery (%)	1.0 µg L ⁻¹ added tap water	Recovery (%)
La	<LOD	0.101 ± 0.004	101	0.996 ± 0.002	99.6
Ce	<LOD	0.096 ± 0.002	96	0.979 ± 0.005	97.9
Pr	<LOD	0.091 ± 0.003	91	0.953 ± 0.01	95.3
Nd	<LOD	0.102 ± 0.003	102	0.992 ± 0.018	99.2
Sm	<LOD	0.097 ± 0.006	97	1.002 ± 0.028	100.2
Eu	<LOD	0.093 ± 0.001	93	0.998 ± 0.010	99.8
Gd	<LOD	0.098 ± 0.005	98	1.015 ± 0.011	101.5
Tb	<LOD	0.092 ± 0.004	92	0.99 ± 0.015	99.0
Dy	<LOD	0.098 ± 0.003	98	0.977 ± 0.018	97.7
Ho	<LOD	0.093 ± 0.009	93	0.992 ± 0.008	99.2
Er	<LOD	0.094 ± 0.007	94	1.005 ± 0.004	100.5
Tm	<LOD	0.090 ± 0.004	90	0.972 ± 0.009	97.2
Yb	<LOD	0.091 ± 0.005	91	0.977 ± 0.006	97.7
Lu	<LOD	0.093 ± 0.002	93	0.946 ± 0.011	94.6

Table 5The analysis of sea water comparing the proposed method with the Zhu et al. method ($n = 3$).

Element	Results obtained using the proposed Method				Results obtained using the method of Zhu et al. [45]				$ x_1 - x_2 $	$t_{\text{spooled}} \sqrt{\frac{N_1 + N_2}{N_1 \cdot N_2}}$
	Measured (ng L ⁻¹)	Added (ng L ⁻¹)	Found (ng L ⁻¹)	R%	Measured (ng L ⁻¹)	Added (ng L ⁻¹)	Found (ng L ⁻¹)	R%		
La	137.8 ± 12.0	50	189.0 ± 5.8	102.4	136.7 ± 27	50	192.1 ± 15	110.8	3.1	25.81
Ce	18.6 ± 2.3	50	62.8 ± 2.0	88.5	19.7 ± 4.8	50	63.3 ± 3.6	87.1	0.5	6.61
Pr	10.1 ± 2.1	50	55.3 ± 1.6	90.4	11.4 ± 6.3	50	61.8 ± 3.4	100.8	6.5	6.03
Nd	10.2 ± 2.1	50	55.8 ± 1.7	91.2	12.9 ± 4	50	58.9 ± 3.3	91.8	3.1	5.96
Sm	7.0 ± 1.8	50	55.9 ± 2.1	97.8	8.3 ± 3.6	50	54.0 ± 4.6	91.4	1.9	8.79
Eu	6.9 ± 2.4	50	56.3 ± 2.5	98.8	7.4 ± 3.8	50	53.1 ± 2.5	91.6	3.2	5.67
Gd	8.8 ± 2.5	50	59.3 ± 2.6	100.9	9.0 ± 3.1	50	55.4 ± 2.8	92.8	3.9	6.13
Tb	7.3 ± 2.5	50	57.5 ± 1.7	100.5	8.1 ± 3.7	50	55.7 ± 2.7	94.3	1.8	5.12
Dy	8.2 ± 2.1	50	58.8 ± 1.9	101.2	8.9 ± 3.9	50	56.8 ± 2.6	95.6	2.0	5.17
Ho	7.5 ± 2.2	50	58.3 ± 2.4	101.8	7.6 ± 2.0	50	56.3 ± 2.6	97.4	2.0	5.68
Er	8.2 ± 2.1	50	61.0 ± 2.7	105.5	8.2 ± 4.1	50	58.0 ± 2.2	99.6	3.0	5.59
Tm	7.6 ± 2.3	50	59.8 ± 1.7	104.3	7.2 ± 3.4	50	57.7 ± 2.2	100.9	2.1	4.46
Yb	8.4 ± 2.4	50	61.5 ± 2.3	106.1	7.1 ± 4.1	50	58.5 ± 3.2	102.9	3.0	6.33
Lu	7.9 ± 2.6	50	63.1 ± 2.3	110.4	8.3 ± 3.2	50	63.6 ± 3.3	110.5	0.5	6.46

(If the difference between this method and Zhu's method's results $|x_1 - x_2|$, is smaller than the computed value $t_{\text{spooled}} \sqrt{(N_1 + N_2)/(N_1 \cdot N_2)}$, no significant difference between experimental and certified results has been accepted at the 95% confidence level. $x_1 - x_2$ column indicates the differences in concentration found between the two methods).

Table 6Comparison of sorption capacities ($\mu\text{mol g}^{-1}$).

Methods (Ref)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu
2,6-Diacetylpyridine functionalized Amberlite XAD-4 (this work)	127.3	124.3	126.3	123.1	117.1	53.4	136.7	108.6	113.5	58.6	106.6	79.2	47.3
8-Quinolinole-immobilized fluorinated metal alkoxide glass [19]	60	-	-	-	36	-	-	-	-	-	-	60	-
Mesoporous TiO ₂ [46]	153.3	98.5	-	-	-	128.3	-	-	102.8	-	-	153.2	-
Nano-sized TiO ₂ [28,47]	74.9	-	-	-	-	79.6	-	-	54.2	-	-	73.9	-
Multiwalled carbonnanotubes [48,49]	59.8	-	-	-	-	62.0	-	-	-	-	-	49.5	-
Amberlite XAD-4 resin functionalized with bicine [50]	350	-	-	400	-	-	-	420	-	-	-	-	-
Poly(dithiocarbamate) resin [51]	200	-	-	270	-	-	-	170	-	-	-	-	-
<i>o</i> -Vanillinsemicarbazone functionalized Amberlite XAD-4 [52]	16.6	17.7	-	-	-	-	-	-	-	-	-	-	-
Alkyl phosphinic acid resin (APAR) [32]	14.3	14.4	14.3	14.0	13.9	14.1	13.9	13.8	13.7	13.4	13.2	13.1	13.5
Maleic acid grafted polytetrafluoroethylene fiber (MA-PTFE) [30]	310	-	-	-	-	-	-	-	-	-	-	-	-
Multi-dentate Ion-Selective AXAD-16-MOPPA Polymer [53]	1310	-	-	-	-	-	-	-	-	-	-	-	-

undertaken for the tap water samples because the aim of this work was to show the ability of the resin for the determination of REEs in seawater samples. To obtain accurate and precise results for the seawater samples, a preconcentration factor of five was required (i.e. the analytes present in 10 mL of sample were eluted using 2 mL of eluent). As a second method of validation, the results obtained from the seawater sample using the proposed method were compared with those obtained using the method described by Zhu et al. [45] (Table 5). In brief, the method described by Zhu and colleagues involved the use of a Chelex-100 resin-packed mini-column for the determination of REEs in seawater. These authors used a preconcentration of 20-fold (with analyte retention from 50 mL of sample and elution using 2.5 mL of eluent). The analytes were determined using inductively coupled plasma mass spectrometry (ICP-MS).

The results obtained were found to be in good agreement, with the student *t*-test indicating that there was no significant difference between the results obtained using the proposed method and the method proposed by Zhu et al.

3.4. Maximum retention capacity of the 2,6-diacetylpyridine functionalized Amberlite XAD-4

The loading capacity of the resin for each metal ion was calculated from the difference between the metal ion concentrations in the solutions before and after sorption. The maximum retention capacities for rare earth elements on this resin are compared with other resins in Table 6. It can be seen from Table 6 that most other studies have not determined all of the REEs. Despite this, the capacity of the resin described in this study exceeded many of those in other studies. The only other study that determined all of the

REEs reported retention capacities approximately an order of magnitude inferior to those in this work. The retention capacity was not found to change significantly even after it had been used for more than 50 samples. The resin was therefore regarded as being very stable.

4. Conclusions

The method developed is very simple, requires only a small sample volume (unless preconcentration is required) and uses few reagents. The 2,6-diacetylpyridine functionalized Amberlite XAD-4 resin could be recycled many times without affecting its sorption capacity. The elution was easily achieved using 0.1 mol L⁻¹ HNO₃. The presence of the major components of seawater, namely Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻, CO₃²⁻ and SO₄²⁻ ions did not interfere with the analysis and therefore, it was concluded that this analysis could be applied to equally to saline and fresh waters. The resin also exhibited improved retention characteristics compared with many of the other materials reported previously. Limits of detection, without any preconcentration, are at the ng L⁻¹ level and since the kinetics of the analyte retention are rapid, large preconcentration factors can be achieved in a relatively short period of time.

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