Flow Injection On-Line Solid Phase Extraction Coupled with Inductively Coupled Plasma Mass Spectrometry for Determination of (Ultra)Trace Rare Earth Elements in Environmental Materials Using Maleic Acid Grafted Polytetrafluoroethylene Fibers as Sorbent

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A new sorbent, maleic acid grafted polytetrafluoroethylene fiber (MA-PTFE), was prepared and evaluated for on-line solid-phase extraction coupled with inductively coupled plasma mass spectrometry (ICP-MS) for fast, selective, and sensitive determination of (ultra)trace rare earth elements (REEs) in environmental samples. The REEs in aqueous samples at pH = 3.0 were selectively extracted onto a microcolumn packed with the MA-PTFE fiber, and the adsorbed REEs were subsequently eluted on-line with 0.9 mol l⁻¹ HNO₃ for ICP-MS determination. The new sorbent extraction system allows effective preconcentration and separation of the REEs from the major matrix constituents of alkali and alkali earth elements, particularly their separation from barium that produces considerable isobaric interferences of ¹³⁴Ba¹⁶O¹H⁺, ¹³⁵Ba¹⁶O⁺, ¹³⁶Ba¹⁶O¹H⁺, and ¹³⁷Ba¹⁶O⁺ on ¹⁵¹Eu⁺ and ¹⁵³Eu⁺. With the use of a sample loading flow rate of 7.4 ml min⁻¹ for 120 s preconcentration, enhancement factors of 69–97 and detection limits (3s) of 1–20 pg l⁻¹ were achieved at a sample throughput of 22 samples h⁻¹. The precision (RSD) for 16 replicate determinations of 50 ng l⁻¹ of REEs was 0.5–1.1%. The developed method was successfully applied to the determination of (ultra)trace REEs in sediment, soil, and seawater samples. (J Am Soc Mass Spectrom 2006, 17, 1258–1264)
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Environmental effects of rare earth elements (REEs), namely lanthanides, have become of great concern owing to their increasing use in industrial products and agriculture [1, 2]. REEs also serve as analogs for the actinide elements (Am and Cm), such that the accurate determination of REEs at low levels is likewise important for predicting the behavior of the radioactive actinides in future radioactive waste repositories [3]. Therefore, it is essential to establish a reliable and sensitive analytical method to determine REEs in environmental materials and, furthermore, to understand how REEs migrate and transfer in the ecological environmental system, which could help in the study of the physiological

actions of REEs and in the prediction of any potential environmental effects.

Inductively coupled plasma mass spectrometry (ICP-MS) has definitely emerged as a powerful technique for element determination owing to its high sensitivity, low detection limits, linear dynamic range of up to nine orders of magnitude, and its capability to measure multi-element and isotope ratio with relative simple spectra interferences [4–6]. However, its application to direct determination of ultratrace REEs in complicated environmental samples is quite limited because highly saline samples can cause both isobaric interferences and matrix effects [7]. Especially, due to significant isobaric interferences (¹³⁴Ba¹⁶O¹H⁺, ¹³⁵Ba¹⁶O⁺, ¹³⁶Ba¹⁶O¹H⁺, ¹³⁷Ba¹⁶O⁺) on ¹⁵¹Eu⁺ and ¹⁵³Eu⁺, one of the low abundance REEs that may fractionate from neighboring REEs in natural systems from changes in oxidation state, good separation of REEs from Ba is a prerequisite for accurate ICP-MS determination of REEs in samples with high ratios of Ba to REEs [8, 9].

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Both off-line (batch-wise mode) [10–16] and on-line [16–19] preconcentration and separation procedures have been developed for ICP-MS determination of (ultra)trace REEs. Compared with those off-line operation counterparts, flow injection (FI) on-line separation and preconcentration systems provide many advantages, such as little risk of analyte loss and contamination, potential improvement of selectivity through kinetic discrimination under chemically nonequilibrated conditions, lower detection limits, improved precision, reduced sample and reagent consumption and waste production, high efficiency, and automation [16, 20]. The most widely used techniques for the on-line separation and preconcentration of trace REEs are those based on solid-phase extraction (SPE) [11, 17–19] due to the advantages of easiness to couple with ICP-MS, rapid phase separation, high enrichment factor, sampling in the field, no formation of emulsion, safety with respect to hazardous samples, low cost, and flexibility [20].

Development of new sorbents with good ability to separate REEs from the major matrix constituents—alkali and alkali earth elements, especially from barium, is of particular significance for reliable determination of ultra-trace REEs in environmental samples by FI on-line solid-phase extraction coupled with ICP-MS. In addition, to allow smooth running of the FI on-line solid-phase extraction preconcentration system, some special requirements for the sorbent materials should be met, such as negligible swelling capacity to resist swelling and shrinking with change in pH and/or solvent conditions, strong mechanical stability to withstand high linear flow rates, and high chemical resistibility to endure harsh conditions [21]. The chemical inertness, elevated resistibility, low friction coefficient, and good swelling resistance of polytetrafluoroethylene (PTFE) make it very attractive as the substrate for the sorbent for FI on-line solid-phase extraction preconcentration systems [22].

The aim of this work is to prepare a new sorbent, maleic acid grafted PTFE fibers (MA-PTFE), and to evaluate it as sorbent for FI on-line, solid-phase extraction coupled with ICP-MS for determination of (ultra)trace REEs in environmental samples.

Experimental

Instrumentation

A Model X 7 ICP-MS system equipped with a glass concentric nebulizer and PlasmaLab software (Thermo Elemental, Waltham, MA) was used throughout. The instrument was optimized daily and operated as recommended by the manufacturer to minimize isobaric interferences of the light REE (La–Gd) oxides on the heavy REEs (Tb–Lu). The nebulizer gas flow rate was adjusted so that the CeO/Ce ratio and BaO/Ba were less than 3%. The “TRA profile mode” data collection mode in the PlasmaLab software was used to monitor the signals of the 14 REEs.

Table 1. Operating conditions and mass spectrometer settings of the X-series ICP-MS for the determination of REEs using on-line solid phase extraction

Parameter	Value
RF power	1250 W
Coolant gas flow rate (Ar)	13.0 l min ^{−1}
Carrier gas flow rate (Ar)	0.77 l min ^{−1}
Nebulizer gas flow rate (Ar)	0.86 l min ^{−1}
Sampling depth	6.0 mm
Sampler	Nickel, 1.1 mm orifice
Skimmer	Nickel, 0.75 mm orifice
<i>Ion lenses</i>	
Extraction	−671
Lens 1	1.0
Lens 2	−25.1
Lens 3	−189.8
<i>Data acquisition</i>	
Scanning mode	Profile TRA
Dwell time	10 ms
Integration mode	Peak area
<i>Detector</i>	
PC detector	2884 V
Analog	1860 V

Peak area was used for quantification. The operating parameters of the ICP-MS system used in this work are given in Table 1.

A model FIA-3110 flow injection analyzer (Vital Instrumental, Beijing, China) was employed for the on-line solid-phase extraction of REEs. Only one pump of the analyzer was employed to propel the sample solution to complete on-line solid-phase extraction. The Peripump of the ICP-MS instrument (Thermo Elemental, Waltham, MA) was employed and controlled automatically by PlasmaLab software. Approximately 40 cm of 0.5 mm i.d. PTFE tubing was used to connect the valve to the Meinhard nebulizer (Grass Expansion Inc., Pocasset, MA) of the ICP-MS instrument. The manifold used for on-line solid-phase extraction of REEs is shown in Figure 1. Tygon peristaltic pump tubing (ISMATEC SA, Glatfbrugg, Switzerland) was employed to propel the sample and reagents.

Reagents

Concentrated HNO₃, HF, and NH₃·H₂O solutions were of ultrapure grade (BV-III, Beijing Institute of Chemical Reagent, Beijing, China). Doubly deionized water (DDW, 18.2 MΩ cm^{−1}) obtained from a WaterPro water system (Labconco Corporation, Kansas City, MO) was used throughout. Single element stock solutions of REEs at 1000 mg l^{−1} and Ba, Mg at 100 mg l^{−1} were obtained from the National Research Center for Certified Reference Materials (NRCCRM, Beijing, China). Stock multi-REEs solution of multi-REEs at 10 mg l^{−1} of each element in 2% vol/vol HNO₃ was prepared by diluting the single element stock solutions. Working multi-REEs solutions were prepared by series dilution of the stock multi-REEs solution immediately before use. All other reagents were of at least analytical grade. All cleaning operations and sample and

(a) Sample loading **(b) Elution**

Figure 1. FI manifold of the developed on-line solid-phase extraction for ICP-MS determination of ultratrace REEs. P1 and P2, peristaltic pumps; MC, microcolumn; valve position (a) fill; (b) injection; W, waste.

reagent chemistries were carried out in a class 100 clean bench.

Synthesis of MA-PTFE

A direct irradiation grafting method [23, 24] was employed to prepare the maleic acid grafted PTFE fibers (20 μm in diameter, Tongchuang Co., Beijing, China). About 150 g of maleic acid was dissolved in 350 ml acetone to produce 30% acetone solution, to which 8 g of cleaned PTFE fibers and 1 g of azo-bis-isobutyronitrile (Shanghai Sihewei Chemicals, Shanghai, China) were added as initiator. The mixture was degassed by bubbling with a high purity nitrogen flow for about 20 min, sealed, and subjected to ^{60}Co irradiation at a dose rate of 0.8 kGy h^{-1} for 48 h. After irradiation the grafted PTFE fibers was filtered, repeatedly washed with 1 mol l^{-1} NaOH, DDW, 1 mol l^{-1} HCl, and DDW three times to remove unreacted monomers and homopolymers, and dipped into 1 mol l^{-1} HCl for 24 h to reduce anhydride to carboxylic groups (Figure 2). The resulting grafted fiber was filtered, washed with DDW to complete removal of the residual acid, then with copious amount of acetone, and dried in a vacuum oven at 50°C for 48 h.

FI On-Line Solid Phase Extraction for ICP-MS determination of REEs

The microcolumn for on-line solid-phase extraction was made from a PTFE tube with an effective length of 2 cm and an i.d. of 3 mm. The MA-PTFE fibers with a length

of $\sim 2 \text{ cm}$ were random-packed tightly onto the microcolumn like a cotton ball. The fibers were held in place by two end-screw connectors. The mass of the fibers tightly filled into the column was measured to be 0.1633 g. The microcolumn was sequentially washed with DDW, 1 mol l^{-1} HNO_3 , and DDW until the effluent contained no REE and other ions.

Figure 1 shows the FI manifold for the operation sequence of the FI on-line solid-phase extraction coupled with ICP-MS. In the prefill step (Figure 1b), the microcolumn was washed with 0.9 mol l^{-1} HNO_3 and the tubing was flushed with sample solution for 10 s. This prefill stage was used only when a new sample was introduced, but omitted for replicate preconcentrations of the same sample. In Step 1, the valve was in the “fill” position, the sample solution was loaded onto the packed column at flow rate of 7.4 ml min^{-1} for 120 s by pump 1; meanwhile 0.9 mol l^{-1} HNO_3 was introduced into the ICP-MS at 0.5 ml min^{-1} for baseline. In Step 2, the injector valve was turned to the “inject” position and pump 1 stopped so that 0.9 mol l^{-1} HNO_3 was introduced at a flow rate of 0.5 ml min^{-1} for 35 s to elute the adsorbed REEs into the ICP-MS for determination. The total time for one replicate on-line preconcentration and analysis was 165 s including 120 s sample loading time.

Samples

The polyethylene bottles used for sampling water were precleaned with detergent, DDW, dilute HNO_3 , and DDW, respectively. Seawater samples were collected from Tianjin, Dalian, and Qingdao, China. River water samples were obtained from Haihe River (Tianjin, China), Jinghang Canal (Cangzhou, China), and Weijin River (Tianjin, China). All samples were filtered through $0.45\text{-}\mu\text{m}$ super filters, acidified to $\text{pH} = 3.0$, and stored at 4°C or measured at once.

Three certified reference materials (CRMs) from NRCCRM, i.e., GBW 07312 (sediment), GBW 07313 (marine sediment), and GBW 07405 (soil), were analyzed to check the accuracy of the developed on-line solid-phase extraction coupled with ICP-MS for determination of REEs in environmental samples.

Sample Digestion

About 0.1 g of the CRMs were thoroughly mixed with 4 ml of 65% HNO_3 , 1 ml 30% H_2O_2 , and 1 ml of 40% HF

Figure 2. Schematic representation of the reaction between PTFE and maleic anhydride.

Figure 3. Effect of the pH of sample solution on the on-line solid-phase extraction of trace REEs and Ba(II).

in a PTFE pressure vessel. The PTFE vessel was closed and left to stand overnight. A microwave program (EPA 0512) was then applied to the vessel for sample digestion. After the PTFE vessel cooled down to room temperature, 0.5 ml of 40% HF was added and the EPA 0512 program was applied again. Once the PTFE vessel cooled down to room temperature, 0.5 ml of 30% H₂O₂ was added to stand for 1 h. Five ml of boric acid solution (5.00 g of H₃BO₃ in 100 ml of DDW) was added to dissolve precipitated fluorides and EPA0512 was applied again [25]. The clear digests were diluted to 500 ml (pH = 3.0, adjusted with 5% vol/vol HNO₃ and diluted NH₃ · H₂O). A blank solution was also prepared in parallel.

Results and Discussion

Determination of the Content of Grafted Groups on the PTFE Fiber

Quantification of the grafted groups was determined by an acid-base back titration method; 0.5 g of MA-PTFE was cut into mm-grade using a stainless scissors, and mixed with 20 ml of 0.2 mol l⁻¹ NaOH solution. After electro-magnetic stirring of the mixture for 3 h, 10 ml of the supernatant was titrated with 0.2 mol l⁻¹ HCl. The content of the -COOH grafted on the PTFE fiber was determined to be 0.61 mmol g⁻¹.

Binding Capacity of the MA-PTFE Fibers

The static binding capacity of the MA-PTFE fiber was determined for La(III) by a batch experiment. 100 mg of the MA-PTFE fiber was equilibrated by shaking for 24 h in the excess La(III) solution (50 ml, 10 mg l⁻¹) at optimum adsorption pH = 3.0. Then, the MA-PTFE fiber was filtered off and the concentration of the remaining La(III) in the solution was determined by ICP-MS. The result of the static capacity for La was determined to be 0.31 mmol g⁻¹.

The dynamic capacity of the MA-PTFE fibers was determined by passing La(III) solution at optimum pH through a cylindrically shaped PTFE microcolumn (2-cm long × 3-mm i.d.) packed with 0.1633 g of the MA-PTFE fibers at a fixed flow rate until the concentration of the metal ions in the effluent was the same as in the influent. Successively fractions of 1 ml effluent aliquots were collected, in which the concentration of La(III) was measured by ICP-MS. The dynamic binding capacity was then calculated according to Wang and Barnes [26].

The effect of sample flow-rate on the dynamic capacity of the MA-PTFE fibers was examined. No remarkable effect of sample flow-rate on the dynamic capacity was observed in a sample loading flow rate range of 1 to 3 ml min⁻¹. The dynamic capacity decreased as the sample flow-rate increased from 3 to 7 ml min⁻¹. Further increase in sample loading flow rate resulted in more rapid decrease in dynamic capacity likely due to the limited retention kinetics and less contact time for retention.

Development of an FI On-Line Solid-Phase Extraction Protocol of for ICP-MS Quantification of (Ultra)Trace REEs in Environmental Materials Using the MA-PTFE Fibers as Sorbent

The effect of the pH of sample solution on the on-line solid-phase extraction of REEs was investigated from pH = 1 to 5. As shown in Figure 3, the optimum pH range for group REEs extraction was in a pH range of 2.8 to 3.6.

To evaluate the ability of the present FI on-line solid-phase extraction system to separate REEs from Ba, the pH dependence of the Ba(II) ion intensity was also examined (Figure 3). Ba(II) can not be preconcentrated below pH = 3.1, and the maximum Ba signal was observed between pH 4.7–5.0. Accordingly, the effect of Ba on the ICP-MS determination of Eu can be eliminated by controlling the pH of sample solution below 3.1.

To find the possibility for eliminating the effect of dissolved salts on the ICP-MS determination, the pH dependence of the on-line solid-phase extraction of Na(I) was investigated in a wide pH range of 1.5 to 10.9 under cool plasma conditions. It was found that the Na signal was at baseline level at pH = 1.5–5.0, and increased rapidly with further increase in pH. Studies on the effect of the pH of sample solution on the on-line solid-phase extraction of Mg(II) under hot plasma conditions showed that the Mg signal was nearly at baseline level at pH ≤ 4.5, and reached maximum at pH > 10.6. Under the condition of pH ≤ 4.5 the matrix interferences from the two main coexisting ions of Na(I) and Mg(II) in natural water, especially in seawater, can be eliminated. For selective group extraction of REEs and effective elimination of the interferences from Ba

Table 2. Analytical figures of merit of the on-line solid phase extraction coupled with ICP-MS for determination of REEs under experimental conditions shown in Table 1

Isotope	Detection limit (3s) ^a /pg l ⁻¹	Enhancement factor ^b	Precision/% (RSD, <i>n</i> = 16) ^c
¹³⁹ La	9	76	0.5
¹⁴⁰ Ce	20	75	0.5
¹⁴¹ Pr	3	79	0.6
¹⁴⁵ Nd	16	81	1.0
¹⁴⁷ Sm	14	84	1.1
¹⁵¹ Eu	13	85	0.7
¹⁵⁷ Gd	12	83	0.9
¹⁵⁹ Tb	2	81	0.5
¹⁶¹ Dy	4	79	0.6
¹⁶⁵ Ho	1	69	0.5
¹⁶⁶ Er	5	69	0.8
¹⁶⁹ Tm	2	97	0.5
¹⁷² Yb	4	88	0.5
¹⁷⁵ Lu	1	80	0.5

^aBased on 3s of 11 replicate determinations of the blank.^bCalculated as the ratio of the slope of the linear portion of the calibration curves after the on-line solid extraction to that without on-line solid extraction.^cBased on 16 replicate preconcentrations of 50 ng l⁻¹ aqueous multi-element standard.

and dissolved salts, the sample solution was adjusted to pH = 3.0.

The effect of sample loading flow rate on the FI on-line solid-phase extraction of 50 ng l⁻¹ REEs and Ba(II) was examined at a sample pH = 3.0 with a sample loading time of 30 s. The signal intensities of REEs increased almost linearly with sample loading flow rate from 2.7 to 7.4 ml min⁻¹, then gradually leveled off with further increase in sample loading flow rate. However, the signal intensity of Ba was always at baseline level as sample loading flow rate increased from 2.7 to 9.6 ml min⁻¹.

Studies of the effect of sample loading time on the on-line solid-phase extraction of 50 ng l⁻¹ REEs and Ba(II) at a sample pH = 3.0 with a sample loading flow rate of 7.4 ml min⁻¹ showed that the signal intensity of each REE increased linearly as sample loading time increased up to 135 s, after which the slope decreased gradually, whereas the Ba signal was still at baseline level and was not affected by the sample loading time. These results indicate that a higher enhancement factor for REEs could be achieved by properly increasing

sample flow rate and/or sample loading time without increasing the interferences from Ba.

Dilute nitric acid was selected for on-line elution of the extracted REEs and transport of the analytes to the ICP-MS system, given its high efficiency for the analyte elution and its low background for ICP-MS analysis. The concentration and flow rate of the nitric acid solution for elution were optimized in light of sensitivity and precision; 0.9 mol l⁻¹ of HNO₃ at a flow rate of 0.5 ml min⁻¹ was selected for elution to ensure good precision and to obtain reasonable sensitivity.

Analytical Performance of the FI On-Line Solid-Phase Extraction Coupled with ICP-MS for (Ultra)Trace REEs Determination

Table 2 summarizes the figures of merit of the on-line solid-phase extraction coupled with ICP-MS for simultaneous extraction and determination of 14 REEs under the conditions given in Table 1. A comparison of the developed FI on-line solid-phase extraction preconcentration and separation system with other previous reported on-line solid-phase extraction preconcentration and separation systems [11, 17–19] for ICP-MS determination of REEs in terms of sample throughput, enhancement factor, detection limit, and precision is made in Table 3. Generally speaking, the developed on-line solid-phase extraction coupled with ICP-MS using the MA-PTFE fibers as sorbent offer lower detection limits, higher sample throughput, better precisions, and higher enhancement factors.

Validation of the Developed Methodology

Owing to the lack of seawater and natural water CRMs for REEs, the accuracy of the developed on-line solid-phase extraction coupled with ICP-MS for determination of (ultra)trace REEs in environmental materials was checked by analyzing a number of CRMs, GBW 07312 (sediment), GBW 07313 (marine sediment) and GBW 07405 (soil). The analytical results for the concentrations of REEs in these CRMs obtained by the developed on-line solid-phase extraction coupled with ICP-MS are compared with those certified in Table 4. Good agreement between the determined concentrations of REEs in these CRMs by

Table 3. Comparison of the developed on-line solid phase extraction system with previous on-line solid-phase extraction systems for ICP-MS determination of REEs

Sorbent	Sample throughput (samples h ⁻¹)	RSD (%)	Detection limits (pg l ⁻¹)	Enhancement factor	Reference
Maleic acid grafted PTFE fibers	22	0.5–1.1 (50 ng l ⁻¹)	1–20	69–97	This work
Amberlite XAD-7 + 8-HQ	5	1.2–2.3 (2 ng l ⁻¹)	1.5–16	Not available	Ref. 11
Iminodiacetate (IDA) based resin	5	5–6 (real sample)	20–50	Not available	Ref. 17
Muromac A-1 (IDA resin)	8.6	2.5–8.9 (1.0 μg l ⁻¹)	40–251	11.1–15.6	Ref. 18
8-HQ immobilized fluorinated metal alkoxide glass	12	4.7–8.0 (10 ng l ⁻¹)	37–297	Not available	Ref. 19

Table 4. Analytical results for the determination of REEs in the certified reference materials

Element	Concentration/ $\mu\text{g g}^{-1}$					
	GBW 07312 (Sediment)		GBW 07313 (Marine sediment)		GBW 07405 (Soil)	
	Determined (mean $\pm$ s, $n = 5$)	Certified	Determined (mean $\pm$ s, $n = 5$)	Certified	Determined (mean $\pm$ s, $n = 5$)	Certified
La	30.8 $\pm$ 0.8	32.7 $\pm$ 2.2	67.5 $\pm$ 1.5	67.8 $\pm$ 5.7	32.4 $\pm$ 0.7	36 $\pm$ 6
Ce	56.4 $\pm$ 1.6	61 $\pm$ 5	83.4 $\pm$ 1.7	92 $\pm$ 14	96.8 $\pm$ 1.8	91 $\pm$ 15
Pr	6.42 $\pm$ 0.14	6.9 $\pm$ 1.2	22.7 $\pm$ 0.6	20.1 $\pm$ 2.5	7.42 $\pm$ 0.16	7.0 $\pm$ 1.3
Nd	25.3 $\pm$ 0.5	26 $\pm$ 4	86.4 $\pm$ 2.0	91.8 $\pm$ 5.4	25.5 $\pm$ 0.7	24 $\pm$ 2
Sm	5.42 $\pm$ 0.10	5.0 $\pm$ 0.5	20.2 $\pm$ 0.4	21.5 $\pm$ 2.0	4.31 $\pm$ 0.10	4.0 $\pm$ 0.6
Eu	0.64 $\pm$ 0.01	0.61 $\pm$ 0.04	4.74 $\pm$ 0.12	5.3 $\pm$ 0.5	0.77 $\pm$ 0.01	0.82 $\pm$ 0.06
Gd	4.71 $\pm$ 0.09	4.4 $\pm$ 0.4	20.1 $\pm$ 0.4	22.0 $\pm$ 1.6	3.33 $\pm$ 0.08	3.5 $\pm$ 0.3
Tb	0.89 $\pm$ 0.02	0.82 $\pm$ 0.08	3.42 $\pm$ 0.06	3.4 $\pm$ 0.5	0.72 $\pm$ 0.01	0.7 $\pm$ 0.2
Dy	4.77 $\pm$ 0.11	4.8 $\pm$ 0.2	17.4 $\pm$ 0.5	19.9 $\pm$ 2.5	3.30 $\pm$ 0.08	3.7 $\pm$ 0.6
Ho	1.02 $\pm$ 0.02	0.94 $\pm$ 0.09	4.03 $\pm$ 0.08	4.3 $\pm$ 0.2	0.91 $\pm$ 0.02	0.8 $\pm$ 0.2
Er	2.91 $\pm$ 0.06	3.1 $\pm$ 0.3	10.8 $\pm$ 0.3	11.0 $\pm$ 1.0	2.33 $\pm$ 0.04	2.4 $\pm$ 0.3
Tm	0.58 $\pm$ 0.01	0.53 $\pm$ 0.07	1.52 $\pm$ 0.04	1.54 $\pm$ 0.17	0.38 $\pm$ 0.01	0.41 $\pm$ 0.05
Yb	3.91 $\pm$ 0.06	3.7 $\pm$ 0.5	10.6 $\pm$ 0.3	9.8 $\pm$ 1.6	2.74 $\pm$ 0.07	2.8 $\pm$ 0.5
Lu	0.65 $\pm$ 0.01	0.58 $\pm$ 0.08	1.27 $\pm$ 0.03	1.46 $\pm$ 0.28	0.44 $\pm$ 0.09	0.42 $\pm$ 0.07

the developed method and those certified indicates the accuracy of the developed methodology.

Application to Natural Water Samples

The developed method was applied to determination of (ultra)trace REE in three seawater samples and three river water samples collected locally. The recoveries of 2 ng l⁻¹ REEs spiked in seawater samples and 10 ng l⁻¹ REEs spiked in river water samples ranged from 90 to 106%. The concentration of the REEs ranged from 0.12 to 8.25 ng l⁻¹ in the seawater samples and 1.26 to 243 ng l⁻¹ in the river water samples. The precisions (RSD) of the concentrations of REEs are in the range 1.2 to 4.8%, which are adequate for the construction of geochemically informative normalized REE patterns [27, 28]. Detailed analytical results for these water samples are supplied in the Supplementary Material section (which can be found in the electronic version of this article).

Conclusions

In summary, the developed FI on-line solid-phase extraction coupled with ICP-MS using the maleic acid grafted PTFE fibers as sorbent allows effective preconcentration and separation of REEs from Ba and other matrix elements, and provides a rapid, simple, automatic, selective, and highly sensitive technique for determination of (ultra)trace REEs in environmental materials. More work should be done on the applicability of the fibers for solid-phase extraction of other metal ions so that the fibers can be commercialized for wider applications in the future.

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