Talanta 134 (2015) 476–481

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A novel ligandless-dispersive liquid–liquid microextraction method for matrix elimination and the preconcentration of rare earth elements from natural waters

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ARTICLE INFO

Article history:
Received 18 August 2014
Received in revised form
25 November 2014
Accepted 28 November 2014
Available online 6 December 2014

Keywords:
Dispersive liquid–liquid microextraction
Inductively coupled plasma mass spectrometry (ICP-MS)
Preconcentration
Rare earth elements (REEs)
Waters

ABSTRACT

A new, simple, efficient and rapid separation method based on ligandless-dispersive liquid–liquid microextraction (LL-DLLME) was developed for the preconcentration of rare earth elements (REEs) (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) in natural water samples, followed by inductively coupled plasma mass spectrometry (ICP-MS) detection. Carbon tetrachloride and acetone were used as extraction solvent and disperser solvent, respectively. The experimental parameters affecting the extraction efficiency such as sample pH, volume of extraction/disperser solvent and concentration of NaCl were investigated and optimized. Under the optimum conditions, detection limits between 0.68 and 26.6 ng L^{-1} for a 5 mL sample volume were determined. The developed method was successfully applied to samples such as tap water, river water and seawater. Satisfactory recoveries were obtained with the percentage recovery values of the REEs for spiked water samples being between 94 and 111 for tap water, between 89 and 118 for river water and between 92 and 124 for seawater.

1. Introduction

Rare earth elements (REEs) have been used in different fields, for example as petrogenetic tracers in geochemistry, as fertilizers in agriculture and as superconductors and supermagnets in industry [1]. They are very important for industrial applications because of their metallurgical, optical and electronic properties. Since they have such widespread use, the pollution of the environment by REEs is increasing and they are accumulating in organisms and therefore have the potential to enter the food chain [2]. Therefore, the determination of trace REEs in biological and environmental samples has attracted considerable interest in recent years.

Several techniques such as inductively coupled plasma–optical emission spectrometry (ICP–OES) [3–5], inductively coupled plasma-mass spectrometry (ICP-MS) [2,6,7], neutron activation analysis (NNA) [8], spectrophotometry [9] and X-ray fluorescence (XRF) spectrometry [10] have been used for the determination of REEs. Of these, ICP-MS is the most powerful analytical techniques for trace/ultratrace REEs determination. It has the capability of multi-element detection over a wide concentration range achieving extremely low detection limits and low mass interference for REEs. However, direct determination of REEs in seawater by ICP-MS is still problematic because of the extremely low natural concentrations (pg mL^{-1}) and the high salt content causing the clogging of introduction systems and serious interferences [11]. Therefore, a separation and/or a preconcentration step prior to the analysis is necessary. For this purpose, various sample pretreatment methods such as liquid–liquid extraction (LLE) [12,13], ion-exchange [14], coprecipitation [15,16], solid phase extraction (SPE) [2,4,17], cloud point extraction (CPE) [18], solidified floating organic drop microextraction (SFODME) [19], and dispersive liquid–liquid microextraction (DLLME) [20–22], have been developed for the separation and preconcentration of trace/ultratrace REEs. Recent developments and different applications of dispersive liquid–liquid microextraction (DLLME) have been reviewed in the literature [23–28].

In recent years, DLLME has become a popular pretreatment and separation method for different sample types having different matrices. This technique has been applied for the extraction of various target organic or inorganic analytes due to advantages such as rapidity, low cost, environmental friendliness because of low consumption of organic solvents and high preconcentration factors [29–33]. The technique of DLLME is based on a ternary component solvent system that is produced by an appropriate mixture of extraction and disperser solvents injecting into the aqueous sample. A cloudy solution forms, allowing the analyte in the sample to transfer into the fine droplets of the extraction

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http://dx.doi.org/10.1016/j.talanta.2014.11.063
0039-9140/

solvent. Centrifugation of this mixture enables phase separation so that the analyte ions in these organic droplets may be used for the determination by instrumental techniques [33]. When using ionic liquids (ILs) as solvents in DLLME, the separation of the droplet has been achieved by cooling in an ice bath [27]. The separation of the droplet has also been accomplished by injecting the dispersive solvent serving as the demulsifier onto the top surface of the aqueous bulk to break down the emulsion and then the separated floating organic extraction solvent was impelled and collected into a pipette tip fitted to the tip of the syringe [34].

The aim of the present work was to develop a new dispersive liquid–liquid microextraction method for the preconcentration of REEs from natural water samples without any chelating agent prior to determination using ICP-MS. Since the fewer reagents used reduce the chances of contamination, a preconcentration method that does not rely on a chelating agent is clearly beneficial.

The parameters that affect the extraction efficiency, such as sample pH, volumes of disperser and extraction solvents and the concentration of NaCl were optimized. The developed method was successfully applied for the determination of REEs in tap water, river water and seawater samples.

2. Experimental

2.1. Instruments

An ICP-MS instrument (X Series 2, Thermo Scientific, Hemel Hempstead, UK) was used for determination of REEs. Operating conditions for the ICP-MS instrument are given in Table 1. The pH values were measured using a digital pH meter (Oakton Instruments, UK). A Sanyo-Centaur 2 centrifuge (Sanyo Gallenkamp, Loughborough, England) was used to separate the cloudy sample solution into the organic droplet and the aqueous solution.

2.2. Reagents and solutions

All chemicals used in this work were of analytical reagent grade and were used without further purification. The laboratory glassware used was kept in 10% (v/v) nitric acid overnight and washed several times with ultrapure water before use. Ultrapure water (18.2 MΩ cm) obtained from a Maxima water system (Elga, Buckinghamshire, UK) was used throughout. Working standard solutions of REEs were prepared on a daily basis by stepwise dilution of the multi-element stock standard solution (100 mg L^{-1}, Romil Ltd. Cambridge, UK). Triton X-100, ammonium chloride, ammonia and acetone from Sigma-Aldrich (St. Louis, MO, USA), nitric acid, hydrochloric acid, sodium bicarbonate and sodium hydroxide from Fisher Scientific, carbon tetrachloride from Merck (Darmstadt, Germany) and potassium chloride, potassium hydrogen phthalate and potassium dihydrogen phosphate from BDH Laboratory Supplies (Aristar, Poole, UK) were used in the experiments. Potassium chloride buffer solution (0.1 M) was prepared by adding an appropriate amount of hydrochloric acid to potassium chloride solution to result in a solution of pH 2.0. Potassium hydrogen phthalate buffer solutions (0.1 M at pH 3.0, 4.0 and 5.0) were prepared using potassium hydrogen phthalate, hydrochloric acid and sodium hydroxide. Phosphate buffer solutions (0.1 M) were prepared by adding an appropriate amount of sodium hydroxide to potassium dihydrogen phosphate solution resulting in solutions of pH 6.0 and 7.0. Finally, ammonium chloride/ammonia buffer solutions (0.1 M) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions with pH between 8.0 and 10.0.

2.3. Ligandless-dispersive liquid–liquid microextraction procedure

Aliquots of 5.0 mL sample solution containing the REE ions were adjusted to pH 9.0 using ammonium chloride/ammonia buffer solution and then placed in a polyethylene centrifuge tube. Then, 0.2 mL acetone (disperser solvent) and 60 μL of CCl_4 (extraction solvent) was added to this sample solution and manually shaken for 2 min. A cloudy solution was formed that was produced by tiny droplets of extraction solvent dispersed in the sample solution. This turbid solution was then centrifuged at 3000 rpm for 7 min, and the dispersed fine droplets of CCl_4 were deposited at the bottom of conical test tube. After removing the aqueous phase, the organic phase was diluted to 2.5 mL with 0.1% triton X-100 prepared in 0.1 M HNO_3 solution. A 25 μL aliquot of a 10 mg L^{-1} internal standard solution comprising indium and iridium was added to this solution and then the analyte concentrations determined using ICP-MS.

Calibration was performed against a blank and different concentrations of aqueous standards that had had the same LL-DLLME procedure applied to them.

2.4. Applications to real samples

The proposed method was applied to tap water from Balıkesir University, river water from Büyük Bostancı river in Balıkesir and seawater from The Aegean Sea near the Edremit Coast in Balıkesir. The accuracy of the method was checked by measuring the recovery of REEs in spiked water samples. The river water and seawater samples were filtered through a cellulose membrane filter with a pore size of 0.45 μm and acidified to pH 2 with nitric acid in order to prevent adsorption of the metal ions on the container walls and stored in pre-cleaned polyethylene bottles until analysis. Tap water samples were taken without pretreatment before determination. The pH of the water samples (5 mL) was adjusted to 9.0 using a few drops of 10% (w/v) sodium hydroxide solution and then maintained using ammonium chloride/ammonia buffer. The procedure developed was applied to the water samples.

Table 1
ICP-MS operating conditions.

RF power (W)	1400
Coolant Ar gas flow rate (L min^{-1})	13
Auxiliary Ar gas flow rate (L min^{-1})	0.70
Nebulizer Ar gas flow rate (L min^{-1})	0.86
Dwell time (ms)	10
Spray chamber type	Sturman-Masters
Nebulizer	V-Groove
Collision cell gas	7% hydrogen in helium at 3.5 mL min^{-1}
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

3. Results and discussion

3.1. Optimization of the experimental variables

Different experimental parameters affecting the proposed DLLME method's efficiency including pH, volume of acetone (disperser solvent) and carbon tetrachloride (extraction solvent) and concentration of NaCl, were optimized before the analysis of the real natural samples to achieve maximum extraction recovery. The analytical parameters were optimized using a 5 mL standard solution containing 5.0 μg L^{-1} of each of the REE ions. The optimization procedure was carried out by varying a parameter while the others were kept constant. All experiments were performed in triplicate.

As preconcentration effectiveness of an analyte with a given DLLME method may vary depending on the analyte solution pH, finding the optimal pH is one of the most crucial issues during the optimization of working conditions. Therefore, the effect of pH on the LL-DLLME extraction of REEs was studied over the pH range of 2.0–10.0. Acetone (300 μL) and 40 μL CCl_4 was added to 5 mL of analyte solution containing 1.0 mL buffer solution. The effect of the sample solution pH on analytical signals is presented in Fig. 1. As can be seen in Fig. 1, the analytical signals slightly increased from pH 2.0 to 7.0 and reached a maximum at pH 9.0 and then decreased. Therefore, pH 9.0 was selected as the optimum value for all further work.

The effect of the volume of extraction solvent on the analytical signals was examined by changing the volume of CCl_4 from 30 to 70 μL, keeping the volume of acetone constant (300 μL). The experimental results showed that the analytical signals of REEs slowly increased when the extraction solvent volume varied from 30 to 60 μL with 10 μL increments, and slowly decreased when the volume was higher than 60 μL. Therefore, 60 μL CCl_4 was used as extraction solvent in the subsequent experiments.

The volume of disperser solvent directly affects extraction solvent solubility in aqueous phase, thus, influencing the efficiency of the microextraction technique. The effect of the volume of acetone on the extraction efficiency of REEs was investigated over the range of 100–400 μL. The results showed that the analytical signals increased up to 200 μL acetone and then slowly decreased. Therefore, 200 μL of acetone was selected as the optimum volume of the disperser solvent.

The addition of salt to the aqueous sample may significantly improve the extraction of several analytes in liquid–liquid extraction (LLE). This is possibly due to the salting-out effect. To evaluate the use of the salting-out effect, the extraction efficiency was studied with the NaCl concentrations over the range 0.0 M to 1.0 M. According to the experimental results obtained, salt addition has no significant effect on the extraction efficiency of REEs. Therefore, all the extraction experiments were carried out without the addition of salt.

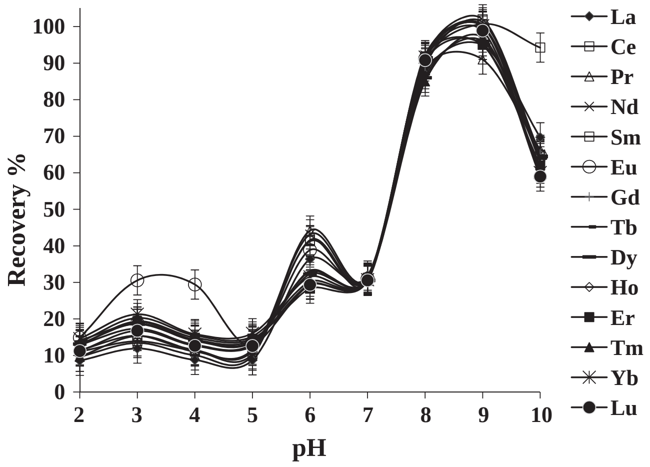

Fig. 1. Effect of pH on the extraction efficiency of rare earth elements.

3.2. Effect of the volume of sample solutions

Obtaining a high preconcentration factor for a method is dependent upon the sample volume. Different volumes of sample solution (5–40 mL) containing 5.0 ng of each REE ion were used to study the effect of sample volume with a constant ratio of sample volume to the volumes of disperser solvent (acetone) and extraction solvent (CCl_4). Therefore, the acetone volume used was 0.2, 0.4, 0.8, 1.2 and 1.6 mL, while the carbon tetrachloride volume used was 60, 120, 240, 360 and 480 μL when the volume of sample was 5, 10, 20, 30 and 40 mL, respectively. The results obtained are presented in Table 2. The applicability of the preconcentration was demonstrated using 40 mL of tap water and 40 mL of tap water spiked with 4.0 ng of each REE ion. The results are also given in Table 2. The percentage recovery was quantitative at all sample volumes. However, if a higher sample volume is used for preconcentration of the REEs from natural waters, it is advisable that the calibration standards and blank should also be prepared using the same volume. This prevents any effects arising from different organic solvent volumes on the sensitivity of the instrument.

3.3. Effect of matrix ions

The effects of foreign ions were studied in two different parts. First, the effect of a seawater matrix was studied using synthetic seawater containing 1270 mg L^{-1} Mg^{2+}, 400 mg L^{-1} Ca^{2+}, 10,800 mg L^{-1} Na^{+}, 390 mg L^{-1} K^{+}, 5100 mg L^{-1} SO_4^{2-}, 600 mg L^{-1} CO_3^{2-} and 16,600 mg L^{-1} Cl^{-} and 620 mg L^{-1} NO_3^{-} by comparing the signal of 5.0 μg L^{-1} of each analyte in the presence and absence of the matrix. The results are shown graphically in Fig. 2 and indicated that there were no significant differences in the analytical signals between sample with and without the addition of the matrix. The results obtained also indicate that the method can be used successfully to extract REEs from high salinity water samples before their determination using ICP-MS.

In the second part of the investigation into the effect of the foreign ions, the potential interference effects from Fe, Al, Sr, Ba, Mn, Ni, Cd, Zn, Co each at a concentration level of 1 mg L^{-1}, which is a significantly higher concentration than exists in virtually all natural waters, were determined. The effect of humic acids on the extraction of the REEs was also investigated, with a concentration of 5 mg L^{-1} being tested. The recovery values for the REE elements in the presence of these ions or with humic acid were between 91 and 105%, confirming the lack of interference caused under the experimental conditions used. The results indicate that this method may readily be applied to the determination of REE in natural water samples including seawater.

3.4. Analytical performance of the method and comparison with other methods

The analytical performance of the proposed method was evaluated under the optimized conditions. Calibration graphs were constructed by performing the proposed LL-DLLME procedure to 5 mL of a blank and the standard solutions containing known amounts of REEs in the concentration range of 0.05–5 μg L^{-1} buffered at pH 9.0. The limits of detection (LOD) were calculated using 3 s/slope from 15 repeat analysis of a solution containing 5.0 μg L^{-1} REE ions. The standard deviations of the signals of the REEs in these solutions were inserted into this equation to calculate the LOD value for each analyte. The detection limits

Table 2
Effect of the sample volume on the recoveries of rare earth elements, $N=3$.

	Recovery (%)					
	5 mL	10 mL	20 mL	30 mL	40 mL	40 mL *
La	102.2 ± 10.1	94.1 ± 6.5	85.8 ± 5.3	92.4 ± 6.3	105.2 ± 1.2	115.9 ± 9.8
Ce	97.6 ± 5.5	90.4 ± 6.2	91.4 ± 3.3	87.4 ± 11.6	87.4 ± 7.2	92.7 ± 5.3
Pr	99.7 ± 10.8	109.8 ± 11.5	90.5 ± 0.9	97.9 ± 4.8	93.9 ± 3.0	95.6 ± 7.8
Nd	93.6 ± 0.1	91.0 ± 9.2	91.9 ± 7.7	100.9 ± 13.1	114.5 ± 8.9	105.1 ± 6.3
Sm	103.9 ± 8.7	110.6 ± 6.1	97.9 ± 12.2	98.5 ± 7.9	103.2 ± 15.7	110.1 ± 9.8
Eu	102.7 ± 6.6	103.6 ± 7.6	94.7 ± 2.3	94.2 ± 4.9	98.6 ± 8.8	111.0 ± 10.5
Gd	102.0 ± 3.8	90.3 ± 2.9	94.0 ± 0.9	99.3 ± 9.1	95.8 ± 3.3	107.3 ± 9.7
Tb	96.1 ± 3.7	90.0 ± 7.1	93.9 ± 11.9	90.8 ± 14.9	90.0 ± 5.6	108.1 ± 8.4
Dy	95.8 ± 4.6	88.0 ± 4.3	96.4 ± 1.3	91.0 ± 15.6	91.0 ± 5.2	100.3 ± 6.5
Ho	106.4 ± 7.1	91.5 ± 9.5	95.7 ± 5.4	100.6 ± 13.1	103.7 ± 0.2	95.6 ± 7.9
Er	102.1 ± 6.9	91.2 ± 7.2	98.6 ± 10.4	95.0 ± 4.4	103.3 ± 12.8	93.5 ± 7.8
Tm	98.7 ± 6.5	93.5 ± 9.8	94.6 ± 15.2	96.0 ± 4.8	95.3 ± 7.7	102.0 ± 10.1
Yb	98.9 ± 7.3	91.0 ± 5.6	94.5 ± 16.4	105.3 ± 11.1	97.8 ± 6.0	96.4 ± 8.4
Lu	97.1 ± 6.2	91.5 ± 7.1	94.0 ± 1.4	91.1 ± 5.0	96.5 ± 1.3	94.2 ± 7.5
CCl_4 volume (μL)	60	120	240	360	480	480
Acetone volume (mL)	0.2	0.4	0.8	1.2	1.6	1.6
Preconcentration factor	2	4	8	12	16	16

* These recovery values were obtained from 40 mL of tap water and 40 mL of tap water spiked with 4.0 ng of each REE ion.

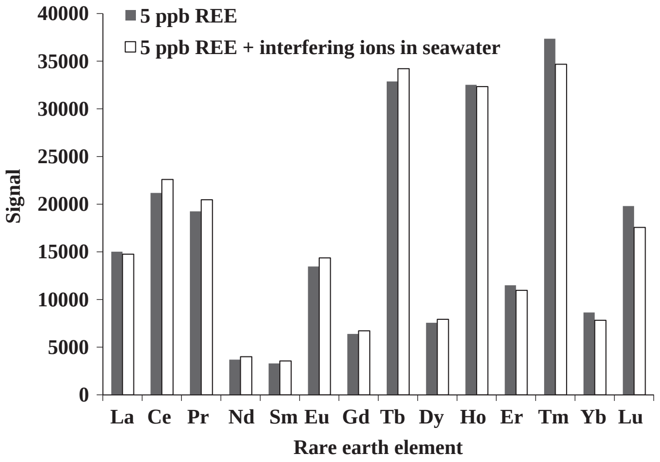

Fig. 2. The effect of interfering ions (1270 mg L^{-1} Mg^{2+}, 400 mg L^{-1} Ca^{2+}, 10,800 mg L^{-1} Na^{+}, 390 mg L^{-1} K^{+}, 5100 mg L^{-1} SO_4^{2-}, 600 mg L^{-1} CO_3^{2-}, 16,600 mg L^{-1} Cl^{-}, and 620 mg L^{-1} NO_3^{-}) on the signal of 5.0 μg L^{-1} of REE ions.

were 7.04, 26.60, 1.77, 5.95, 9.77, 4.40, 5.51, 1.08, 3.53, 0.76, 3.77, 0.68, 3.96 and 0.91 ng L^{-1} for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, respectively, while for 5 mL sample solution the preconcentration factor was 2. The correlation coefficients of the calibration graphs for REEs were in the range from 0.9973 to 0.9999. As shown in Table 2 the proposed method yielded very good recovery values and a preconcentration factor of 16 for 40 mL of the sample solution. Therefore, the detection limits obtained would 8 fold lower than the LOD values quoted above.

The real extraction efficiencies of the method have been checked measuring the concentrations of REEs in a solution containing 5 μg L^{-1} of REEs in 0.1% Triton X-100 prepared in 0.1 M HNO_3 and 60 μL of CCl_4 using calibration graphs prepared using the proposed method. Real recoveries were between 86 and 100% for the REEs. Since the calibration was performed against a blank and different concentrations of aqueous standards that had undergone the same LL-DLLME procedure, if the real extraction efficiencies of the samples were less than 100%, it would be cancelled by the same flaw with the calibration standard and hence there would be no effect on the result of the REEs.

Table 3 compares the characteristic data of the developed method with other preconcentration methods for REEs reported in the literature. Although the detection limits that are obtained in this method are higher than some of the other methods given in Table 3, the extraction time of the proposed method is shorter than most of the other methods. Also, the proposed method requires a use of small sample volume. Additionally, in most of the DLLME pretreatment methods for trace elements (with the exception of ionic liquids), the organic droplets were heated until the entire organic matrix has evaporated and the residue was then dissolved in acid solution followed by detection of the analytes with different spectroscopic techniques. However, in the proposed method, a solution containing 0.1% Triton X-100 in 0.1 M HNO_3 was added to the organic droplets and this final solution was measured directly by ICP-MS. Therefore, the proposed method is straightforward and simple to apply.

3.5. *Application of the method to water samples*

In order to evaluate the applicability of the proposed method, it was applied to the determination of REE ions in tap, river and seawater samples, and the recoveries of spikes of the REE ions were also studied. The analytical results and the recoveries for the spiked samples are given in Table 4. Good agreement was obtained between the spiked and the recovered concentrations of the analytes. Recovery values between 94 and 111% for tap water, 89 and 118% for river water and 92 and 124% for seawater were determined. These results demonstrate the applicability of the method for the determination of REEs in natural water samples.

4. Conclusions

In the present work, a new dispersive liquid–liquid microextraction method for the preconcentration of REEs was developed that did not require a chelating agent. The developed method with ICP-MS detection was applied successfully for simultaneous extraction, preconcentration and determination of the REEs in tap water, river water and seawater samples. The method has the advantages of simplicity, efficiency, rapidity, high sensitivity, good accuracy and minimum organic solvent consumption.

Table 3
Comparative data from some recent studies on preconcentration–separation of REEs.

Analyte	Method [a]	Detection technique[b]	Sample	Detection limit (LOD) (ng L^{-1})	Preconcentration factor	Sample volume (mL)	Extraction time (min)	Ref.
Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	PMCME	On-line MCN- ICP-MS	Human serum and urine	0.08–0.97	20	1	7	[6]
La, Eu, Yb	SFODME	ETV-ICP-MS	Biological and natural water samples	0.65–2.1	500	10	30	[19]
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	DLLME	ICP-QMS	Groundwater samples	0.05–0.55	93.8–101.8	50	10	[20]
Sm, Eu, Gd, Dy	DLLME	ICP–OES	Uranium dioxide powder	340–1290	19.34–86.04	80	6	[21]
Sm, Eu, Gd, Dy	DLLME	ICP–OES	–	–	78–103	–	60	[22]
La, Eu, Gd, Yb	SPE	ICP-MS	Tea leaves and mussel	0.36–0.60	25	50	33	[35]
La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y	LPE	ICP-MS	High-purity cerium oxide	3–26	–	–	30	[36]
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu	SPE	ICP-MS	Tap water and seawater	3.2–10.3	–	2	5	[37]
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	LL-DLLME	ICP-MS	Water samples	0.68–26.6	2	5	9	This work
				0.085–3.33	16	40	9	

[a] LL-DLLME: Ligandless-dispersive liquid–liquid microextraction, SPE: Solid phase extraction, SFODME: Solidified floating organic drop microextraction, DLLME: Dispersive liquid–liquid microextraction, PMCME: Polymer monolithic capillary microextraction, LPE: Liquid phase extraction.

[b] ICP-MS:Inductively coupled plasma mass spectrometry, ETV-ICP-MS: Electrothermal vaporization inductively coupled plasma mass spectrometry, ICP-QMS: Inductively coupled plasma quadrupole mass spectrometry, MCN-ICP-MS: Microconcentric nebulization inductively coupled plasma mass spectrometry.

Table 4
Analytical results of water samples and the recovery of spiked analyte ($\bar{x} \pm s$, N=3).

Element	Added μg L^{-1}	Tap water (μg L^{-1})	R (%)	River water (μg L^{-1})	R (%)	Seawater (μg L^{-1})	R (%)
La	–	< LOD	–	0.042 ± 0.005	–	0.088 ± 0.003	–
	0.1	0.111 ± 0.028	111.0	0.145 ± 0.011	103.0	0.196 ± 0.038	108.0
	5	5.11 ± 0.20	102.2	4.52 ± 0.21	89.6	5.20 ± 0.11	102.2
Ce	–	< LOD	–	< LOD	–	0.074 ± 0.005	–
	0.1	0.094 ± 0.020	94.0	0.097 ± 0.018	97.0	0.177 ± 0.014	103.0
	5	4.89 ± 0.20	97.8	4.75 ± 0.30	95.0	5.26 ± 0.17	103.7
Pr	–	< LOD	–	0.080 ± 0.018	–	0.085 ± 0.009	–
	0.1	0.110 ± 0.022	110.0	0.171 ± 0.09	91.0	0.209 ± 0.037	124.0
	5	4.83 ± 0.19	96.6	5.83 ± 0.06	115.0	5.25 ± 0.35	103.3
Nd	–	< LOD	–	0.033 ± 0.008	–	0.070 ± 0.003	–
	0.1	0.104 ± 0.023	104.0	0.145 ± 0.005	112.0	0.173 ± 0.035	103.0
	5	4.85 ± 0.25	97.0	4.70 ± 0.25	93.3.0	5.46 ± 0.16	107.8
Sm	–	< LOD	–	0.028 ± 0.005	–	< LOD	–
	0.1	0.110 ± 0.025	110.0	0.139 ± 0.008	111.0	0.119 ± 0.007	119.0
	5	4.76 ± 0.27	95.2	4.80 ± 0.41	95.4	5.21 ± 0.34	104.2
Eu	–	< LOD	–	< LOD	–	< LOD	–
	0.1	0.104 ± 0.025	104.0	0.094 ± 0.011	94.0	0.105 ± 0.027	105.0
	5	4.82 ± 0.22	96.4	4.85 ± 0.33	97.0	5.48 ± 0.16	109.6
Gd	–	< LOD	–	< LOD	–	0.053 ± 0.001	–
	0.1	0.103 ± 0.028	103.0	0.099 ± 0.003	99.0	0.145 ± 0.009	92.0
	5	4.91 ± 0.29	98.2	4.73 ± 0.26	94.6	5.57 ± 0.13	110.3
Tb	–	< LOD	–	0.019 ± 0.006	–	< LOD	–
	0.1	0.107 ± 0.028	107.0	0.127 ± 0.011	108.0	0.114 ± 0.017	114.0
	5	4.88 ± 0.27	97.6	4.75 ± 0.27	94.6	5.52 ± 0.17	110.4
Dy	–	< LOD	–	0.046 ± 0.009	–	0.026 ± 0.004	–
	0.1	0.108 ± 0.030	108.0	0.164 ± 0.008	118.0	0.130 ± 0.007	104.0
	5	4.99 ± 0.28	99.8	4.72 ± 0.30	93.5	5.37 ± 0.19	106.9
Ho	–	< LOD	–	< LOD	–	0.050 ± 0.003	–
	0.1	0.106 ± 0.026	106.0	0.093 ± 0.002	93.0	0.162 ± 0.031	112.0
	5	4.98 ± 0.26	99.6	4.97 ± 0.32	99.4	5.30 ± 0.21	105.0
Er	–	< LOD	–	0.042 ± 0.009	–	0.094 ± 0.011	–
	0.1	0.107 ± 0.025	107.0	0.147 ± 0.015	105.0	0.196 ± 0.06	102.0
	5	5.01 ± 0.26	100.2	5.11 ± 0.35	101.4	5.17 ± 0.23	101.5
Tm	–	< LOD	–	< LOD	–	< LOD	–
	0.1	0.106 ± 0.027	106.0	0.104 ± 0.018	104.0	0.114 ± 0.013	114.0
	5	5.01 ± 0.24	100.2	4.50 ± 0.22	90.0	4.99 ± 0.19	99.8
Yb	–	< LOD	–	< LOD	–	0.035 ± 0.008	–
	0.1	0.100 ± 0.017	100.0	0.109 ± 0.011		0.136 ± 0.006	101.0
	5	4.92 ± 0.30	98.4	4.55 ± 0.28	91.0	4.91 ± 0.26	97.5
Lu	–	< LOD	–	< LOD	–	< LOD	–
	0.1	0.103 ± 0.028	103.0	0.094 ± 0.008	94.0	0.112 ± 0.006	112.0
	5	5.03 ± 0.32	100.6	4.45 ± 0.26	89.0	4.75 ± 0.21	95.0

Acknowledgements

The authors are thankful for the financial support from the Unit of the Scientific Research Projects of Balıkesir University (Project no: 2013/82). İbrahim Çelik is grateful to the ERASMUS Lifelong Learning Programme for Training.

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