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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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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.

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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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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