



# Mixed micelle-mediated extraction approach for matrix elimination and separation of some rare earth elements



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## ARTICLE INFO

### Article history:

Received 17 January 2016

Received in revised form 18 February 2016

Accepted 18 February 2016

Available online 27 February 2016

### Keywords:

Rare earth elements

Mixed micelle-mediated extraction

Alizarin red S

Amphibolite rock sample

Inductively coupled plasma optical emission spectrometry

## ABSTRACT

A selective mixed micelle-mediated extraction procedure was investigated for simultaneously separation of Y(III), La(III), Nd(III), Sm(III), Gd(III), Ho(III), Er(III), and Yb(III) from different matrices prior to their determination using inductively coupled plasma optical emission spectrometry (ICP-OES). The proposed procedure is based on the complexation of the target metal ions with Alizarin Red S and cetyltrimethylammonium bromide (CTAB) at pH 6 and then entrapped in Triton X-114 in the presence of KI at room temperature (25 °C). Under optimized extraction conditions, the limits of detection were ranged from 0.04 ng mL<sup>-1</sup> (Yb) to 0.92 ng mL<sup>-1</sup> (La). The developed procedure exhibited high enrichment factors (90–97-fold). Furthermore, the interference of diverse ions accompanying the target metal ions in their ores is tolerated by controlling the pH. The accuracy of the procedure has been validated through recovery experiments on spiked water samples and synthetic mixtures. The procedure was successfully applied for the determination of the studied metal ions in Amphibolite rock sample.

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## 1. Introduction

Rare earth elements (REE) provide performance that has not yet to be replaceable by alternative materials due to their unique physical and chemical characteristics, so these elements are indispensable in cutting-edge technology products. In particular, they have been widely used in numerous industrial applications such as manufacturing automotive catalytic converters, phosphors that are used in color TV sets and flat-panel displays, electronic components, permanent magnets, metallurgical additives, and superconductors [1–3]. Furthermore, REE have many applications in green technological areas for examples, reducing carbon dioxide emissions and manufacturing of next-generation batteries such as rechargeable lanthanum–nickel–hydride (La–Ni–H) batteries which replace environmentally less friendly cadmium and lead batteries [4]. Rapid growth in these industrial areas could result in heightened global demand for REE. Thus, more and more attention is paid to the separation and determination of REE. Inductively coupled plasma-mass spectrometry (ICP-MS) is one of the most powerful analytical techniques for REE determination. It has low detection limits and low mass interference for REE, but the high cost limits its extensive application. ICP-OES is undoubtedly one of the most effective techniques for the determination of REE because of the capability for rapid multi-element detection with relatively low detection limits over a wide linear dynamic range. However, direct ICP-OES

determination of REE in geological and environmental samples by instrumental techniques is still one of the most difficult and complicated tasks, the problem is encountered in their determination at trace levels in the presence of a large number of diverse ions. The complexity of concomitant ions of these samples raised the possibility that spectral interference may introduce errors in determination of REE. Hence, there is a pressing need to develop robust pre-concentration techniques capable of providing quantitative determination of REE in variety of sample matrices with several instrumental techniques. Many techniques have already been proposed for the pre-concentration and separation of REE, including co-precipitation [5,6], solid-phase extraction [7,8], ion exchange [9,10], liquid–liquid extraction [11,12], cloud point extraction [13–17], chromatographic separation [18], liquid phase microextraction [19,20], and capillary microextraction [21].

Cloud point extraction (CPE) has been shown to be a promising, viable alternative to the current classical separation methods. It is considered a particular case of aqueous–two phase systems similar to liquid–liquid extraction but it differs in that the system begins as a single phase and utilizes a surfactant, in place of an organic solvent, for phase separation. CPE has been demonstrated to have several advantages such as simplicity, low cost, speed, selectivity, and excellent pre-concentration factors. Likewise, the ability of CPE to be coupled with different analytical instruments (e.g., atomic absorption, spectrochemical, chromatographic, and electrochemical analyses) allows for elaborating high-sensitive analytical methods [22,23]. Moreover, it complies with the principles of green chemistry [24]. Thus, the use of CPE for separation and pre-concentration of metal ions from different matrices is of

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continuing progress [25,26]. The main limitation of CPE is the relatively low partition coefficients of several metal ions with hydrophilic chelates. For charged micelles, the clouding phenomenon rarely occurs, presumably because electrostatic repulsion prevents phase separation in most cases. In order to accomplish both ideal hydrophobic and non-ideal electrostatic interactions, a mixed micelle-mediated extraction (mixed-MME) system has been applied. The interaction of ionic surfactant with a charged complex leads to formation of neutral molecules which could be extracted by non-ionic surfactant [27,28]. Therefore, a mixed-MME system is becoming important for separation and pre-concentration of many metal ions [29,30].

The aim of the present work is to introduce a new simple and selective mixed-MME procedure for quantitative separation of some REE from the concomitant ions, especially Ti(IV), UO<sub>2</sub>(II), Th(IV), Zr(IV), Hf(IV), Fe(III), Al(III), and Sc(III). The use of chromogenic reagent Alizarin Red S (ARS) seems to be efficient. The presence of sulphonate group in the ARS moiety inhibits the formation of sufficient hydrophobic complexes to be extracted in the non-ionic surfactant (Triton X-114). So, the mixed-MME approach is suggested. This could be verified by using the cationic surfactant cetyltrimethylammonium bromide (CTAB) to neutralize the hydrophilicity of ARS. The use of electrolytes is also essential in such cases. To increase the selectivity and applicability of the proposed procedure, the interference of different concomitants will be extensively studied through the study of the effect of the pH and the preceding separation of the interfering ions. In the view of optimization and interference studies, the proposed procedure will be applied for separation and pre-concentration of the target metal ions from water samples, synthetic mixtures, and Amphibolite rock sample prior to their determination using inductively coupled plasma optical emission spectrometry (ICP-OES).

## 2. Experimental

### 2.1. Instrumentation

All ICP-OES analyses of REE were elaborated using a Perkin Elmer ICP-OES (Optima 8300, USA). The instrumental operating parameters are summarized in Table 1. The pH measurements were performed using a Hanna instrument model 8519 pH meter (Hanna instruments, Germany) furnished with a combined glass-saturated calomel electrode. A CH90-2 centrifuge (Hinotek Technology Co. Ltd., China) was utilized to accelerate the phase separation of the cloudy sample into surfactant-rich phase and aqueous phase. A JSR Model JSSB-30T temperature-controlled water bath was used for keeping solution mixtures at the desired temperature for mixed-MME experiments.

### 2.2. Reagents and solutions

Otherwise noted, all reagents used were of analytical reagent grade. Aqueous solutions were prepared with double distilled water. Stock solutions of 1000 µg mL<sup>-1</sup> yttrium and some lanthanide ions were prepared by dissolving the appropriate amount of their pure oxides

(BDH, England) in a few ml of perchloric acid and evaporating to dryness. The resulting residues were dissolved in double distilled water and standardized by EDTA titration. A solution of  $5 \times 10^{-3}$  mol L<sup>-1</sup> ARS (Merck, Germany) was prepared by dissolving 1.801 g of C<sub>14</sub>H<sub>7</sub>NaO<sub>7</sub>·5H<sub>2</sub>O in double distilled water and diluting to 1000 mL. The surfactants, Triton X-114 (from Sigma-Aldrich, USA) and CTAB (Acros Chemicals, Ottawa, ON, Canada) were used without further purification. A 1.822 g of CTAB was dissolved in 1000 mL double distilled water to obtain a  $5 \times 10^{-3}$  mol L<sup>-1</sup> of CTAB solution. A solution of (2.0% w/v) Triton X-114 was prepared by diluting 20 g of Triton X-114 in 1000 mL of double distilled water. Acetate buffer solutions were prepared by adding adequate volumes of 0.5 mol L<sup>-1</sup> sodium hydroxide to 0.5 mol L<sup>-1</sup> acetic acid solutions to result in solutions with pH between 3.0 and 5.5. Borate buffer solutions were made by mixing appropriate volumes of 0.5 mol L<sup>-1</sup> solutions of boric acid and sodium hydroxide resulting in buffer solutions of pH from 6.0 to 8.0. The pH value of each solution was adjusted. Appropriate concentrations of interfering ions were prepared by dissolving their nitrate salts in double distilled water.

### 2.3. Recommended procedure of mixed-MME

For metal distribution studies, an aliquot of sample solution containing target metal ion standard solution was transferred to 50 mL centrifuge tube followed by the addition of 5 mL of borate buffer solution pH 6. Then, 1 mL of  $5 \times 10^{-3}$  mol L<sup>-1</sup> ARS, 1 mL of  $5 \times 10^{-3}$  mol L<sup>-1</sup> CTAB, 2 mL of (2.5% w/v) Triton X-114, and 5 mL of 1 mol L<sup>-1</sup> KI were added. The final volume of micellar solution is brought up to 50 mL using double distilled water. After the addition of all reagents, the solution was shaken and left to stand at room temperature (25 °C) for 3 min. Following this equilibration period, the solution was centrifuged at 3500 rpm for 10 min. After it was waited in an ice bath for 5 min, the surfactant-rich phase became viscous and retained bottom of tubes so the surfactant-rich phase was easily separated from supernatant aqueous phase by removing the latter phase. For multi-elemental analysis, the surfactant-rich phase was dissolved and diluted to 2.0 mL of acidified methanol solution with HNO<sub>3</sub> (5: 1) to reduce its viscosity and increase the sample volume for the ICP-OES measurement.

### 2.4. Sample preparation

#### 2.4.1. Water samples

Tap, river, and sea water samples were collected from different locations in Egypt and filtered through a 0.45 µm pore size membrane filter to remove the suspended solids. Spiked water samples were prepared by introducing a definite amount of standard metal ion in variable concentrations to evaluate the accuracy of the proposed procedure. 25 mL of spiked water samples were transferred into 50 mL centrifuge tubes and the recommended procedure given above was applied without further treatment.

#### 2.4.2. Amphibolite rock sample

Amphibolite rock sample (Eastern Desert, Wadi Barud, Egypt) was delivered from the Geology Department, Faculty of Science, Mansoura University. Full analysis of Amphibolite rock sample was elaborated in the laboratories of the department of the geological sciences, Durham University, England, United Kingdom, using ICP-MS (Perkin Elmer, ELAN 6000). Amphibolite rock sample was dried at 100 °C for 2 h., ground, passed through a sieve of 120 meshes, and homogenized. For the digestion, 100 mg of the sample was weighed transferred into a Teflon cup. After adding 3 mL of aqua regia, the mixture was slowly heated to near dryness. This step was repeated twice using another 3 mL of aqua regia every time. The residues were then dissolved with 3 mL concentrated hydrofluoric acid and the solution was heated to almost dryness. Afterwards, 1 mL concentrated sulphuric acid was added dropwise and heated to volatilize excess hydrofluoric acid. The

**Table 1**  
The optimized conditions for ICP-OES measurements.

|  |  |
|--|--|
| RF generator power(W)                          | 1350   |
| Plasma gas flow rate (L min <sup>-1</sup> )    | 15   |
| Auxiliary gas flow rate (L min <sup>-1</sup> ) | 0.2  |
| Nebulizer gas flow rate (L min <sup>-1</sup> ) | 0.45   |
| Pump rate (mL min <sup>-1</sup> )              | 2.5  |
| Sample uptake rate (mL min <sup>-1</sup> )     | 2.5  |
| Delay time (s)                                 | 7  |
| Integration time (s)                           | 3  |
| The number of measurements                     | 3  |
| Wavelength (nm)                                | Y 324.228, Gd 335.047, Sm 330.639,<br>Nd 401.225, La 408.672, Er 337.271,<br>Ho 345.600, Yb 328.937. |

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