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Determination of trace rare earth elements in environmental samples by low temperature electrothermal vaporization inductively coupled plasma mass spectrometry after synergistic extraction with dimethylheptyl methyl phosphate and 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5

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Abstract

Synergistic extraction of trace rare earth elements (REEs) from nitrate solutions using mixtures of dimethylheptyl methyl phosphate (P350) and 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (PMBP) in hexamethylene has been investigated. The factors affecting the synergistic extraction of rare earth ions, such as pH, organic solvent and phase ratio of organic phase to aqueous phase were systematically studied. The synergistic enhancement factors of P350 and PMBP for REEs were calculated to be 4.3–5.8. After the synergistic extraction, the postextraction organic phase was directly introduced into the graphite furnace for electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) determination. It was found that PMBP along with P350 has an obvious chemical modification for REEs, and the limits of detection (LODs) for 15 REEs were in the range of 0.02–0.09 ng L^{-1}. The proposed method was found to be more suitable for the analysis of environmental samples with complex matrix.

Keywords: Rare earth elements; Synergistic extraction; Electrothermal vaporization inductively coupled plasma mass spectrometry; Environmental samples

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1. Introduction

In China, rare earth elements (REEs) are very large and important natural resources, which have been widely used in agricultural and industrial activities. Therefore, more and more REEs have been transferred and accumulated in the environment, such as soil and natural water, and finally enter the human body through food chain. Up to the present day, the bioavailability and toxicity of REEs are still unclear to a certain extent. Therefore, it is very necessary to monitor the contents of REEs in environmental samples.

Several analytical techniques have been used for the determination of trace REEs in environmental samples. Of all these, inductively coupled plasma optical emission spectrometry (ICP-OES) [1,2] and inductively coupled plasma mass spectrometry (ICP-MS) [3–5] are the most powerful analytical tools currently available. However, ICP-OES has some limitations especially during the analysis of ultra-trace REEs in some environmental samples with very complex matrix. In 1980, Houk et al. [6] first used ICP for mass analysis, and since then ICP-MS has been widely used in elemental analysis. Compared with ICP-OES, the analytical sensitivity of ICP-MS is improved by 2–3 orders of magnitude. Nowadays, ICP-MS has been the preferred method for the analysis of environmental samples due to its high sensitivity, good selectivity, large dynamic linear range, multi-element capability, and the possibility to perform isotopic measurements.

However, when conventional pneumatic nebulization (PN)-ICP-MS was used for the determination of trace REEs in some environmental samples, it may be associated with some problems including: (1) very low nebulization efficiency; and (2) the mass interferences of polyatomic ions (MH^+, MO^+, and MOH^+) and the matrix effects (lead to a signal suppression) caused by

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the complex matrix. Employing electrothermal vaporization as a sample introduction technique for ICP-MS may provide a solution to reduce the above problems. ETV is a micro-sampling technique with introduction efficiency up to 80%. Since the vaporization and atomization steps are separated, in-situ matrix removal could be achieved by optimizing the heating program [7,8]. Gray and Date [9] first combined micro-sampling ETV and high sensitivity ICP-MS in 1983, nowadays ETV-ICP-MS has been developed a very powerful method for trace/ultra-trace analysis. It should be pointed out, when ETV-ICP-MS was used for the determination of refractory elements and easily forming carbides elements (including REEs), incomplete vaporization of the analytes and memory effects were the major difficulties [10,11]. The application of a suitable chemical modifier has been proved to be one of the most efficient methods. In our previous works [12–15], several chelating reagents have been used as chemical modifier in ETV-ICP-OES/MS, and satisfactory results have been obtained.

Synergistic extraction systems [16–18] have been applied to REEs numerous times, with a large increase in the extraction efficiency being observed. Moreover, synergistic systems also improved the extraction in different medium. Jia et al. [19] studied the synergistic effect of PMBP and triisobutylphosphine sulphide (TIBPS) in the extraction of REEs from chloride solution in detail. Matsubayashi et al. [20] also investigated the thermodynamic parameters in the synergistic extraction of REEs with 2-thenoyltrifluoroacetone (TTA) and benzoic acid. β-diketones have been widely used as chelate reagents in solvent extraction to extract transition metals [21,22] and REEs. However, it was found that metal chelates extracted with β-diketones contained several water molecules in solvent extraction system. Fortunately, the water molecules coordinated to the metal ions in metal-β-diketones chelates could be easily substituted by the Lewis base. Therefore, a synergistic extraction system of β-diketones and a Lewis base could show larger synergistic effects in magnitude.

The aim of the present work was to develop a new synergistic extraction system with P350 and PMBP as extracting reagents for ETV-ICP-MS determination of trace REEs. The factors affecting the synergistic extraction and the vaporization behaviors of REEs were investigated. Under the optimized conditions, REEs were extracted from nitrate solutions at pH 6 using mixtures of P350 and PMBP in hexamethylene with obvious synergistic extraction effects, and then determined by ETV-ICP-MS at a low vaporization temperature of 1200 °C. The proposed method was used for the determination of REEs in environmental samples with satisfactory results.

2. Experimental

2.1. Apparatus

An Agilent 7500a ICP-MS (Agilent, Japan), equipped with a modified commercially available WF-4C graphite furnace (Beijing Second Optics, China) was used as electrothermal vaporizer. The transfer line consisted of a laboratory-built connecting interface [23] and a polyethylene tube (6 mm id) with total length of 70 cm, so that the adsorption and condensation in the transfer line were minimized. The optimized operating conditions for ICP-MS and ETV are given in Table 1. A Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) was used for pH value measurements. A WX-3000 microwave accelerated digestion system (EU Chemical Instruments Co. Ltd., Shanghai, China) was used for sample digestion.

Table 1
Equipment and operating parameters

ICP-MS plasma	
Rf power	1250 W
Outer gas flow rate	15 L min^{-1}
Intermediate gas flow rate	0.9 L min^{-1}
Nebulizer gas flow rate	0.7 L min^{-1}
Sampling depth	7.0 mm
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
Time-resolved data acquisition	
Scanning mode	Peak-hopping
Dwell time	20 ms
Integration mode	Peak area
Points per spectral peak	1
Elements and istopes	^{89}Y, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{155}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu
Electrothermal vaporizer	
Sample volume	10 μL
Carrier gas flow rate	0.4 L min^{-1}
Drying step	130 °C ramp 10 s\hold 10 s
Pyrolysis step	600 °C hold 20 s
Vaporization step	1200 °C hold 3 s
Cleaning step	2700 °C hold 3 s

2.2. Reagents

The stock standard solutions (1 g L^{-1}) of REEs were prepared by dissolving their SpecPure® oxides (Merck, Darmstadt, Germany) or nitrates using the conventional method, and diluting to a certain volume with high purity deionized water. 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (PMBP) and dimethylheptyl methyl phosphate (P350), supplied by Shanghai Chemical Reagent Factory, were directly used without further purification. Standard reference material of soil sample GBW07401 (Perambulation Institute of Physical Geography and Geochemistry of the Geological and Mineral Ministry, Langfang, China) was used. 0.1 mol L^{-1} sodium hydroxide and 0.1 mol L^{-1} HNO_3 were used for pH adjustment. Hexamethylene and other chemical reagents used in this work were of analytical grade, and high purity deionized water was used throughout.

2.3. Sample digestion

The digestion recipes of standard reference material GBW07401 and real soil sample were based on the recommended methods in literature [24]. 5 mg of sample was weighed into a PTFE vessel, and 2 mL HNO_3 and 1 mL HF were added. All solid particles attached to the wall of the PTFE vessel were rinsed down with the acids. The heating program was performed