

Preconcentration Enhancement of Some Lanthanides Using Dispersive Liquid-Liquid Microextraction Method

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Abstract

In this Preconcentration method, the appropriate mixture of extraction solvent, disperser solvent and chelating agent was rapidly injected by syring into the aqueous solution containing Samarium, Europium, Gadolinium and Dysprosium. Therefore, a cloudy solution formed. In fact, it is consisted of fine particles of extraction solvent which is dispersed entirely into aqueous phase. At this stage, Samarium, Europium, Gadolinium and Dysprosium ions react with chelating and therefore, hydrophobic complex from which are extracted into the fine droplets of extraction solvent. After centrifugation, these droplets were sedimented at the bottom of the conical test tube. Then later phase preconcentration, cations rich phase was diluted up to 5.0 mL and determined simultaneously by inductively coupled plasma. Major factors affecting the Preconcentration of Samarium, Europium, Gadolinium and Dysprosium ions are extraction and dispersive solvent type and their volume, extraction time, PH, concentration of ions, concentration of chelating agent and their types, centrifuge rotation, drying temperature of complex and interfering cations.

Keyword

Samarium, Europium, Gadolinium and Dysprosium, dispersive liquid-liquid Microextraction

1. Introduction

The most important method for preconcentration the rare-earth element are ion-exchange (1-4), precipitation (5-6), extraction (7-8). Solvent extraction methods have played a major role in the preconcentration of lanthanides. More recently, these methods have been extended to include novel and powerful supercritical fluid extraction, SCF chromatographic and DLLME methods. Preconcentration based on dispersive liquid-liquid Microextraction is a modified solvent extraction method and its acceptor-to-donor



phase ratio is greatly reduced comparing with the other methods. In dispersive liquid-liquid Microextraction, the appropriate mixture of the extraction, disperser solvents and chelating agent are rapidly injected by a syringe into an aqueous solution containing their complexes. A cloudy solution formed consequently. In fact, it is consisted of fine particles of extraction solvent which is dispersed entirely into the aqueous phase. The cloudy solution must be centrifuged. Then fine droplets precipitate at the bottom of the conical test tube (9). For the first time in this study we reported simultaneous preconcentration of Samarium, Europium, Gadolinium and Dysprosium. Several variables affecting efficiency and preconcentration capability of the technique were investigated. too, The simultaneous preconcentration method can refine inadequacy of high detection limit of inductively coupled plasma instrument in determination of Samarium, Europium, Gadolinium and Dysprosium and can lead to a higher confidence level and easy determination of the trace amounts of this elements.

Experimental

Carbon tetrachloride (analytical grade for determination with dithizone), chloroform (analytical grade for determination with dithizone) and carbon disulfide (for spectroscopy) as extraction solvent , methanol (for spectroscopy), acetone(suprasolv) and acetonitrile (HPLC grade) as dispersive solvent, HNO_3 (65% , suprapur), lanthanides salts in oxide form and 1-(2-pyridylazo)-2-naphthol(PAN) (analytical grade) were obtained from Merck. All solutions were prepared using double-distilled water. The stock solutions of samarium, europium, gadolinium and dysprosium were prepared at a concentration of 5.00×10^{-2} M of ions by dissolving an appropriate amount of its salts in 20 mL of 12.8 M HNO_3 solution and the solutions were evaporated carefully at low temperatures (not above 60°C) to dry. The residues were dissolved in 26.42 mL of 7.57 M nitric acid solution and diluted to 200 mL. For all ions a similar manner were followed. to prepare a 0.01 M solution of 1-(2-pyridylazo)-2-naphthol (PAN), 0.25 gr of PAN was dissolved in 100 cm^3 of ethanol 95%. An ammonium solution (1% w/w) was used for adjusting the pH. All vessels used for trace analysis were kept in a 1.00 M HNO_3 solution at least 24 h and subsequently washed twice with double-distilled water before use. A simultaneous inductively coupled plasma (Optima 2100 DV) was used. The pH values were measured with a Schoct pH-meter (CG 841) and syringe (gastight, Hamilton, Reno, Nevada, USA). Phase separation was assisted using a centrifuge (Mistral 1000, MSB 100/CE 1.4) and a furnace (EHRET) was used to heat for drying of the precipitate phase. 20 mL of a solution containing Samarium, Europium, Gadolinium and Dysprosium at a concentration 5.00×10^{-5} M ion and 1.00 M HNO_3 which its pH was fixed by ammonium solution (0.1 M) at 8.5-9 were placed in a 100 mL screw cap glass test with conic bottom. 10 mL of methanol as disperser solvent which contains 400 μL of chloroform as extraction solvent and 1 mL 0.001M of 1-(2-pyridylazo)-2-naphthol (PAN) solution as chelating agent was injected rapidly into a sample solution using a 0.5 mL syringe for several times. A cloudy solution was formed in test tube. In this step, samarium, europium, gadolinium and dysprosium ions react with chelating agent (PAN) and extract into the fine droplets of chloroform. The mixture was then centrifuged for 60 min at 3000 rpm. After this process the dispersed fine droplets of chloroform were precipitated at the

bottom of conical test tube (0.5 mL). This precipitate phase was dried by a furnace in 80 °C. Then, it was diluted to 0.5 mL by adding 1.0 M HNO₃ solution.

Results and Discussion

In the present study, Preconcentration factor was calculated using the following equation:

$$PF = C_{sed} / C_0$$

Where PF, C_{sed} and C_0 are preconcentration factor, concentration of the analyte in the precipitate phase and initial concentration of the analyte in the aqueous sample respectively that were determined by inductively coupled plasma (ICP-OES). This study represented the dispersive liquid-liquid Microextraction technique results under the best of operating conditions. Inductively coupled plasma results showed that the optimum condition under which the dispersive liquid-liquid Microextraction technique was done was suitable for simultaneous preconcentration of Samarium, Europium, Gadolinium and Dysprosium (Table1). Under the optimum conditions the simultaneous preconcentration factors of 80.2, 99.56, 102.98 and 78.12 were obtained for Samarium, Europium, Gadolinium and Dysprosium, respectively. The results will be presented and discussed.

Table1. The best of operating conditions

Condition operated	Extraction solvent type (amount)	Dispersive solvent type (amount)	Extraction time	Ligand type (amount)	Centrifuge rotation	Drying temperature of complex
Results	Carbon tetrachloride (600 µL)	Methanol (8 mL)	60 min	1-(2-pyridylazo)-2-naphthol(PAN) (0.8 mL)	3000 RPM	100 °C

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