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SEPARATION AND PRE-CONCENTRATION OF TRACE AMOUNTS OF CERIUM(III) ON OCTADECYL SILICA MEMBRANE DISCS MODIFIED WITH 1,3,5-TRITHIACYCLOHEXANE AND ITS SPECTROPHOTOMETRIC DETERMINATION BY ARSENAZO(III)

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ABSTRACT

A simple and reliable method for rapid and selective separation and determination of trace amounts of Ce^{3+} ions from aqueous samples using octadecyl-bonded silica membrane discs modified with 1,3,5-trithiacyclohexane (TTCH) and spectrophotometry with arsenazo(III) is presented. Extraction efficiency and the influence of sample matrix, pH of sample solution, type and

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minimum amount of stripping acid, and flow-rates were investigated. The maximal capacity of the membrane discs modified with 15 mg of TTCH was found to be 547 μg of cerium. The limit of detection of the proposed method is 2 ng/mL. The effects of various cationic interferences on the percent recovery of cerium in binary mixtures were studied. The method was applied to the recovery of Ce^{3+} ions from synthetic samples.

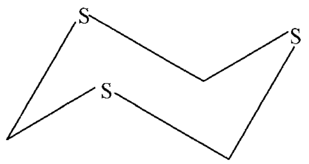
Key Words: Ce(III) separation; Solid phase extraction; Octadecyl silica discs; 1,3,5-Trithiacyclohexane; Arsenazo(III); Spectrophotometry

INTRODUCTION

Cerium and other rare earth elements are widely used in industrial products such as fluorescent devices, magnetic substances, and alloys. They are also used as gasoline-cracking catalysts, polishing compounds, carbon arcs, etc.[1] The determination of trace amounts of cerium ions in aquatic ecosystem has been of increasing concern because of its increasing discharge, toxic properties, and other effects on receiving water. Thus, the separation and determination of trace amounts of cerium from different matrices is of great importance. Although the atomic absorption spectrometry (AAS)[2] and spectrophotometric methods[3,4] are among the most widely used methods for the cerium determination, in most cases, their sensitivity is insufficient for monitoring the low levels of cerium ion. Consequently, pre-concentration and matrix elimination is usually required. Liquid–liquid extraction of cerium with organic solutions containing different chelating agents such as tributylphosphate,[5] triocylphosphine oxide,[6] 5,7-dibromo-8-quinolinol,[7] 1,10-phenanthroline,[8] and iodine[9] has attracted considerable attention. However, these classical extraction methods are usually time-consuming, labor-intensive, and require large volumes of high purity and toxic organic solvents. Solid phase extraction (SPE) is an alternative technique that reduces solvent usage and exposure, disposal cost, and extraction time for sample preparation.[10] Recently, hydrophobic SPE discs have been used extensively for the determination of organic and inorganic environmental pollutants.[11–16] These discs, made of 90% (w/w) octadecyl silica in an inert polytetrafluoroethylene matrix, have a typical diameter of 47 mm and a thickness of 0.5 mm. Typical capacity of a disc for well-retained compounds ranges from 10 to 20 mg. Proclaimed major advantages of the SPE discs are as follows: (1) shorter sample processing time, due to the large cross-sectional area of the disc and decreased pressure drop, allowing the sample to process at higher flow-rates, (2) decreased plugging by particles due to large cross-sectional area of the disc, and (3) reduced channeling resulting from the use of smaller diameter sorbent and a greater mechanical stability of the sorbent bed.[10]

In recent years, we have employed octadecyl silica membrane discs modified with different noncyclic and macrocyclic ligands to develop simple, fast, and reliable methods for the selective separation, concentration, and determination of Ba^{2+},[14] Pb^{2+},[17,18] and UO_2^{2+}[19,20] from aqueous solutions.

The present work describes the first application of modified SPE discs for the selective separation, pre-concentration, and determination of ultra trace amounts of cerium by a spectrophotometric method, using octadecyl silica membrane discs modified with 1,3,5-trithiacyclohexane (TTCH).



TTCH

EXPERIMENTAL

Reagents

Hydrobromic acid, hydrochloric acid, sulfuric acid, acetic acid, nitric acid, and high-purity methanol (all from Merck) were used as received. Analytical grade cerium nitrate and nitrate salts of other metal ions (all from Merck) were of the highest purity available and were dried in vacuum over P_2O_5. TTCH was purchased from Fluka and used as received.

Apparatus

All absorbance measurements were carried out using a Shimadzu UV-2100 spectrophotometer. A model 624 digital Metrohm pH meter equipped with a combined glass–calomel electrode was used for pH determinations. The AAS determination of different cations was performed under the recommended conditions for each metal ion.

Sample Extraction

Extraction was performed with $47 \times 0.5\,\mathrm{mm}^2$ (diameter × thickness) Empore membrane discs containing octadecyl-bonded silica (8 μm particles 60 Å pore size, 3M Co., St. Paul, MN). The discs were used in conjunction with a standard Millipore 47 mm filtration apparatus.

To remove potential interferences and to ensure optimal extraction of the analyte of interest, the disc cleaning and conditioning should be done before its use. Thus, after placing the membrane disc in the filtration apparatus, 10 mL of methanol was poured onto the disc immediately and drawn through the disc by applying a slight vacuum. After all of the solvent has passed through the disc, air was passed through it for few minutes. The disc conditioning was then performed by pouring 10 mL of methanol onto the disc. Immediately, a low vacuum was applied and the solvent was drawn through the disc until the solvent surface almost reached the surface of the disc. The disc should not be allowed to soak without vacuum, and the air should not be allowed to contact the disc surface. Then, 10 mL of water was introduced onto the disc and was drawn through the disc. The disc was then dried under vacuum for 5 min, this is especially important for the discs that are used for the first time. Finally, a solution of 15 mg of TTCH dissolved in 1 mL of methanol was introduced onto the disc so that the solution was spread on the whole disc surface. The solution was allowed to penetrate inside the membrane completely without applying any vacuum. After about 1 min, the filtration funnel containing the modified disc was transferred into an oven and the solvent was completely evaporated at 60°C. Then the sample solution containing Ce(III) was passed through the membrane. After the extraction, cerium ion was stripped from the membrane disc using appropriate amounts of a nitric acid solution. Then the cerium concentration was determined spectrophotometrically by arsenazo(III).

RESULTS AND DISCUSSION

TTCH with three donating sulfur atoms in its structure is insoluble in water at various pH values. Recently, we have successfully used TTCH as an excellent neutral ionophore in construction of a novel Ce(III) ion-selective membrane electrode.[21] Thus, in this work, we decided to examine the capability of TTCH as a suitable reagent for selective separation and pre-concentration of Ce^{3+} ions with SPE by using octadecyl-bonded silica membrane discs. Thus, some preliminary experiments were undertaken to investigate the quantitative retention of cerium ion by the membrane discs in the absence and presence of TTCH, after the recommended washing, wetting, and conditioning procedures were carried out. It was found that, while the conditioned membrane disc itself retained negligible amount of Ce^{3+} ions, the membrane disc modified by TTCH is capable of retaining Ce^{3+} ions in the sample solution quantitatively.

In order to choose a proper eluent for the retained cerium ions after the extraction of 10 μg cerium in 50 mL solution by the modified discs, the retained cerium ions were stripped with varying volumes of different acid solutions of varying concentrations (Table 1). From the data given in Table 1 it is immediately obvious that both the nature and the concentration of acids used as eluent influence the recovery of Ce^{3+} from the modified discs. Obviously, among five different acid solutions used, 20 mL of 3.0 M nitric acid can accomplish the quantitative elution of cerium from the membrane disc while other acids used are ineffective for the complete elution of cerium. Moreover, the observed increase in the recovery of cerium by increasing volume of different eluents could be due to the penetration of hydrated cerium ion and its TTCH complex into the C_{18} structure.

The influence of flow-rates of the sample and stripping solutions from the modified membrane disc on the retention and recovery of cerium(III) ion was investigated. It was found that, in the range 1–20 mL/min, the retention of cerium by the membrane disc is not affected by the sample solution flow-rate considerably. Similar results for the extraction of organic and inorganic materials by octadecyl silica discs have already been reported in the literature.[12–20] On the other hand, quantitative recovery of Ce^{3+} ions from the modified membrane discs was achieved in a flow-rate range 1.0–10 mL/min, using 20 mL of 3.0 M nitric acid as a stripping solution. However, at higher flow-rates, larger volumes of 3.0 M nitric acid were necessary for quantitative stripping of Ce^{3+} ions.

In order to investigate the optimum amount of TTCH on the quantitative extraction of cerium by membrane disc, the SPE of 8 μg cerium ion in 100 mL water was conducted by varying the amount of ligand from 0 to 20 mg and results are summarized in Table 2. As seen, the extraction of cerium is quantitative using

Table 1. Percent Recovery of Cerium from the Modified Membrane Discs Using Different Stripping Acid Solutions[a]

	% Recovery			
Stripping Acid Solution	5 (mL)	10 (mL)	15 (mL)	20 (mL)
HNO_3 (1.5 M)	28	58	76	92
HNO_3 (3 M)	49	92	98	100
CH_3COOH (3 M)	17	39	59	77
HCl (3 M)	26	51	76	90
H_2SO_4 (3 M)	12	28	49	63
HBr (1 M)	19	40	62	80

[a] Initial samples contained 8 μg Ce^{3+} ion in 100 mL water.

Table 2. Effect of Amount of TTCH on Ce^{3+} Ion Extraction

Amount of TTCH (mg)	% Recovery
0	0
2	15.3 (1.8)[a]
5	55.2 (1.3)
10	85.5 (1.5)
15	100.3 (1.1)
20	100.5 (1.9)

Initial samples contained 8 μg Ce^{3+} ion in 100 mL water.

[a] Values in parentheses are RSDs based on three replicate analyses.

15 mg of TTCH or higher. Hence, subsequent extraction experiments were carried out with 15 mg of TTCH.

The influence of the pH of aqueous samples on the recovery of 20 μg Ce^{3+} from 100 mL solutions was studied in a pH range 2.0–8.0. The pH was adjusted by using 0.1 *M* of either nitric acid or sodium hydroxide solutions. The results are shown in Fig. 1. As seen, at a pH range 4.0–8.0, the modified membrane disc can retain the Ce^{3+} ions quantitatively. Higher pH values (>8.0) were not tested because of the possibility of the hydrolysis of octadecyl silica in the discs.

The breakthrough volume of sample solution was tested by dissolving 8 μg of cerium(III) in 25, 50, 100, 250, 500, 1000, and 2000 mL water and the recommended procedure was followed. In all cases, the extraction by modified membrane disc was found to be quantitative. Thus, the breakthrough volume for the method should be greater than 2000 mL. Consequently, pre-concentration factors >200 are easily attainable by the proposed method.

The limit of detection (LOD) of the proposed method for the determination of cerium was studied under the optimal experimental conditions. The LOD obtained from $C_{\mathrm{LOD}} = K_{\mathrm{b}}S_{\mathrm{b}}/m$[22] for a numerical factor $K_{\mathrm{b}} = 3$ was 2 ng/mL.

Maximum capacity of the membrane disc modified by 15 mg of TTCH was determined by passing 100 mL portions of an aqueous solution containing 4000 μg cerium through the disc, followed by the spectrophotometric determination of the retained metal ions. The maximum capacity was found to be 547 ± 7 μ; g of Ce^{3+} ions on the disc.

In order to investigate the selective separation and determination of Ce^{3+} ion from its binary mixtures with diverse metal ions, 25 mL of aqueous solutions containing 8 μg Ce^{3+} and various amounts of other cations were taken and the recommended procedure was followed. The results are summarized in Table 3. It

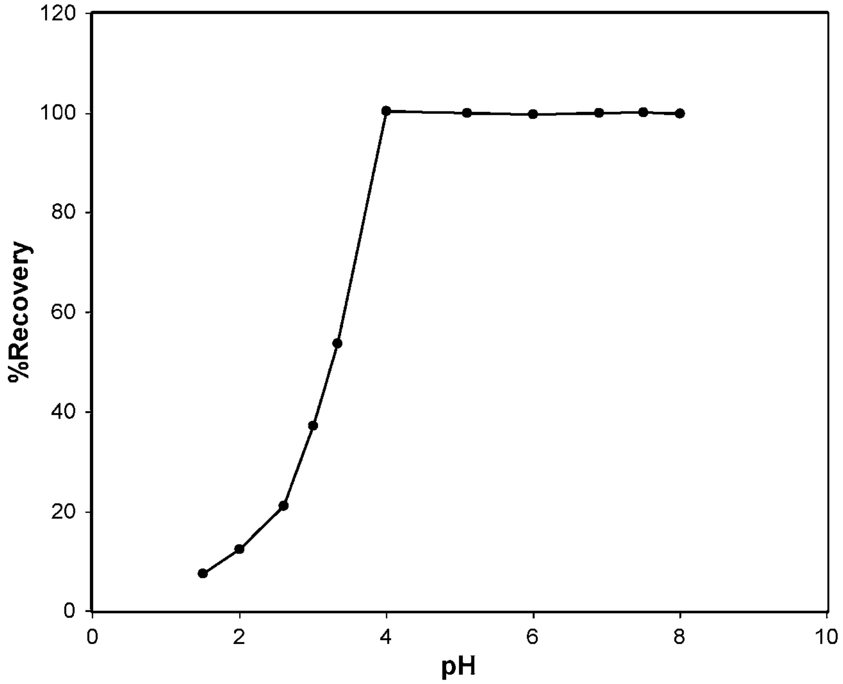


Figure 1. Effect of pH on recovery of Cerium(III).

Table 3. Separation of Cerium from Binary Mixtures

Diverse Ion	Amount Taken (mg)	% Found	% Recovery of Ce^{3+} Ion
Na^+	20	NADP[a]	99.9 (1.2)[b]
K^+	20	NADP	98.9 (1.1)
Mg^{2+}	20	NADP	100.1 (1.4)
Ca^{2+}	20	NADP	99.8 (1.5)
Cu^{2+}	1.0	NADP	99.1 (1.6)
Co^{2+}	1.5	0.5 (0.2)	99.7 (1.4)
Cd^{2+}	1.5	0.5(0.1)	99.7 (1.2)
Ni^{2+}	1.5	0.1 (0.1)	99.8 (1.5)
Pb^{2+}	1.5	0.8 (0.3)	100.3 (1.4)
Zn^{2+}	1.0	0.9 (0.4)	99.1 (1.1)

Initial samples contained 8 μg Ce^{3+} ion in 100 mL water.

[a] No adsorption, passes through disc.

[b] Values in parentheses are RSDs based on three replicate analyses.

Table 4. Recovery of 8 μg Cerium Added to 100 mL Solution of the Synthetic Samples

Sample	% Recovery of Ce^{3+} Ions
Synthetic sample 1 (Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, and Ni^{2+}, 1 mg of each cation)	98.9 (1.5)[a]
Synthetic sample 2 (Na^{+}, K^{+}, Mg^{2+}, and Ca^{2+}, 20 mg of each cation)	99.7 (1.1)

[a] Values in parentheses are RSDs based on three replicate analyses.

is seen that the cerium ions in different binary mixtures can be retained almost by the modified membrane disc almost completely. Meanwhile, retention of other cations by the disc is very low and they can be separated from Ce^{3+} ion.

In order to assess the applicability of the method to real samples with different matrices containing varying amounts of a variety of diverse ions, it was applied to the separation and recovery of cerium ions from three synthetic samples. Table 4 shows the recovery of 8 μg of the added cerium ion from 100 mL solutions of different synthetic samples. As can be seen, the results of three replicate analyses of each sample show that the cerium recovery is almost quantitative.

CONCLUSION

In this work, trace amounts of Ce(III) ions in aqueous solutions were selectively separated and pre-concentrated on the octadecyl silica membrane discs modified with TTCH as a novel cerium complexing agent. Arsenazo(III) was used as a suitable reagent for the spectrophotometric determination of cerium ions. The proposed method has the following advantages. The method is rapid, the time taken for the separation and analysis of cerium in a 250 mL water sample is at the most 25 min. It can selectively separate Ce^{3+} ions from other metal ions associated, even at much higher concentrations. The method can be successfully applied to separation and determination of cerium in real samples.

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