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TECHNICAL NOTE

Separation of Barium from Alkali and Alkaline Earth Metal Ions Using Octadecyl Silica Membranes Modified by Dibenzo-18-crown-6

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ABSTRACT

A simple method for rapid and selective separation of Ba^{2+} ion from alkali and alkaline earth metal ions by using octadecyl silica membrane disks modified with dibenzo-18-crown-6 in the presence of 0.01 M picric acid is presented. The influence of picric acid concentration, nature of the macrocyclic ligands, flow rates, and nature of the stripping acid have been investigated. Maximum capacity of the membrane disks modified by 10 mg crown ether was found to be 900 μg of Ba^{2+} ions. The method was applied to the recovery of barium ion from three different water samples and a certified reference material.

Key Words. Barium separation; SPE; Octadecyl silica disks; Dibenzo-18-crown-6; Picric acid

INTRODUCTION

Rapid and precise determination of barium in many industrial and environmental samples such as fission products, lubrication oils, rocks, min-

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erals, marine organisms, and bone is of vital importance. However, these samples often contain large amounts of alkali and alkaline earth metals other than barium which may interfere in the determination of Ba^{2+} ion (1–4). Thus, for the precise determination of barium, it is essential to separate it from other elements. Among different methods used for the separation of Ba^{2+} ion from the associated elements (1), solvent–solvent extraction (5–10) and extraction–chromatographic methods (11–13) using macrocyclic ligands have attracted considerable attention. However, these methods suffer from problems such as need for large amounts of macrocyclic ligands and high purity solvents, disposal of organic solvents, long procedural time, need for expensive packing, and leaching of the ligands from the columns.

Recently, different trapped ligands on a variety of solid matrices have been successfully used for the separation and sensitive determination of trace metal ions (14–18). Moreover, hydrophobic solid-phase extraction (SPE) disks have been used extensively for the determination of organic environmental pollutants (19–23). These disks, made of 90% (w/w) octadecyl silane in an inert polytetrafluoroethylene matrix, have a typical diameter of 47 mm and a thickness of 0.5 mm. Typical capacity of a disk for well-retained compounds ranges from 10 to 20 mg. The proclaimed major advantage of the SPE disks over their cartridge and tube counterparts is their ability to retain organic compounds even when high flow rates are utilized. In a previous publication (24), we showed that hydrophobic crown ethers such as benzo-15-crown-5, benzo-18-crown-6, and dicyclohexyl-18-crown-6 can be retained completely by octadecyl silica disks from 500 mL aqueous samples.

For this paper we used an octadecyl silica membrane disk modified by dibenzo-18-crown-6 for the selective separation of Ba^{2+} ion from alkali and alkaline earth cations in a picric acid medium. Parameters such as type of crown ether, concentration of picric acid as counterion, type and volume of suitable eluents, and the effect of sample and eluent flow rates on the extraction efficiency of the modified membrane disks were investigated.

EXPERIMENTAL

Reagents

All solvents and acids used were of HPLC grade from Aldrich Chemical Company. Reagent grade benzo-15-crown-5 (B15C5), benzo-18-crown-6 (B18C6), dicyclohexyl-18-crown-6 (DC18C6), and dibenzo-24-crown-8 (DB24C8) (all from Merck) were used as received. Analytical grade picric acid, barium carbonate, and nitrate salts of lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, and strontium (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Doubly distilled deionized water was used throughout.

Apparatus

All alkali and alkaline earth determinations were carried out with a Philips Pye Unicam 22100 atomic absorption spectrophotometer. The atomic absorption measurements were made under the recommended conditions for each metal ion.

Sample Extraction

Extractions were performed with 47 mm diameter × 0.5 mm thickness Empore membrane disks containing octadecyl-bonded silica (8 μm particle, 60 Å pore size) from J. T. Baker. The disks were used in conjunction with standard Millipore 47 mm filtration apparatus.

Before extraction, each membrane was washed with 10 mL methanol to remove all contaminants arising from the manufacturing process and from the environment. After placing the membrane in the filtration apparatus and drawing air through the disk for several minutes, it was dried inside an oven at 50°C. Then a solution of 10 mg crown ether dissolved in 2 mL methanol was introduced to the reservoir of the apparatus and allowed to penetrate inside the membrane completely. The solvent was evaporated at 50°C. The membrane disk modified by crown ether is now ready for sample extraction.

The general procedure for the extraction of Ba^{2+} ions on the membrane disk was as follows. The modified disk was first washed with 10 mL water followed by washing with 5 mL 0.01 M picric acid for preconditioning. Then 5 mL of the sample solution containing 126 μg Ba^{2+} and 0.01 M picric acid was passed through the membrane (flow rate = 2 mL/min). The extracted barium was then stripped from the membrane disk using an appropriate amount of suitable mineral acids. Fractions were collected and the barium content was determined by AAS using a calibration graph.

RESULTS AND DISCUSSION

In some preliminary experiments which were carried out to investigate the quantitative retention of Ba^{2+} ions by the octadecyl silica membrane disks under different experimental conditions, the following results were obtained. First, the membrane disk itself did not show any tendency to extract Ba^{2+} ions from the sample solutions. On the other hand, the recovery data obtained by the membrane disks either modified by DB18C6 or only preconditioned with 0.01 M picric acid revealed that they could retain some 36 and 10% of barium ion in the sample solutions, respectively. However, a membrane disk modified by 10 mg DB18C6 and preconditioned with 5 mL of 0.01 M picric acid solution was found capable of retaining all the barium ions in the sample solution. It is noteworthy that picrate ion is well known to act as an excellent counteranion for the solvent–solvent extraction of a variety of metal ions with macrocyclic ligands (9, 10).

In order to investigate the optimum concentration of picric acid on the quantitative retention of Ba^{2+} ion by the membrane disk modified with DB18C6, barium ion extraction was conducted by varying the picric acid concentration from 1×10^{-5} to 1×10^{-2} M (Table 1). The extraction of barium was found to be quantitative at 1×10^{-2} M picric acid. It is interesting to note that at this concentration level of picric acid, washing the membrane disk containing barium ion with 5 mL water before its stripping does not affect the quantitative retention of the cation. This is very important in the elution of interfering ions associated with Ba^{2+} ion from the membrane disks. Hence, subsequent extraction experiments were carried out at a picric acid concentration of 1×10^{-2} M.

After extraction, Ba^{2+} ions were stripped from the membrane disk with varying volumes of 1 M concentration of different acids such as nitric acid, hydrochloric acid, and acetic acid, and the results are summarized in Table 2. It is seen that the elution of barium from the membrane disk

TABLE 1

Percent Recovery of Barium from the Modified Membrane Disk Using Different Concentrations of Picric Acid[a]

Picric acid concentration (M)	% Recovery	% Recovery after washing with 5 mL water
0	34.5	16.5
1×10^{-5}	44.3	19.4
1×10^{-4}	48.6	23.8
1×10^{-3}	74.8	63.7
5×10^{-3}	92.1	86.3
8×10^{-3}	98.2	97.0
1×10^{-2}	100.0	100.0
2×10^{-2}	100.0	100.0

[a] Initial samples contained 126 μg Ba^{2+} ion and 0.01 M picric acid in 5 mL water.

TABLE 2
Percent Recovery of Barium from the Modified Membrane Disk Using Varying Volumes of 1 M Solutions of Different Acids[a]

Volume (mL)	% Recovery		
	Nitric acid	Hydrochloric acid	Acetic acid
5	60.2	36.7	8.6
10	76.6	51.5	24.1
15	85.6	61.4	42.0
20	94.4	68.8	58.2
25	100.0	79.4	74.2
35	100.0	100.0	100.0

[a] Initial samples contained 126 μg Ba^{2+} ion and 0.01 M picric acid.

was quantitative with 25 mL of 1 M HNO_3, while this can be done with at least 35 mL of the two other acids. In other experiments it was found that the lower the concentration of acid, the larger the volume of acid solution needed for the quantitative stripping of the cation. Considering the above results, 25 mL portions of 1 M nitric acid were used for further studies. It should be noted that when nitric acid of higher concentration (>1 M) was used, there was some leaching of the crown ether from the disk.

Since the octadecyl silica membrane disk is shown to be able to completely retain different hydrophobic crown ethers such as benzo-15-crown-5 (B15C5), benzo-18-crown-6 (B18C6), and dicyclohexyl-18-crown-6 (DC18C6) (24), we were interested in modifying the membrane disk with different crown ethers. The results of such studies are shown in Table 3. As seen, except with B15C5, all the other crowns used can retain Ba^{2+} ion completely. Among these, DC18C6 and DB18C6 will release the retained barium quantitatively after washing the extracted barium ions with 25 mL of 1 M nitric acid. However, due to the much cheaper price of DB18C6 compared with DC18C6, it was selected for further studies.

The influence of flow rates of the sample and stripping solutions from the membrane disk on the retention and recovery of barium ion was investigated. It was found that in the range of 1 to 80 mL/min, the retention of barium by the membrane disk is not significantly affected by the sample solution flow rate. However, quantitative stripping of Ba^{2+} ion from the disk is achieved in a flow rate range of 0.5 to 2 mL/min. Thus, in all cases, a flow rate of 2 mL/min was employed for the elution of Ba^{2+} ion from the disk with 1 M nitric acid solution.

TABLE 3
Percent Recovery of Barium from the Membrane Disks Modified with 10 mg of Different Crown Ethers[a]

Crown ether	% Retained by the membrane	% Recovery after elution with 25 mL of 1 M HNO_3
Benzo-15-crown-5	62.3	62.3
Benzo-18-crown-6	100.0	86.6
Dibenzo-18-crown-6	100.0	100.0
Dicyclohexyl-18-crown-6	100.0	100.0
Dibenzo-24-crown-8	100.0	51.8

[a] Initial samples contained 126 μg Ba^{2+} ion and 0.01 M picric acid in 5 mL water.

The capability of the membrane disk for the concentration of Ba^{2+} ions from more dilute sample solutions was investigated by dissolving 126 μg of the cation in 100 mL of water (instead of 5 mL water as given in the procedure) containing 0.01 M picric acid, and then performing the general procedure. In this case it was found that Ba^{2+} ions can also be quantitatively retained by the disk.

The maximum capacity of the membrane disk modified by 10 mg of DB18C6 was studied by passing 5 mL portions of an aqueous solution containing 2000 μg barium and 0.01 M picric acid through the disk, followed by determination of the retained metal ions in the eluting solution using AAS. The maximum capacity for the modified disk was found to be 900 μg of Ba^{2+} ion on the disk.

In order to investigate the selective separation of Ba^{2+} ion from its binary mixtures with alkali and alkaline earth cations, an aliquot of aqueous solutions containing 126 μg barium and mg amounts of other cations was taken, and picric acid was added so that its concentration was 0.01 M in a total volume of 5 mL, and the recommended procedure was followed. The results are summarized in Table 4. The results show that Ba^{2+} ions in binary mixtures are retained almost completely by the membrane disk, even in the presence of up to 13 mg of the diverse ions. The retention of foreign cations by the disk is negligible.

In order to assess the applicability of the method to real samples containing different amounts of alkali and alkaline earth cations (and possibly some trace amounts of other metal ions), it was applied to the separation and recovery of Ba^{2+} ions from three different water samples (tap water, well water, and river water) as well as a certified reference material (IAEA's lake sediment, obtained from the International Atomic Energy

TABLE 4
Separation of Barium from Binary Mixtures. Amount of Ba^{2+} Taken Is 126 μg

Foreign ion (added as nitrate)	Amount taken (mg)	% Recovery of foreign ion[a]	% Recovery of barium[a]
Li^+	12.7	0.2 (0.4)	99.9 (0.5)
Na^+	10.3	1.0 (0.2)	96.4 (1.1)
K^+	3.8	0.8 (1.0)	95.9 (0.8)
Rb^+	12.4	2.7 (0.7)	95.4 (0.3)
Cs^+	8.6	0.1 (3.3)	98.2 (1.3)
Mg^{2+}	12.9	0.5 (2.7)	94.0 (0.4)
Ca^{2+}	13.0	0.3 (1.3)	96.0 (2.0)
Sr^{2+}	6.7	0.6 (1.0)	99.8 (0.4)

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

Agency, P.O. Box 100.0-1400, Vienna, Austria). The sample was dissolved according to a procedure described elsewhere (25).

The water samples were first analyzed by AAS to determine their alkali and alkaline earth contents. The results are summarized in Table 5. As can be seen, the amounts of Li^+, Cs^+, and Ba^{2+} ions in the three samples are negligible, while the amounts of other alkali and alkaline earth cations in the samples range from 0.4 to 70 μg/mL.

In the next step, barium ion (126 μg) and picric acid (0.01 M) were added to 5 mL of each sample and the recommended procedure was followed. It was found that all species other than Ba^{2+} passed through the modified membrane disk almost completely (some of them after washing the disk with 5 mL doubly distilled deionized water). The retained Ba^{2+} ions were eluted with 25 mL of 1 M HNO_3, and the percentage of barium recovery

TABLE 5
Alkali and Alkaline Earth Content of the Three Water Samples as Determined by AAS[a]

	Concentration (μg/mL)								
Sample	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Tap water	n	16.6	0.2	1.3	n	12.8	37.6	0.4	n
Well water	n	42.9	0.8	1.4	n	15.8	70.2	0.9	n
River water	n	46.5	0.4	1.5	n	14.2	54.0	0.7	n

[a] n = negligible amount.

TABLE 6
Recovery of 126 μg Barium Added to 5 mL of the Water Samples Based on Three Replicate Analyses

Sample	Ba^{2+} found (μg)	% Recovery	%RSD
Tap water	130.7	103.7	3.7
Well water	135.4	107.5	1.4
River water	128.0	101.6	2.8

was determined by AAS. The results of triplicate analyses (Table 6) show that barium recovery is almost quantitative in all three water samples.

The alkali and alkaline earth content of the certified sample in μg/mL are: Li^+, 29.0; Na^+, 1.72×10^2; K^+, 1.50×10^3; Rb^+, 1.13×10^2; Cs^+, 7.0; Mg^{2+}, 2.90×10^2; Ca^{2+}, 2.50×10^2; Sr^{2+}, 80.0; Ba^{2+}, 6.39×10^2. The amount of barium determined in this sample by the proposed method is 6.44×10^2 μg/mL which is in satisfactory agreement (%RSD of 3.2) with the reported value of 6.39×10^2 μg/mL.

CONCLUSION

The proposed method has the following advantages. The method is rapid as compared with previously reported procedures (9, 10); the time taken for the separation and analysis of barium is at the most 40 minutes. It can selectively separate Ba^{2+} ion from alkali and other alkaline earth cations, even when they are present at much higher concentrations. The method can be applied to the separation of barium at trace levels and at higher concentrations. It is a simple, rapid, highly selective, and reproducible method for the separation of barium ion. The reproducibility of the procedure is 2% at the most.

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