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# DETERMINATION OF BARIUM IN THE PRESENCE OF A LARGE AMOUNT OF CALCIUM BY MEANS OF THE COMBINATION OF THE SOLVENT EXTRACTION BY 18-CROWN-6 WITH THE ATOMIC ABSORPTION SPECTROPHOTOMETRY

Yasuyuki TAKEDA, Shōji SUZUKI, and Yoshihiko OHYAGI
Depertment of Chemistry, Faculty of Science, Chiba University, Yayoi-cho, Chiba 260

A small amount of barium ($2.0\times10^{-5}$- $5.00\times10^{-4}$M) in the presence of a large amount of calcium ($5.00\times10^{-2}$M) was easily and precisely determined by means of the combination of the solvent extraction procedure by 18-crown-6 with the atomic absorption spectrophotometry using the dinitrogen oxide-acetylene flame. Average recovery of barium was 100±3%.

The determination of barium in environmental samples, such as calcium carbonate, rocks, minerals, marine organism and bone, is very important in terms of geochemistry and biochemistry. However, these environmental samples often contain a large amount of calcium, and it causes considerable spectral interferences on the emission and the atomic absorption spectrophotometric determination of barium. In order to solve this problem, several methods have been reported, for example, flame emission spectrophotometry using the background correction procedure by means of wavelength modulation[1)], flame atomic absorption one by the use of nitrogen free dinitrogen oxide-acetylene flame[2)], flameless atomic absorption one by the graphite rod atomization procedure[3)], and graphite furnace emission one with automatic background correction[4)]. On the other hand, it is suggested that the separation of barium from calcium before analysis is necessary for the precise determination of barium by means of atomic absorption spectrophotometry[5,6)]. Some pre-separation methods, for instance, co-precipitation and ion-exchange chromatography have been reported. However, solvent extraction methods have been scarcely done. In the present study, solvent extraction procedure with 1,4,7,10,13,16 - Hexaoxacyclooctadecane(18-crown-6 (18C6)) was applied for the separation of barium from a large amount of calcium, and the determination of barium was carried out by atomic absorption spectrophotometry using a dinitrogen oxide-acetylene flame.

It is known that typical crown ethers consist of hydrophilic cavities linked with oxygen atoms and hydrophobic exteriors, and that some of them form stable complexes particularly with alkali and alkaline earth metal ions by holding the ions in the central cavities and moreover exhibit a striking selectivity for one of these ions in each series at a homogeneous system[8,9,10,11)]. The similar selectivity of a certain crown ether toward the alkali metal ions was also shown in recent solvent extraction studies[12,13)]. The relative size of the ion and the cavity of the crown ether has been pointed out for one of the most important factors which influence this selectivity and the stability of the complex[8,9,10,11,12]. Generally, the high selectivity and the most stable complex of the crown ether for a given cation can be obtained when the cation fits well into the cavity of the crown ether. In this study 18C6 was chosen as the extractant of barium in the presence of calcium, since the cavity size of 18C6 (2.6-3.2Å[10]) is larger than the ionic diameter of calcium (1.98Å[14]) and nearly equal to that of barium (2.70Å[14]), and the difference between the stability constant values for the 1:1 complex of $Ba^{2+}$ and that of $Ca^{2+}$ with 18C6 in an aqueous solution is much larger than that of the dicyclohexyl-18-crown-6 and dibenzo-18-crown-6 systems[9]. Nitrobenzene was used as a extraction solvent because of its polar property.

18C6 was purchased from the Nisso Co., Ltd., and was used without any further purification. Nitrobenzene, $HNO_3$, $Ca(NO_3)_2 \cdot 4H_2O$, and $Ba(NO_3)_2$ were analytical grade reagents from Wako-Pure Chemicals Co., Ltd., and picric acid was analytical grade one from Koso Chemical Co., Ltd. Nitrobenzene was washed three times with distilled water before use.

Emission and atomic absorption measurements were carried out by a Seiko model SAS-725 atomic absorption spectrophotometer equipped with a Seiko 8cm slot dinitrogen oxide burner head. The optimum flow-rates of the fuel and oxidant were about 13.5 and 8.0 l/min respectively. The most suitable height of the light beem from the burner top was 7.0 mm, and the slit width was 0.4 nm.

Spectral interferences of calcium on the emission and atomic absorption of barium at the wavelength of 553.6 nm by means of dinitrogen oxide-acetylene flame are shown in Fig. 1. It may be noted from Fig. 1 that the spectral interferences of calcium on the atomic absorption of barium are less than those on the emission, and that the interferences of calcium are scarcely found in the atomic absorption at the calcium concentrations lower than about $1 \times 10^{-4}$M. Therefore the atomic absorption spectrophotometry by means of dinitrogen oxide-acetylene flame was employed in this study.

The overall extraction procedure to separate barium ($2.0 \times 10^{-5}$ - $5.00 \times 10^{-4}$M) from calcium ($5.00 \times 10^{-2}$M) is given in Fig. 2. The aqueous phase of the sample solution contained $2.0 \times 10^{-5}$ - $5.00 \times 10^{-4}$M barium, $5.00 \times 10^{-2}$M calcium ions, and $1.2 \times 10^{-2}$M picric acid (pH 2.2 - 2.4). The organic

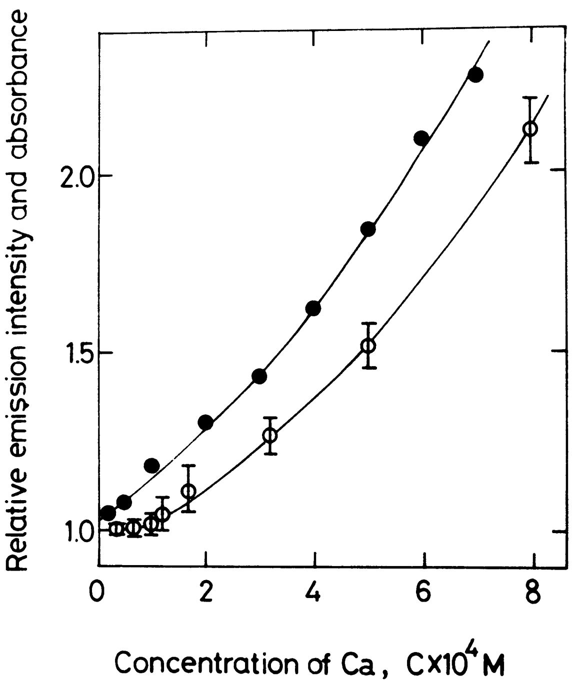

Fig. 1. Spectral interferences of calcium on the emission and atomic absorption of barium at the wavelength of 553.6 nm by means of dinitrogen oxide-acetylene flame. Barium concentration $1.0 \times 10^{-4}$M.

● : Relative emission intensity

o : Relative absorbance

phase of the sample solution was the nitrobenzene solution of 18C6, and the concentration of 18C6 was about three times as large as that of the barium ion in the aqueous phase of the sample solution in every case. The volume of each phase in the sample solution was 10 ml. The two phases in a stoppered glass tube (volume 30 ml) were shaken in a thermostated water bath for about 30 min at 25±0.2 °C, and then separated by centrifugation. A 8 ml portion of the organic phase in the sample solution (org. phase-1) and an equal volume of the aqueous solution containing picric acid ($1.8 \times 10^{-2}$M) were placed in another stoppered glass tube. The two phases were agitated under the same conditions as described above and then centrifuged. A 6 ml portion of the organic phase (org. phase-2) and an equal volume of the aqueous solution containing picric acid ($1.8 \times 10^{-2}$M) were placed in another stoppered glass tube. The two phases were shaken under the same conditions as described above and then separated by centrifugation. A 5 ml portion of the organic phase (org. phase-3) was transferred into another stoppered glass tube and shaken with an equal volume of the 1M nitric acid solution in order to back-extract the barium ions into the aqueous phase. The concentration of the barium ion in the aqueous phase-4 was determined by atomic absorption spectrophotometry.

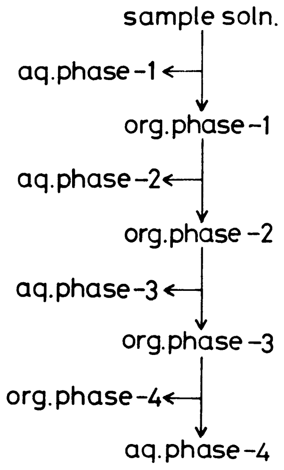

Fig. 2. Overall extraction procedure for the separation of barium from calcium.

The results are given in Table 1. From Table 1 it is found that in each case, the experimentally found concentration of the barium in the aqueous phase-4 well agrees with the one initially added to the sample solution, and that the

Table 1. The determination of barium in calcium-rich samples by means of atomic absorption spectrophotometry using a dinitrogen oxide-acetylene flame

| Initial concn. of calcium ($\times 10^{-2}$M) | Initial concn. of barium ($\times 10^{-4}$M) | Calcium found in aq. phase-4 ($\times 10^{-5}$M) | Barium found in aq. phase-4 ($\times 10^{-4}$M) | Recovery (%) |
|---|---|---|---|---|
| 5.00 | 0.20 | 2.93 | 0.20 | 100 |
| 5.00 | 0.40 | 3.26 | 0.40 | 100 |
| 5.00 | 0.60 | 3.30 | 0.58 | 97 |
| 5.00 | 0.80 | 3.09 | 0.80 | 100 |
| 5.00 | 1.00 | 2.96 | 1.03 | 103 |
| 5.00 | 1.40 | 2.18 | 1.44 | 103 |
| 5.00 | 1.80 | 1.83 | 1.76 | 98 |
| 5.00 | 2.20 | 1.32 | 2.20 | 100 |
| 5.00 | 3.00 | 1.20 | 3.08 | 103 |
| 5.00 | 4.00 | 1.17 | 3.91 | 98 |
| 5.00 | 5.00 | 1.26 | 5.04 | 101 |

concentration of the calcium in the aqueous phase-4 was about $10^{-4}$ part of that in the initial sample solution. The average recovery of barium in these systems was 100±3%.

This method seems to be more rapid than the ion exchange chromatography$^{6)}$ and to be simpler than the co-precipitation one$^{5,7)}$.

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