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Original Scientific Paper

Determination of Barium in Uranium Compounds by Conductometric Titration

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A method for the determination of barium by conductometric titration in the precipitates of the system uranyl nitrate — potassium hydroxide — barium nitrate, is proposed. The precipitates were dissolved in concentrated nitric acid and uranium separated by means of continuous extraction with tetrahydropyrane. Barium could be determined from 0.6 to 7 mg with a standard error of about 0.12 mg Ba. The lowest gramatomic ratio Ba/U was 1.8×10^{-4}.

INTRODUCTION

The precipitation system: uranyl nitrate — potassium hydroxide — neutral electrolyte[1], has a number of interesting properties. The addition of an indifferent electrolyte, *e.g.* barium nitrate, causes precipitation from initially clear solutions of uranyl nitrate and potassium hydroxide. For the interpretation of the mechanism of precipitation and for a quantitative study of the composition of the precipitates obtained, the determination of small amounts of barium in the presence of large amounts of uranium proved necessary. Kolthoff[2] described the conductometric titration as the method for the determination of barium chloride with lithium sulphate in concentrations from $10^{-3}M$ to $5 \times 10^{-2}M$. This method was used for the determination of micro amounts of barium in uranium precipitates[1]. Since the presence of uranium interferes with the conductometric determination of barium, the major part of uranium present in the form of uranyl nitrate was extracted by tetrahydropyrane[3] before titration.

EXPERIMENTAL

For the measurement of conductance, a PYE Conductance Bridge (Cat. No 11700), and water jacketed conductance cells were used. All titrations were performed at constant temperature of 25 ± 0.1^0 C, in a volume of 15 ml. All chemicals used were of analytical grade. For titrations an aqueous $0.5M$ solution of lithium sulphate was used. The titrant was added from a microburet, which was constructed and calibrated in the manner described[4]. 1 mm of microburet scale corresponded to 0.331 μl. The procedure of quantitative separation of uranium is as follows: the sample containing barium and uranium was dissolved in distilled water and nitric acid added up to 4 *M*. Continuous extraction with tetrahydropyrane in micro-extractors[5] was performed during 50 minutes. The aqueous phase from the extraction vessels was evaporated, dissolved in 4 *M* nitric acid, and extracted again during the next 50 minutes. After this procedure, uranium was quantitatively separated from barium in the aqueous phase[3]. A few drops of concentrated nitric acid and hydrogen peroxide were added to the evaporated samples in order to decompose traces of tetrahydropyrane and other organic substances. After that, samples were carefully dissolved in 15 ml of 30% (v/v) ethanol, and then the solutions were titrated.

RESULTS AND DISCUSSION

The obtained regression of the quantity of barium present in the form of barium nitrate, upon microburet additions of 0.5 *M* lithium sulphate, can be expressed as:

$$y = (0.0228 \pm 0.0003)\, x \qquad (1)$$

where x = volume of 0.5 *M* lithium sulphate added in mm of microburet scale

y = quantity of barium dissolved in 15 ml 30% (v/v) ethanol in mg.

The slope of the regression line was found to be 0.0228. Statistical analysis proved that the regression line passes through the origin[6]. This indicates that no loss of barium occurred in the process of preparating the samples. Results shown in Table I are mean values of two parallel determinations.

TABLE I

Determination of Barium after Extraction of Uranium

No.	Barium taken (mg)	Uranium taken (mg)	Ba/U ratio 10^{-3}	Microburet reading (mm)	Barium found (eq. 1)	Difference (%)
1	0.63	2.0	0.3	24	0.55	—12.7
2	0.98	0.2	4.9	41	0.94	— 4.1
3	1.25	2.0	0.6	52	1.19	— 4.8
4	1.95	0.2	9.7	87	1.99	+ 2.0
5	2.50	2.0	1.3	111	2.54	+ 1.6
6	3.25	0.2	16.2	146	3.34	+ 2.7
7	3.75	1.0	3.8	159	3.64	— 2.9
8	4.56	0.2	22.8	207	4.72	+ 3.5
9	5.00	2.0	2.5	225	5.13	+ 2.6
10	6.51	0.2	32.5	278	6.34	— 2.6

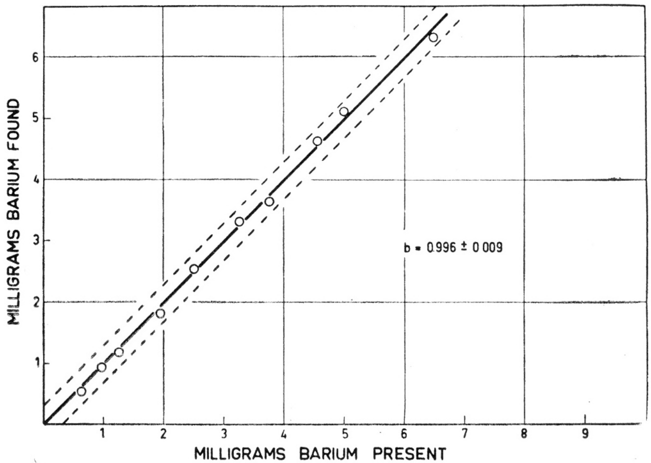

Fig. 1 The regression of milligrams of barium found against milligrams of barium present, and the corresponding 99% confidence limits.

The results of the determination of barium, after removal of uranyl nitrate are represented in Fig. 1., by plotting the quantities of barium found versus barium present. The quantities of barium found were obtained from titration data and eq. (1). Fig. 1. shows the linear regression and the corresponding 99% confidence limits. The results show that about 0.4 mg Ba in 15 ml is the lower limit for the determination by the method proposed. In Fig. 2. the standard error (curve 1), and the relative standard error (curve 2), as functions of the quantity of barium present are shown.

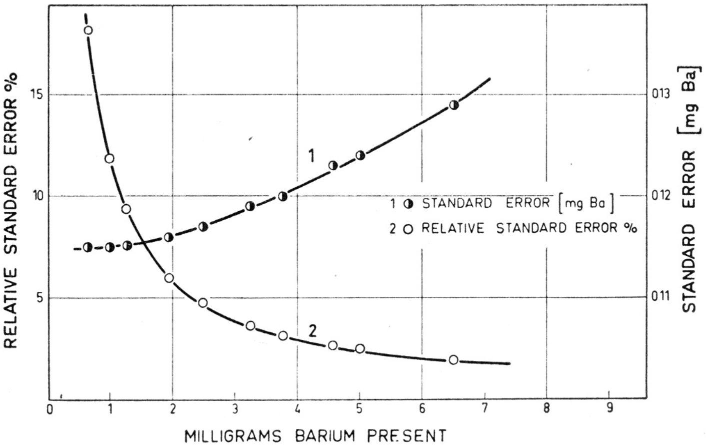

Fig. 2. The standard error (curve 1) and the relative standard error (curve 2) as functions of quantity of barium present.

The use of the method described can be illustrated by an example of analysis of the solid phase obtained from the precipitation system of $10^{-3}\,M$ uranyl nitrate — $2.3 \times 10^{-3}\,M$ potassium hydroxide — $2 \times 10^{-3}\,M$ barium nitrate[1]. The precipitate formed was dried to constant weight at 110° C.

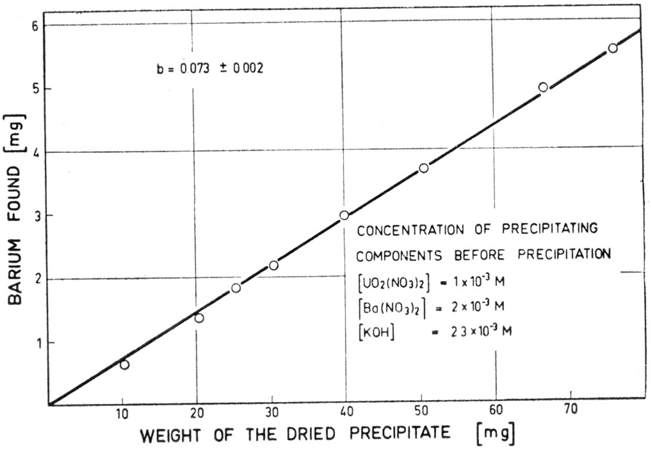

Fig. 3. Results of barium analyses in the precipitate obtained in the system: $10^{-3}M$ uranyl nitrate — $2.3 \times 10^{-3}M$ potassium hydroxide — $2 \times 10^{-3}M$ barium nitrate. Milligrams of barium found against milligrams of precipitate, dried at 110° C to constant weight.

Fig. 3. shows the results of barium analyses in the mentioned uranate precipitate. With the regression coefficient of $b = 0.073 \pm 0.002$, it could be concluded that the content of barium in the analysed sample is $7.3 \pm 0.2\%$.

The presence of other alkaline earth elements interferes with the determination of barium by the method described.

Using the proposed procedure, it was possible to determine from 0.6 to 7 milligrams of barium in uranium precipitates with a standard error of about 0.12 mg Ba. The gramatomic ratio of Ba/U, in the analyzed concentrates could be as low as 1.8×10^{-4}.

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IZVOD

Određivanje barija u talozima urana konduktometrijskom titracijom

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Predložena je metoda određivanja barija konduktometrijskom titracijom u talozima sistema uranil nitrat — kalijev hidroksid — barijev nitrat. Talozi su otapani u koncentriranoj dušičnoj kiselini, a uran je separiran kontinuiranom ekstrakcijom sa tetrahidropiranom. Barij se može određivati od 0.6 do 7 mg uz standardnu pogrešku od oko 0.12 mg Ba. Najniži gramatomski odnos barija prema uranu iznosi $1{,}8 \times 10^{-4}$.

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