Analytical Chemistry by means of Oxalic Acid. II. On the Quantitative Analysis of Barium(1)

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(Received April 7, 1952)

The methods of precipitating barium as barium oxalate or its various hydrates have been studied by many authors.(2) As to the application of the reaction for determining barium, several investigations(3) have been published, but the results were not effective. The present writer employed 50% alcohol as washing liquid of barium oxalate, and established a method in which barium is estimated gravimetrically as barium oxalate hemihydrate or volumetrically by titrating oxalic acid combined with barium with potassium permanganate.

1. Gravimetric Method.—Procedure:—To 25ml. of hot 0.1 M barium chloride solution which is acidified with dilute hydrochloric acid so that a large quantity of barium oxalate precipitate once formed may be dissolved, a definite quantity of hot 5% ammonium oxalate solution is added with constant stirring. When dilute ammonia water is added drop by drop to the solution until the latter becomes just pink with phenolphthalein, the solution being well agitated all the while, a crystalline precipitate is produced. Now the whole mass in the beaker covered with watch glass is warmed on the water-bath for about 2 hrs., and is left to stand over night. The precipitate after being washed several times by decantation using 50% alcohol solution is filtered with a 1. G. 5. glass filter. Then the precipitate is dried at 100°—105°C. for 2 hrs. in the air-bath, and weighed as barium oxalate hemihydrate.

A) Influences of Amounts of Amm. Oxalate and Dilution of Sample Solution—. In order to find out the most suitable amount of ammonium oxalate which should be taken for the precipitation of barium oxalate and also to learn the influence of dilution of the sample solution, a series of experiments were carried out, the results of which are shown in Table 1.

Table 1

(Ba used is 0.3434 g.)

Water added	5% amm. oxalate		$BaC_2O_4\cdot$ 1/2H_2O	Ba found	Error
ml.	ml.	molar ratio to Ba	g.	g.	mg.
—	10	1.4	0.5860	0.3434	±0
—	20	2.8	0.5858	0.3433	−0.1
—	40	5.6	0.5853	0.3430	−0.4
—	60	8.4	0.5843	0.3424	−1.0
—	80	11.2	0.5834	0.3419	−1.5
25	10	1.4	0.5852	0.3429	−0.5
50	10	1.4	0.5824	0.3413	−2.1
100	10	1.4	0.5805	0.3402	−3.2

When the molar ratio of ammonium oxalate to barium exceeds 2.8 and the concentration of the sample solution is less than 0.1 M, the precipitation is not complete. A large quantity of ammonium oxalate seems to form a complex salt of ammonium barium oxalate.(4) So the precipitant should be used in a slight excess, and the sample solution should not be diluted to less than 0.1 M with water.

Solubilities of Barium Oxalate.—The precipitate of barium oxalate prepared by the above method is dissolved in a solvent, and from the quantity of the precipitate dissolved the solubility of barium oxalate is calculated. Table 2 shows the solubilities of barium oxalate in distilled water as well as in 50% alcohol at 25°—26°C.

Table 2

Solvent	Time that solvent is in contact with ppt.	$BaC_2O_4\cdot$ 1/2H_2O dissolved in 50 ml	Solubility (25°—26°C)		Solubility product
	hr.	mg.	mg./l.	mol/l.	
water	8	6.1	121	5.4×10^{-4}	2.9×10^{-7}
	24	6.3			
	32	6.3			
50% alc.	8	trace	3.9	1.7×10^{-5}	2.9×10^{-10}
	24	0.2			
	32	0.2			

From the above results it has been found that the 50% alcohol solution is suitable to the washing

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(1) Read before at the 6 th Ordinary Meeting of the Chugoku-Shikoku Branch of the Chemical Society of Japan in January, 1952.

(2) A. Souchay and E. Lenssen, *Ann.*, **99**, 36 (1856); Groschuff, *Chem. Ber.*, **34**, 3313 (1901); Herz and Muss, *Chem. Ber.*, **36**, 3718 (1903).

(3) Barbu N. Angelescu, *Bulet. Soc. de Chimie din Romania*, **5**, 12 (1923); J. Haslam, *Analyst*, **60**, 668 (1935), C. Diaz Villamil, *An. Soc. espan. Fisica Quim.*, **34**, 580.

(4) R. Scholder, E. Gadenne and H. Niemann, *Chem. Ber.*, **60**, 1489 (1927).

of barium oxalate. Moreover the solubility of this salt in water is 3.8×10^{-4} mol/l. (18°C.) according to F. Kohlrausch⁽⁵⁾ and 6.8×10^{-4} mol/l. (26°C.) to Herz and Muss.⁽⁶⁾

B) Influence of Various Salts Present.—In order to observe the influence of various salts on the precipitation of barium oxalate, 25 ml. of 0.1 M barium chloride solution was mixed with a definite quantity of various salts, and this solution was treated in the manner described before. The results are shown in Table 3.

Table 3

(Ba used is 0.3434 g.)

Salt mixed	g.	$BaC_2O_4\cdot1/2H_2O$ g.	Ba g.	Error mg.
NaCl	2	0.5857	0.3432	−0.2
〃	〃	0.5859	0.3433	−0.1
KCl	2	0.5859	0.3433	−0.1
〃	〃	0.5860	0.3434	±0
KNO_3	2	0.5858	0.3433	−0.1
〃	〃	0.5859	0.3433	−0.1
NH_4Cl	2	0.5857	0.3432	−0.2
〃	〃	0.5860	0.3434	±0
NH_4NO_3	2	0.5855	0.3431	−0.3
〃	〃	0.5852	0.3429	−0.5
〃	5	0.5825	0.3413	−2.1
〃	〃	0.5830	0.3416	−1.8

Sod. chloride, pot. chloride, pot. nitrate and amm. chloride show almost no bad influence, but amm. nitrate seems to form a complex salt with barium oxalate, which makes the value of barium a little low.

2. Volumetric Method.—J. Haslam⁽⁷⁾ studied the titration of the barium oxalate which was formed in perchloric acid solution. The present writer applied the following method to the volumetric analysis of barium.

Procedure:—From a definite volume of 0.1 M barium chloride solution the precipitate of its oxalate is prepared under the best condition required in the former method. When dilute nitric acid is added to the precipitate in a glass filter, oxalic acid is liberated. Then the solution in the filter is filtered out with suction and the filter is well washed with distilled water. All the filtrate is kept in a measuring flask and diluted accurately to 250 ml. 10 ml. of the filtrate, acidified with sulfuric acid, is titrated with 0.1 N potassium permanganate in the usual way. The results are shown in Table 4.

Table 4

Ba taken	(0.1M-$BaCl_2$)	0.1N-$KMnO_4$ (factor = 0.9479)	Ba found	Error
g.	(ml.)	ml.	g.	mg.
0.3434	(25)	52.65	0.3428	−0.6
0.3434	(25)	52.72	0.3432	−0.2
0.3434	(25)	52.70	0.3431	−0.3
0.1374	(10)	21.08	0.1372	−0.2
0.1374	(10)	21.05	0.1370	−0.4
0.1374	(10)	21.08	0.1372	−0.2
0.0687	(5)	10.52	0.0685	−0.2
0.0687	(5)	10.55	0.0687	±0
0.0687	(5)	10.48	0.0682	−0.5

It has been found that the volumetric analysis by means of oxalic acid produces almost satisfactory results.

Summary

(1) Quantitative precipitation of barium as its oxalate hemihydrate was made possible by employing 50% alcohol as washing solution and by drying the precipitate at 100°—105°C. for 2 hrs.

(2) Sod. chloride, pot. chloride, pot. nitrate and amm. chloride produce little influence on this determination, while amm. nitrate positively effects the estimation.

(3) It was found that barium can be determined volumetrically by titrating with potassium permanganate the oxalic acid which is formed when the barium oxalate is decomposed with nitric acid.

The writer wishes here to express his hearty thanks to Prof. Masayoshi Ishibashi in Kyoto Univ. for his kind guidance and encouragement throughout this experiment. The expenses to this research have been defrayed from the Grant in Aid for Fundamental Scientific Research from the Department of Education, to which the writer's thanks are due.

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(5) Landolt-Boernstein, "Physik. Chem. Tabellen" (1905-36).

(6) Herz and Muss, *Chem. Ber.*, **36**, 3718 (1903).

(7) J. Haslam, *Analyst*, **60**, 668 (1936).