Analytical Chemistry by Means of Oxalic Acid. I. On the Quantitative Analysis of Strontium⁽¹⁾

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The method of determining a metal as its oxalate had been employed only in the case of calcium. The present writer applied this method to strontium, which is similar to calcium.(2)

Precipitating strontium as its oxalate was studied by Souchay, Lenssen, Herz, Muss and others(3), (4) who got various hydrates of strontium oxalate which were fairly soluble in water. The present writer tried the following experiments in order to apply the precipitate of strontium oxalate to gravimetric as well as volumetric analysis. In the gravimetric method strontium oxalate was weighed as its monohydrate, while in the volumetric determination the oxalic acid in strontium oxalate was titrated with potassium permanganate.

Experimental

Preparation of 0.1 M strontium nitrate was as follows:—Ishizu Chemicals' strontium nitrate was recrystallized. On analysing 50 ml. of the solution containing 10 g. of this salt, there were found no heavy metals, no alkali earths but strontium, and no alkalis in the sample. One litre of 0.1 M

Table 1

No.	$SrSO_4$ g.	Sr		Error mg.
		Found g.	Calc. g.	
1	0.4583	0.2186	0.2189	−0.3
2	0.4582	0.2186	0.2189	−0.3
3	0.4585	0.2187	0.2189	−0.2
mean	0.4583	0.2186	0.2189	−0.3

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

(2) Souchay and Lenssen, *Ann.*, **100**, 313 (1856).

(3) Souchay and Lenssen, *Ann.*, **102**, 35 (1857).

(4) Souchay. Lenssen, Herz and Muss, *Ber.*, **36**, 3717 (1903).

solution was prepared by dissolving 21.150 g. of this salt in distilled water, and 25 ml. of this solution was employed for each determination. In the first place the strontium in 25 ml. of this solution was determined by the ordinary sulfate method. The results are shown in Table 1.

1. Gravimetric Method.—In order to precipitate strontium as its oxalate, 5% ammonium oxalate solution was employed.

Procedure for precipitating strontium oxalate:—To 25 ml. of hot 0.1 M strontium nitrate solution which is acidified with dilute hydrochloric acid so that a small quantity of strontium oxalate precipitate once formed is redissolved, a definite quantity of hot 5% amm. oxalate solution is added and the whole is well stirred. When dilute ammonia is added drop by drop to the solution agitating strongly all the while, until the latter becomes just pink with phenolphthalein, a crystalline precipitate is produced. Now the whole is warmed in the water-bath for about 2 hrs., left to stand over night and filtered with 1.G.4. glass filter. The precipitate is washed with 1% amm. oxalate, distilled water or 50% alcohol, dried at 100—105°C. for 2 hrs. in the air-bath, and weighed.

A) Influence of washing solution.—In this case, 10 ml. of hot 5% amm. oxalate solution was employed for each determination. The precipitate was washed by decantation with one of the following washing liquids.

(1) 100 ml. of distilled water.

(2) 30 ml. of 1% amm. oxalate first, and 70 ml. of distilled water.

(3) 100 ml. of 50% alcohol.

The results are shown in Table 2.

Table 2 (Sr used is 0.2189 g.)

Washing liquid	$SrC_2O_4 \cdot H_2O$ g.	Sr Found g.	Sr Error mg.
water 100 ml.	0.4791	0.2168	−2.1
	0.4790	0.2167	−2.2
	0.4790	0.2167	−2.2
1% amm. oxalate 30 ml. and water 70 ml.	0.4810	0.2177	−1.2
	0.4812	0.2177	−1.2
	0.4813	0.2178	−1.1
50% alcohol 100 ml.	0.4837	0.2189	±0
	0.4835	0.2188	−0.1
	0.4835	0.2188	−0.1

The washing with distilled water (1) produces a remarkable negative error, the solubility of strontium oxalate being fairly large, while 50% alcohol (3) is found to be most effective, better results being given than by the ordinary sulfate method (Table 1). The error found in the case of washing with 1% amm. oxalate and water (2) is about the mean value of (1) and (3).

For the above reason, in the case where 50% alcohol is employed as the washing liquid, the determination of strontium can be carried out quantitatively.

Solubility of strontium oxalate.—The precipitate of strontium oxalate prepared by the above process and completely washed in hot water is put in a 300 ml. Erlenmeyer flask together with 200 ml. of solvent. The whole is set in a thermostat and shaken till the solution is saturated. After a definite time the solution is filtered, 50 ml. of the filtrate is put in the beaker and evaporated to dryness in the water-bath. The residue is dried at 100—105°C for 1 hr. and weighed. Table 3 shows the solubilities of strontium oxalate in distilled water, and 50% alcohol at 25—26°C.

Table 3

Solvent	Time in contact with solvent and precipitated, hr.	$SrC_2O_4 \cdot H_2O$ dissolved in 50 ml. mg.	Solubility (25-26°C) mg./l.	Solubility (25-26°C) mol/l.
water	8	2.0	43.5	2.5×10^{-4}
	24	2.4		
	35	2.3		
50% alcohol	8	0.2	3.6	—
	24	0.3		
	35	0.2		

B) Influence of amount of amm. oxalate.—To find out the most suitable amount of amm. oxalate for precipitation of strontium oxalate and also to study the influence of dilution of the sample solution, a series of experiments were carried out, the results of which are shown in Table 4. In these experiments 100 ml. of 50% alcohol was employed as the washing solution.

Table 4 (Sr used is 0.2189 g.)

Water added ml.	5% Amm. Oxalate ml.	5% Amm. Oxalate molar ratio to Sr	$SrC_2O_4 \cdot H_2O$ g.	Sr found g.	Error mg.
—	10	1.4	0.4835	0.2188	−0.1
—	20	2.8	0.4836	0.2188	−0.1
—	40	5.6	0.4835	0.2188	−0.1
—	80	11.2	0.4838	0.2189	±0
50	10	1.4	0.4835	0.2188	−0.1
100	10	1.4	0.4834	0.2187	−0.2

The amounts of amm. oxalate and the partial dilution of the sample solution do not affect the exactness of the analysis.

C) Influence of *p*H.—To 25 ml. of 0.1 M strontium nitrate, a suitable indicator is added, and *p*H of the solution is adjusted to a certain value with dilute ammonia or hydrochloric acid. Then, with 10 ml. of hot 5% amm. oxalate solution the precipitate of strontium oxalate is formed.

From the results shown in Table 5, it is evident that the precipitation is completely carried out if the *p*H value of the sample solution is larger than 3.

Table 5 (Sr used is 0.2189 g.)

pH (Indicator)	$SrC_2O_4 \cdot H_2O$ g.	Sr g.	Error mg.
11.0 (Nitramine)	0.4835	0.2188	−0.1
8.2 (Phenolphthalein)	0.4835	0.2188	−0.1
6.3 (Methyl red)	0.4837	0.2189	±0
3.1 (Methyl orange)	0.4835	0.2188	−0.1
1.2 (Thymol blue)	0.4778	0.2162	−2.7
0.1 (Methyl violet)	none	—	—

D) Influence of various salts present.—The influence of various salts such as sodium chloride, potassium chloride, potassium nitrate, ammonium chloride or ammonium nitrate was examined. In each experiment, 25 ml. of 0.1 M strontium nitrate solution was mixed with a definite quantity of the salt, and this solution was treated in the manner described before. The results are shown in Table 6.

Table 6 (Sr used is 0.2189 g.)

salt	Mixed g.	$SrC_2O_4 \cdot H_2O$ g.	Sr g.	Error mg.
NaCl	2	0.5998	0.2714	+52.5
KCl	1	0.5324	0.2409	+22.0
KNO_3	2	0.5381	0.2435	+24.6
NH_4Cl	2	0.4833	0.2187	− 0.2
NH_4NO_3	2	0.4836	0.2188	− 0.1

Sod. chloride, pot. chloride, and pot. nitrate seem to be adsorbed in the precipitate of strontium oxalate so that the value of strontium is made very high. Amm. chloride and nitrate have no influence.

2) Volumetric Method.—When the strontium oxalate prepared by the above method is decomposed by sulfuric acid, oxalic acid is formed in the solution. By titrating this oxalic acid with potassium permanganate, the amount of strontium in the sample solution can be determined. The present writer applied this method to the volumetric analysis of strontium, and compared the results with those obtained by the gravimetric method.

Procedure:—From 25 ml. of 0.1 M strontium nitrate solution the precipitate of strontium oxalate is prepared under the best condition required in the former method. When 6 N sulfuric acid is added to the precipitate in a glass filter, strontium sulfate is formed and it is filtered out with suction, being stirred continuously with a glass rod. As the strontium sulfate probably adsorbs the oxalic acid, it should be washed well with distilled water. All the filtrate is kept in a measuring flask and diluted accurately to 250 ml. The 25 ml. of the filtrate, acidified with sulfuric acid, is titrated with 0.1 N potassium permanganate and from its volume the amount of strontium may be calculated.

Table 7 (Sr used is 0.2189 g.)

Gravimetrically		Volumetrically		
$SrC_2O_4 \cdot H_2O$ g.	Sr g.	0.1N-$KMnO_4$ (factor = 1.0046) ml.	Sr found g.	diff. to grav. mg.
0.4837	0.2189	49.70	0.2188	−0.1
0.4835	0.2188	49.66	0.2186	−0.2
0.4835	0.2188	49.71	0.2188	±0

The results are shown in Table 7. Judging from the fact that the amount of strontium determined by the volumetric method is nearly equal to that given by the gravimetric, it may be said that the volumetric analysis by means of oxalic acid brings on satisfactory results.

Summary

1. Quantitative precipitation of strontium as its oxalate monohydrate is made possible by employing 50% alcohol as the washing solution and by drying the precipitate at 100-105°C for 2 hrs., and as a consequence a new method for determining strontium gravimetrically was established.
2. It was found that strontium can be determined volumetrically by titrating with potassium permangante the oxalic acid which is formed when the strontium oxalate prepared by the above method is decomposed with sulfuric acid.

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