XXXVIII. THE MICRO-DETERMINATION OF BARIUM.

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IN the estimation of the barium present in barium hexosephosphates the ordinary macro-method on a small scale has been employed in this laboratory in the past. Sufficient of the salt to give about 20 mg. BaSO_4 was used, the barium precipitated in the boiling solution by the addition of very dilute sulphuric acid, and the barium sulphate filtered, ignited in the usual way and weighed on a micro-balance. The results obtained were often somewhat low and the agreement among duplicates was not always as good as was desirable. An investigation of the probable sources of error was made.

The error due to the use of coal gas for heating the barium sulphate.

It was found that heating the small platinum crucible to redness by means of a Bunsen burner to drive off the excess sulphuric acid after treatment of the incinerated residue with hydrochloric and sulphuric acids caused a considerable and variable loss in weight, due to reduction of some of the barium sulphate to barium sulphide in the presence of the hot, reducing gases from the burner. This loss can be eliminated by heating electrically at this stage, as shown by Table I.

Table I.

Weight of barium sulphate (mg.)		Manner of heating
17.200	.	Gas
21.300	.	Gentle gas heating, no blasting
20.205		Gas. " "
17.625		Gas. Blasting
16.850		"
18.275		"
19.395		Electrical
19.346		"
Another sample	18.654	Electrical
	18.646	"
	15.185	Gas
	18.667	Electrical

Between each of the weighings recorded above the barium sulphate was treated with 4 drops of $2N$ HCl , followed by 4 drops of $2N$ H_2SO_4 and the moisture driven off by gently heating the crucible lid prior to heating, in the manner indicated in Table I, to drive off the sulphuric acid. In every case

after gas-heating there was a strong odour of H_2S on adding the hydrochloric acid, whereas after electrical heating there was no odour.

The error due to incomplete filtration.

It was found that loss of barium sulphate due to incomplete filtration could be eliminated by heating the precipitated barium sulphate and supernatant liquid for 6 to 8 hours at incipient boiling, in the usual manner, leaving at 0° overnight, filtering cold and re-filtering the filtrate through the same paper (Whatman 44). Previously, it had been found that on filtering hot and without re-filtration the loss from three barium determinations, each of which gave rise to about 18 mg. BaSO_4 , was 4.162 mg. This loss was determined by evaporating to dryness the combined filtrates from the three determinations and subtracting the weight due to solid impurities in the reagents employed. Barium chloride had been used as the source of barium so this was permissible.

In order to demonstrate the accuracy of the method the following experiment was performed. Approximately 10 mg. of recrystallised barium chloride were dissolved in 100 cc. of water. Six 2 cc. samples were taken with an Ostwald pipette. Three of these were treated according to Pregl's method for the micro-estimation of chlorine. The other three were treated according to the method to be described for the estimation of barium:

BaSO ₄ obtained, mg.	22.530	22.503	22.530
After re-treating with HCl and H ₂ SO ₄ and re-heating	22.535	22.515	22.530
Average	22.525 mg.		
AgCl obtained, mg.	27.720	27.760	27.715
Average	27.732		
Calculated as BaSO ₄	22.581 mg.		

The combined filtrates (*ca.* 100 cc.) from the three barium determinations were evaporated to dryness and the residue weighed. The same quantities of the same reagents used in the three barium determinations were evaporated to dryness and the residue weighed. Results:

Residue obtained from the three filtrates	1.268 mg.
Residue obtained from the reagents	1.054 mg.
BaSO ₄ in the combined filtrates	0.214 mg.
Loss of BaSO ₄ in each determination ($\frac{1}{3} \times 0.214$ mg.)	0.071 mg.

Thus, the weight of barium sulphate found agrees closely with the figure obtained by calculating the equivalent weight in barium sulphate of the silver chloride found, and the loss of barium sulphate is not more than 0.3 % of the total weight. This loss may be even less than that shown since any soluble impurity which may have been present in the recrystallised barium chloride could not be determined, and would, of course, be present in the residue obtained on evaporation of the combined filtrates. Also, agreement is found in the weights of barium sulphate before and after re-treatment with hydrochloric and sulphuric acids and re-heating. It may be noted that even when

evaporated to a small volume the combined filtrates from the three barium determinations showed no sign of precipitate even on standing for 24 hours.

Details of the method employed.

Place sufficient of the material to be analysed to give about 20 mg. BaSO_4 in a 150 cc. beaker, add water to 100 cc. and heat to incipient boiling. In a bulb of about 15 cc. capacity, which has been drawn down to a capillary at one end, place 10 cc. of water containing one drop of $2N \text{ H}_2\text{SO}_4$ and allow this solution to drip slowly into the solution in the beaker. Then add 1 cc. of $2N \text{ H}_2\text{SO}_4$ in 10 cc. of water in the same manner. Finally, add 1 cc. of $2N \text{ H}_2\text{SO}_4$ directly to the beaker. Cover the beaker with a clock-glass and maintain it at approximately 90° for 6 to 8 hours, thereby reducing the volume of the solution to about 20 cc. Set aside over night at 0° . Filter through a small filter-paper (4 to 5 cm.), stirring up the precipitate before each addition of liquid to the funnel. Never allow the surface of the liquid in the funnel to rise closer than 1 mm. to the top of the paper, thereby avoiding a ring of barium sulphate on the glass. When the liquid has all been filtered return the filtrate to the original beaker and repeat the filtration. In this way most of the precipitate is transferred to the paper. Transfer the remainder by using small portions of the filtrate. Finally, wash the beaker and precipitate with distilled water. Dry the filter-paper in the funnel in an oven at 100° and transfer it to a small, weighed platinum crucible. Char the paper slowly by heating the projecting lid only of the crucible with a small flame, never allowing the paper to burn. When charred, increase the heat gradually, finishing with strong heating to complete the incineration. Allow the crucible to cool. Add 2 drops of distilled water, making sure that the precipitate and filter ash are wet. (Otherwise, spattering will occur due to vigorous liberation of hydrogen sulphide on the addition of hydrochloric acid.) Add 1 drop of $2N \text{ HCl}$. Wait till the usual effervescence has moderated before adding 3 or 4 more drops. Add 4 or 5 drops of $2N \text{ H}_2\text{SO}_4$. Drive off the moisture by heating the projecting lid only of the crucible with a very small flame, avoiding any approach to boiling. Finally, heat the crucible for 20 to 25 minutes on an electric heater to drive off the sulphuric acid. Placing the crucible as close as possible to a coil of red-hot resistance wire has been found to provide sufficient heat. It is advisable to remove the lid and heat it separately since, unless an electrically heated muffle is used, there is a tendency for the sulphuric acid to condense on the lid. Place the crucible on the copper block as used by Pregl. After 10 minutes transfer it to the micro-balance case and weigh it after a further 15 minutes. The empty crucible should, of course, have been weighed in the same manner. Repeat the operations from the point where the hydrochloric acid was added. The second weight should agree with the first within 0.03 mg.