CXXXVI. A METHOD FOR THE MICRO- DETERMINATION OF MAGNESIUM.

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Two organic chemical reagents are convenient for the detection and estimation of small amounts of magnesium, *viz.* *op*-dihydroxyazo-*p*-nitrobenzene and 8-hydroxyquinoline. Kahn and Vieweg [1927] have described an accurate gravimetric determination of magnesium with the aid of 8-hydroxyquinoline. Hough and Ficklen [1930] have worked out the ranges over which this reagent can be used for the estimation of magnesium gravimetrically, volumetrically and colorimetrically. They used the gravimetric method for quantities from 10–1 mg. At the lower end of the range the error was about 10 %. Their colorimetric method had a range of 5–0.5 mg. but here again the percentage error at the lower end of the range was high. The volumetric method, involving titration with permanganate, was employed over a range 5–0.1 mg.; above 0.2 mg. the results were good but below this the method became inaccurate.

For physiological work an accurate method for determining quantities of magnesium down to 0.05 mg. (50 γ) in ashed residues was desirable. This has been worked out and analyses down to 20 γ are described in this communication. The useful application of a method of magnesium determination requires that calcium shall not interfere; it will be shown that 50 γ of magnesium can be accurately determined in presence of more than 200 γ of calcium.

The method involves formation of the magnesium complex of 8-hydroxyquinoline, its hydrolysis, and subsequent determination of free hydroxyquinoline, by bromination with excess bromine and determination of excess halogen. Hydroxyquinoline is brominated readily and quantitatively to 5:7-dibromo-8-hydroxyquinoline. Berg [1927] made use of this fact to determine 8-hydroxyquinoline in acid solution by titrating in a standard bromide-bromate solution until excess bromine was indicated by indigocarmine and determining this excess. Kolthoff [1927] employed the same method but used methyl red to indicate the excess bromine. Recently Harden and Wirjodihardjo [1934], using methyl red as an indicator, carried out a direct titration with a standard bromide-bromate solution. They estimated quantities of magnesium in soil from 24.01 to 5.55 mg. and gave the error as -0.18 to $+0.24$ mg. Modification of this method to deal with quantities of the order of 20–100 γ was found by the author to be impracticable owing to the unsatisfactory nature of the end-point.

The method finally used for the analyses of quantities of magnesium down to 20 γ is based on Berg's [1927] principle of adding a known excess of bromide-bromate solution and determining the residual bromine by titration with sodium thiosulphate after the addition of excess potassium iodide, starch being used as an indicator. Such iodimetric titrations of minute quantities of bromine can be accurately and conveniently carried out with the Conway micro-burette.

which delivers volumes of 0.1 ml. with the same percentage accuracy as 1.0 ml. is delivered from the standard 2 ml. Bang burette. The micro-technique involved required the introduction of several modifications in the procedure heretofore employed by workers using 8-hydroxyquinoline. These include the method of obtaining the complex free from the excess of 8-hydroxyquinoline, bromination without loss of bromine and the method of titration.

EXPERIMENTAL.

Formation of magnesium complex of 8-hydroxyquinoline. Three ml. or less of the fluid containing the magnesium to be estimated are introduced directly into a small centrifuge-tube of about 4 ml. capacity. A moderate excess of 8-hydroxyquinoline reagent (soln. 1) is added, and the fluid volume is brought up to approximately 3.5 ml. with distilled water. The centrifuge-tube is corked with a rubber stopper through which a capillary tube passes. This arrangement allows the air to escape on heating, and at the same time prevents the solution from overflowing owing to frothing. The centrifuge-tube is then placed in a small beaker (100 ml.) of water which comes about three-quarters of the way up the tube. The water is gradually heated to 90–95°, the magnesium 8-hydroxyquinoline complex separating out. The tube and its contents are maintained at the above temperature for a few minutes, then cooled and centrifuged for ten minutes. The supernatant liquid is syphoned off leaving only about 0.1 ml. This is diluted to about 3.5 ml. with approximately *N* ammonia solution. The sediment is disturbed to free it from any excess of the reagent and the tube is centrifuged again. As before the supernatant liquid is siphoned off. It may be shown that no disturbing excess of 8-hydroxyquinoline remains after the one washing.

Bromination of the equivalent amount of 8-hydroxyquinoline. To the washed precipitate a volume of standard bromide-bromate solution (soln. 2), sufficient to give an excess of bromine is added. When 100γ of magnesium are present 2.0 ml. of the bromide-bromate solution will be found to give a convenient excess, while 0.5 ml. will suffice when 20γ of magnesium are being determined. The volume is made up to approximately 2.5 ml. with distilled water and 1 ml. of 4*N* hydrochloric acid is added. This hydrolyses the complex, giving an equivalent of free hydroxyquinoline, and liberates bromine from the bromide-bromate solution. The centrifuge-tube is immediately stoppered and inverted for a moment while the sediment is disturbed by gentle tapping. The bromine is left in contact with the 8-hydroxyquinoline at room temperature for three minutes during which time the 8-hydroxyquinoline is converted quantitatively into 5:7-dibromo-8-hydroxyquinoline.

Estimation of excess bromine. A crystal of potassium iodide is added to the solution and the free iodine is titrated, using a micro-burette as described by Conway [1934] containing standard sodium thiosulphate solution (approx. *N*/40; see below) which is added until the colour of the iodine almost disappears. A drop of starch solution is then added and the titration is continued until the blue colour disappears. When the end-point is approached the rate of delivery of the burette may be slowed down, if it is inconveniently fast for accurate regulation, by reducing the delivery pressure of the burette as described by Conway [1934].

The colour change at the end-point can be seen quite clearly on adding about 0.002 ml. of *N*/40 thiosulphate solution which corresponds to about 2–3 graduations on the burette scale. This amount is in turn equivalent to

approximately 0.15% of magnesium. The end-point may therefore be regarded as satisfactory.

A blank determination for the whole procedure must be carried out simultaneously.

Solution 1. (8-hydroxyquinoline reagent): 1 g. of 8-hydroxyquinoline is dissolved in 89 ml. of absolute alcohol and 10 ml. of ammonia (sp. gr. 0.880) and 1 ml. of hydrochloric acid (sp. gr. 1.180) are added. 0.2 ml. of this reagent will suffice for the estimation of 100% of magnesium. Corresponding amounts of the reagent may be used for less quantities.

Solution 2 (bromide-bromate): About 2.7 g. of potassium bromate and about 25 g. of potassium bromide are dissolved in 500 ml. of distilled water and the solution diluted 1 : 10. This will give approximately 1.6 mg. of bromine per ml. and is accurately standardised against the thiosulphate solution.

NOTE. Various methods of testing for an excess of bromine after bromination were tried. The most satisfactory found was to remove a small platinum loopful of the solution and bring it into contact with potassium iodide solution containing starch on a white background. A blue colour indicates excess of bromine.

Solution 3 (sodium thiosulphate): Using a micro-burette with a graduated tube of about one mm. bore, approximately *N*/40 thiosulphate will be found convenient. This is made up by dissolving about 6 g. of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in one litre of distilled water. The solution may be standardised against *N*/200 potassium iodate solution (0.1775 g. KIO_3 per litre). One ml. of this is introduced into a centrifuge-tube, using an Ostwald pipette. A crystal of potassium iodide and a few drops of *N*/10 sulphuric acid are added. The titration is carried out in the usual way, using a drop of starch solution towards the end-point.

The absolute normality of the thiosulphate solution is not determined, but it is standardised in terms of length of fluid column in the graduated tube of the Conway burette, corresponding to 1 mg. or to 1 % of bromine.

RESULTS.

The above method was used in the micro-determination of magnesium in standard solutions of magnesium sulphate containing about 6 g. of pure crystalline $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 ml. of distilled water. The exact quantity of magnesium in 10 ml. of this solution is determined in duplicate by precipitating as magnesium ammonium phosphate, igniting and weighing as magnesium pyrophosphate. The solution thus made up and standardised for its exact magnesium content is suitably diluted and the requisite volumes used in the analyses.

Table I shows the results of analyses which were carried out using the method described with varying amounts of standard magnesium solution. It will be seen that down to 20% the method may be relied on to give a result of an individual determination to within 10 % of the theoretical quantity.

Table I.

Theoretical amount of mg.	Analyses. Mean value	Number of analyses	% deviation of mean value from theoretical	Coefficient of varia- tion of individual determinations
γ	γ			
114.2	120.4	6	+5.0	1.2
76.1	74.3	6	-2.4	2.9
50.8	53.5	7	+5.3	3.9
25.4	24.2	6	-4.7	4.7
19.0	20.2	6	+6.3	4.3
12.7	13.2	6	+7.9	10.3
5.1	5.5	6	+7.8	6.1
3.8	3.3	5	+13.2	14.5
Blank	1.5	13	—	27.5

Table II gives individual analyses carried out on 25.4% of magnesium. The percentage deviation of each analysis from the mean is given and it will be seen

that the greatest is -7.0 . The percentage deviation of the mean value of the six analyses from the theoretical is -4.7 .

Table II. *Six estimations of 25.4 γ Mg.*

Volume of bromide-bromate soln. used (ml.)	Thiosulphate soln. Divisions on micro- burette scale	Mg as estimated. Corrected for blank* (γ)	Deviation from mean γ	% deviation from mean
0.7	10.87	23.6	-0.6	-2.5
0.6	5.89	25.3	+1.1	+4.5
0.6	6.82	23.9	-0.3	-1.2
0.6	6.24	24.8	+0.6	+2.5
0.6	7.73	22.5	-1.7	-7.0
0.6	5.84	25.4	+1.2	+5.0

* Corrected by subtracting blank value = 1.5 γ .

1 division (100 small graduations on) microburette scale used = 0.04435 ml.

1 ml. bromide-bromate solution is equivalent to 1.58 mg. Br.

1 division (100 small graduations) on micro-burette scale used, containing approximately N/80 thiosulphate solution is equivalent to 0.041 mg. Br. (A weaker thiosulphate solution was used here than was subsequently considered more generally suitable.)

Mean value of the six analyses of 25.4 γ of magnesium is 24.2 γ .

Six determinations of the blank value were carried out, using 0.1 ml. of 8-hydroxyquinoline and seven estimations using 0.2 ml. The mean values of these two series were practically the same (1.5 γ) though individual values varied from 1.0 γ to 2.5 γ . This blank value is due to the glass and it will be seen that the variation between the individual blanks (up to 1.0 γ from the mean) may account to a large extent for the high deviation of individual analyses where quantities less than 20 γ are determined.

Determination of magnesium in the presence of calcium.

Table III gives the results of determinations of magnesium in presence of varying amounts of calcium.

Table III.

Wt. of calcium added γ	Mean value of four analyses γ	Apparent increase of magnesium due to presence of calcium γ
0	53.5	—
10	54.4	0.9
25	54.5	1.0
80	53.9	0.4
100	53.1	-0.4
200	55.8	2.3

In each case four analyses were carried out and the mean value of these determinations is given in column 2 of Table III. From these figures it will be seen that the analysis of 50 γ of magnesium in 3.5 ml. may be carried out without any appreciable error due to the presence of four times this quantity of calcium.

SUMMARY.

1. A method is described whereby quantities of magnesium down to 20 γ in 3 ml. or less can be reliably determined in standard solutions or in solutions from ashed residues.

2. Analyses were carried out on known quantities of magnesium varying from 114.2 down to 3.8 γ . The results of these analyses are given and the figures show that over a range 114 to 20 γ the coefficient of variation of the individual determination is 1.2 at the higher and 4.3 at the lower level. An individual

analysis therefore down to 20γ of magnesium may be relied on to within 10 % of the theoretical quantity. With this amount of magnesium the error of estimate is chiefly due to the glass of the centrifuge-tubes used.

3. It has been shown that, by the method described, 50γ of magnesium in 3.5 ml. can be determined in the presence of four times as much calcium without any increased error due to the calcium.

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