unaffected. That the color was not due to oxidation of the ferrous sulphate is shown by the fact that the change took place in (*b*) in an atmosphere of carbon dioxide, but the paper was unaffected in (*c*), which contained air.

The coloration of a solution of *a*-naphthylamine and sulphanilic acid in acetic acid, noted by Marie[1] and Marquis, was confirmed. Hence the evidence points decidedly towards the conclusion that nitrous acid is liberated from a solution of potassium, sodium or silver nitrite by carbon dioxide.

CHEMICAL LABORATORY,
UNIVERSITY OF MISSOURI.

THE COLORIMETRIC ESTIMATION OF MAGNESIUM.[2]

BY OSWALD SCHREINER AND WILLIAM S. FERRIS.

Received May 11, 1904.

IN THE course of certain investigations the problem of the determination of small amounts of magnesium in aqueous solutions was presented. It was thought that a possible solution of the difficultly could be found in precipitating the magnesium as magnesium ammonium phosphate, as is done in the ordinary gravimetric procedure, and after washing, to redissolve the precipitate in nitric acid and then to estimate the magnesium indirectly by determining the phosphate with ammonium molybdate, according to the well-known colorimetric method.[3] The idea was tested by evaporating 50 cc. of a magnesium salt solution to a very low bulk or to dryness and using sodium hydrogen phosphate in excess as precipitant, and ammonium hydroxide as wash-liquid. The results were discouragingly high, owing, no doubt, to the difficulty in washing out the sodium hydrogen phosphate from the precipitate and the filter. The more soluble potassium phosphate was, therefore, substituted with far more encouraging results, as will be seen in Table I. In the first two columns in the table are given the actual amounts of magnesium present and found in the tests of 50 cc. of solution used, and in the last two columns the parts of

---

[1] *Compt. Rend.*, **138**, 694.

[2] Published by permission of the Secretary of Agriculture.

[3] See West-Knights: *Analyst*, **5**, 197 (1880); Lepierre: *Bull. Soc. Chim.* (3), **15**, 1213 (1896); Jolles and Neurath: *Monatsh. Chem.*, **19**, 5 (1898); Jolles: *Arch. f. Hygiene*, **34**, 22 (1899); Woodman and Cayvan: This Journal, **23**, 96 (1901); Woodman: *Ibid.*, **24**, 735 (1902); Veitch: *Ibid.*, **25**, 169 (1903); Schreiner: *Ibid.*, **25**, 1056 (1903).

magnesium per million parts of solution. The four tests had been treated with varying amounts of phosphate as precipitant, the quantities in Nos. 3 and 4 being many times in excess of the required amount.

TABLE I.—PRELIMINARY TEST.

Gram magnesium.		Parts Mg per million of solution.	
Present.	Found.	Present.	Found.
0.000247	0.000241	4.94	4.82
0.000247	0.000244	4.94	4.88
0.000247	0.000273	4.94	5.46
0.000247	0.000259	4.94	5.18

A more thorough series of tests, both with solutions containing only magnesium, as well as those in which other salts were present, was then undertaken. A great many details of procedure had to be worked out, but it is needless, in this connection, to give every step in the development of the procedure. All the determinations, however, are given in Table II, although many were obtained under unfavorable circumstances for the best results.

TABLE II.—RESULTS OBTAINED WHILE DEVELOPING THE METHOD.

Gram magnesium.		Parts Mg per million of solution.	
Present.	Found.	Present.	Found.
0.000316	0.000296	6.32	5.92
0 000316	0.000289	6.32	5.78
0.000316	0.000252	6.32	5.04
0.000316	0.000255	6.32	5.10
0.000158	0.000148	3.16	2.96
0.000158	0.000152	3.16	3.04
0.000158	0.000143	3.16	2.86
0.000158	0.000141	3.16	2.82
0.000079	0 000102	1.58	2.04
0.000079	0.000078	1.58	1.46
0.000079	0.000101	1.58	2.02
0.000040	0.000070	0.80	1.40
0.000040	0.000057	0.80	1.14
0.000040	0.000056	0 80	1.12

The most serious difficulty expected was the effect of the presence of calcium, which, it was thought, would also precipitate phosphoric acid; but it was found that the calcium was readily prevented from taking part in the reactions by adding a few drops of a solution of ammonium oxalate before adding the phosphate reagent. The facts ascertained while running the above series led to the adoption of the following procedure:

METHOD FOR DETERMINING MAGNESIUM COLORIMETRICALLY.

The following reagents will be required:

(1) *Ammonium Molybdate Solution.*—Fifty grams of the pure salt in 1 liter of solution.

(2) *Nitric Acid.*—Specific gravity 1.07.

(3) *Standard Phosphate Solution.*—0.5045 gram of pure freshly crystallized sodium phosphate, $Na_2HPO_4.12H_2O$, is dissolved in water, 100 cc. of nitric acid (sp. gr. 1.07) added, and the whole diluted to 1 liter. The nitric acid is added to lessen the contamination with silica from the glass. One cc. = 0.0001 gram P_2O_5, = 0.0000342 gram Mg.

(4) *Standard Colorimetric Solution.*—This is prepared by diluting 10 cc. of the standard phosphate solution (3) to about 80 cc. and then adding 9 cc. of nitric acid (2) and 8 cc. of ammonium molybdate solution (1) and making up to 100 cc. After standing twenty minutes it is ready for use. Each cubic centimeter of this colorimetric solution is equal to 0.00001 gram P_2O_5, = 0.00000342 gram Mg.

(5) *Ammonium Hydroxide.*—Reagent.

(6) *Ammonium Hydroxide Wash Liquid.*—One part of strong ammonia water (sp. gr. 0.9) and 9 parts of water. This liquid should be practically free from silica, and for this reason is best prepared from redistilled ammonia water.

(7) *Ammonium Oxalate.*—Saturated solution.

(8) *Phosphate Reagent.*—Dissolve 17.4 grams of potassium hydrogen phosphate, K_2HPO_4, 100 grams of ammonium chloride, NH_4Cl, in about 900 cc. of water, add 50 cc. of strong ammonia water (sp. gr. 0.9) and dilute to 1 liter. One cc. of the solution will precipitate 2.4 milligrams of magnesium.

(9) *Filter-paper.*—This must be free from silica. Schleicher and Schüll's No. 589 or 590 7 cm. has been found to be very satisfactory for this colorimetric work.

Colorimeters.—Two different colorimeters were used in the course of the work. The first instrument was similar to the one described and illustrated by Whitson.[1] It consists of a tube of colorless glass 1 x 10 inches, with a side delivery tube near the bottom to connect by means of a rubber tube with a sliding reservoir for quickly changing the length of the standard colorimetric solution;

---

[1] Bulletin 85. Wis. Agr. Expt. Station.

a comparison tube, also of colorless glass and as nearly as practicable of the same dimensions as the measuring tube. It is provided with a 50 cc. and 100 cc. mark. The measuring tube is graduated so that one division of the scale is exactly equal to 0.01 of the distance between the bottom of the comparison tube and the 100 cc. mark. Both tubes have accurately ground and polished bottoms. The whole is mounted in a suitably constructed camera. A reflector of white paper, in place of the mirror of the Whitson instrument, at the top of the camera, illuminates the two solutions alike, while the images are viewed in a mirror below.

In the second instrument the length of the standard solution column is varied by means of an immersion tube inside the standard tube. The tube containing the unknown solution is placed below a similar tube, but not touching the liquid. This tube is used so as to give identically the same kind and size of image for comparison with the image from the standard tube. The length of the standard column is then varied by sliding the comparison tube up or down until its color intensity equals that of the unknown solution. The solutions are illuminated by a white reflector from below and the images are viewed in a mirror above, placed at an angle of 45°. A more detailed description of this colorimeter, together with the use of standard colored glasses instead of colorimetric solutions in connection with it, will appear elsewhere.

The procedure for the method is as follows: Measure out a convenient volume of the solution to be estimated, usually 50 cc., into an evaporating dish, add 1 drop of ammonia water (5), and 2 or 3 drops of the ammonium oxalate solution (7); evaporate to dryness on a water-bath. To the cooled dish add 1 cc. of the phosphate reagent (8), and work up the residue well with a glass rod, and then allow to stand about two hours. The precipitated magnesium ammonium phosphate is then washed as follows: Add about 5 cc. of the ammonium hydroxide wash liquid (6) to the dish, washing down the sides, and then pour the liquid through a small filter (9). Repeat this operation five times, then wash down the filter and funnel until the filtrate measures approximately 50 cc. Then rinse the dish once with about 5 cc. of cold water and pour through the filter in such a way as to wash the filter. Reject the washings and put a clean salt-mouth bottle or other receptacle under the funnel. Add 5 cc. of nitric acid (2) to the dish, working this about with the glass rod and pour through the funnel in such a manner as to wet all the inside of the funnel. Then wash the dish five times with hot water (about 5 cc. each) and continue washing the filter until about 45 cc. of the filtrate have been obtained. To the cooled liquid add 4 cc. of the ammonium molybdate solution (1), and, after twenty minutes, read against the standard colorimetric phosphate solution (4).

When the color developed is too strong for direct comparison with the standard solution, an aliquot part is read. Great care must be taken to insure a sufficient amount of the molybdate reagents when dealing with larger amounts of magnesium, comparatively speaking. The amounts of nitric acid (5 cc.) and ammonium molybdate solution (4 cc.), given above, are safe only up to about 0.0003 gram of magnesium. Should a larger amount have been used for the test, as indicated by the amount of the precipitate or development of color, it will be necessary to add a second portion of these reagents in order to develop the full color, diluting at the same time with water in such a manner as to keep the concentration of the reagents the same, namely, 5 cc. of nitric

TABLE III.—TEST RESULTS.

Gram magnesium.		Parts Mg per million of solution.	
Present.	Found.	Present.	Found.
0.001265	0.001311	25.30	26.22
0.000949	0.000984	18.98	19.68
0.000632	0.000610	12.64	12.20
0.000632	0.000619	12.64	12.38
0.000474	0.000490	9.48	9.80
0.000316	0.000315	6.32	6.30
0.000316	0.000313	6.32	6.26
0.000253	0.000240	5.06	4.80
0.000253	0.000243	5.06	4.86
0.000190	0.000190	3.80	3.80
0.000190	0.000190	3.80	3.80
0.000158	0.000176	3.16	3.52
0.000158	0.000160	3.16	3.20
0.000127	0.000143	2.54	2.86
0.000127	0.000147	2.54	2.94
0.000127	0.000134	2.54	2.68
0.000063	0.000081	1.26	1.62
0.000063	0.000076	1.26	1.52
0.000063	0.000074	1.26	1.48
0.000063	0.000070	1.26	1.40
0.000025	0.000045	0.50	0.90
0.000025	0.000038	0.50	0.76

acid and 4 cc. of ammonium molybdate solution in every 50 cc. of the solution. This procedure was followed in the case of the first five results given in Table III, the first two of which required even more of these reagents. These larger amounts, comparatively speaking, were included so as to show the range of the method. With the smaller amounts, where the coloration to be read is small, it was found very convenient and much more satisfactory to use a standard for comparison of only half the above strength.

In Table III a series of results obtained with solutions of varying concentrations of magnesium and containing at the same time calcium and potassium sulphates, chlorides and nitrates, is given. As before, in the first two columns the actual amounts of magnesium used in making the test are given, and in the last two columns the parts of magnesium per million of solution.

These results, as well as the earlier series, show that in this procedure the magnesium, and magnesium only, is completely precipitated by the phosphate reagent, and that the loss of the resulting magnesium ammonium phosphate in the course of this brief washing with ammonia water must be exceedingly slight even with the smallest amounts of magnesium used. The tendency towards high results with the exceedingly weak solutions is, no doubt, due to the error introduced by the almost unavoidable color of the reagents themselves, an effect which is wholly negligible and in part compensated by the reagents in the standard, when stronger solutions are used. The actual error, however, as is readily seen by an examination of the figures is no greater in these low concentrations than in the higher ones, although it is naturally a much greater per cent. of the amount present.

As silica gives the same coloration with the molybdate reagents, it is, of course, essential that this disturbing factor be removed. As an alkaline fluid is used throughout the procedure, it is evident that the dissolved silica will remain throughout in solution and be removed in the rejected wash liquors. As ammonia water always contains traces of dissolved silica, the last washing, as directed above, is always made with pure water. In order to show experimentally that silica, present in the original solution, is completely removed in the procedure, a series of solutions of varying concentrations in magnesium, but all containing more than five parts of silica per million of solution, were made. Calcium and potassium salts were also present. The results of the magnesium determinations are given in Table IV.

TABLE IV.—TEST SERIES CONTAINING SILICA.

Gram magnesium.		Parts Mg per million of solution.	
Present.	Found.	Present.	Found.
0.000316	0.000313	6.32	6.26
0.000316	0.000316	6.32	6.32
0.000158	0.000147	3.16	2.94
0.000158	0.000151	3.16	3.02
0.000079	0.000094	1.58	1.88
0.000079	0.000088	1.58	1.76
0.000040	0.000055	0.80	1.10
0.000040	0.000054	0.80	1.08

The results clearly show that the silica has been entirely removed in the washing process.

The practical handling of the method as routine work by the assistants in charge of the investigations requiring the accurate determination of small amounts of magnesium has proven very satisfactory and expedient. With proper attention to details one man is able to make twenty determinations, including all calculations, in a working day of seven hours.

BUREAU OF SOILS,
U. S. DEPT. OF AGRICULTURE,
WASHINGTON, D. C.

THE ESTIMATION OF SMALL AMOUNTS OF FERRIC IRON BY ACETYLACETONE (ESPECIALLY APPLIED TO WATER ANALYSIS).

BY H. B. PULSIFER.

Received June 28, 1904.

IT IS less than twenty years ago that Combes[1] first prepared acetylacetone and its metallic salts. He mentioned that acetylacetone gives an intense red coloration with ferric salts.

The following was undertaken to ascertain the limits and conditions attending this color reaction, and to compare its value with that of other reagents commonly used to estimate iron qualitatively and quantitatively.

Acetylacetone is a colorless liquid, boiling at 137°. Combes showed its structure to be $CH_3.CO.CH_2.CO.CH_3$. One of the hydrogen atoms attached to the middle carbon atom is easily replaceable by the common metals.

---

[1] *Compt. Rend.*, **105**, 868.