[CONTRIBUTION FROM THE CHEMICAL LABORATORY, THE TRAVELERS INDEMNITY COMPANY AND THE TRAVELERS INSURANCE COMPANY]

DETERMINATION OF MAGNESIUM WITH 8-HYDROXYQUINOLINE—GRAVIMETRICALLY, VOLUMETRICALLY AND COLORIMETRICALLY

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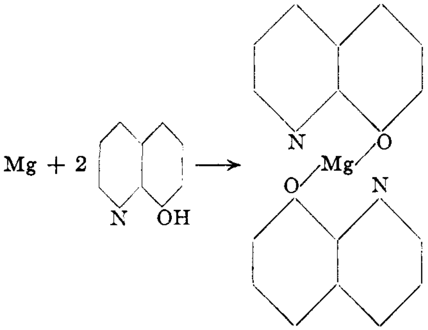
In an attempt to develop a quick method for the determination of magnesium in dilute solutions, particularly in boiler feed water analyses, the quantitative reaction which takes place in alkaline solution between the magnesium ion and a molar equivalent of 8-hydroxyquinoline with the formation of a light green precipitate was used.

Strebinger and Reif filtered off this salt through a Pregl filter tube, dried it at 105° for twenty minutes, and weighed it as $Mg(C_9H_6ON)_2 2H_2O$.[1]

The following methods diverge from that of Strebinger and Reif beyond the point where the green magnesium salt of 8-hydroxyquinoline is precipitated.

The reaction which takes place between the magnesium ion and 8-hydroxyquinoline is as follows



One part by weight of magnesium reacts with 11.9 parts by weight of 8-hydroxyquinoline.

An accurate standard solution of a magnesium salt which contained 0.1 gram of magnesium per liter was prepared.

The solution of 8-hydroxyquinoline was prepared by dissolving 0.5 g. in 100 cc. of alcohol and diluting to 1 liter. The solution obtained is of a bright yellow color.[2]

I. Gravimetric Method (N. B. Calcium must first be precipitated as oxalate and filtered off).—Take a sample containing at least 0.001 g. of magnesium and bring this sample to a volume of from 50 to 150 cc. Make ammoniacal with 20 cc. of ammonia reagent. Heat to 70° and add 100

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[1] Strebinger and Reif, *Chemical Abstracts*, **24**, 2397 (1930).

[2] Allen, "Commercial Organic Analysis," Vol. V, p. 657.

cc. of a solution of 8-hydroxyquinoline containing 0.5 of this salt per liter. If the amount of magnesium present exceeds 0.004 g., add a larger amount of 8-hydroxyquinoline solution for completeness of precipitation, and, if necessary, add more 8-hydroxyquinoline. An excess of 8-hydroxyquinoline is made evident by the yellow color in the filtrate. Wash the precipitate with a weak solution of ammonium hydroxide, ignite strongly for thirty minutes in a porcelain crucible, and weigh as magnesium oxide.

Various amounts of the standard magnesium solution from 10 cc. (0.0010 g.) to 75 cc. (0.0075 g.) were run as above, and the actual results varied slightly from the theoretical. On the higher ranges the agreement was highly satisfactory. On the lower ranges the slight inaccuracies were due to the limitations inherent in the gravimetric method—such as error in weighing and taring, loss through slight solubility of the salt, loss through escape during ignition, and possible variance in the tare of filter paper ash.

Amounts of magnesium less than 0.0010 g. are not determined to good advantage gravimetrically, on account of the magnification of the above mentioned errors in consequence of the small quantity of magnesium present.

The table shows how results obtained compared with the theoretical.

TABLE I

COMPARISON OF RESULTS

Mg taken, mg.	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	7.5	10.0
Mg found, mg.	1.1	1.7	2.3	2.7	3.1	3.3	3.9	4.3	5.0	7.5	9.9

Magnesium taken as solution containing 0.1 mg. per cc.

II. Volumetric Methods.—Reagents: Solution of potassium permanganate, 4.17 g. per liter; *N* sulfuric acid. Precipitate the magnesium salt as described above, and wash with ammonium hydroxide. Dissolve the precipitate in 100 cc. of hot *N* sulfuric acid by immersing filter paper and precipitate in the acid and stirring. Titrate against the potassium permanganate solution until the pink color persists for two minutes. When the end-point is approached, the permanganate solution should be added, 0.5 cc. at a time, and the fading timed with a watch. Each cubic centimeter of potassium permanganate solution used is equivalent to 0.0001 g. of magnesium.

Various amounts of the standard magnesium solution from 1 cc. (0.0001 g. of magnesium) to 50 cc. (0.0050 g. of magnesium) were run, and up to 0.0025 g. of magnesium the results were very accurate. Larger amounts of magnesium than 0.0025 g. caused the end-point to be obscured by colored oxidation products imparting a brown color to the solution. Magnesium in amounts up to 0.0025 g. is determined to very good advantage by this method. In amounts larger than this, the gravimetric method is preferable. Of course, the sample can be diluted and an aliquot taken in order to bring the amount of magnesium into the effective range if it is too high to work to good advantage volumetrically. The table shows how results obtained compared with the theoretical.

TABLE II

COMPARISON OF RESULTS

Each milligram of magnesium taken represents 10 cc. of sample; each milligram found represents 10 cc. of potassium permanganate solution

Mg taken, mg.	0.10	0.20	0.30	0.40	0.50	0.80	1.00	1.20	1.40
Mg found, mg.	.14	.20	.33	.41	.48	.80	0.98	1.17	1.36
Mg taken, mg.	1.60	1.80	2.00	2.50	3.00	3.50	4.00	4.50	5.00
Mg found, mg.	1.60	1.84	2.03	2.55	3.16	3.75	4.45	5.05	5.75

III. Colorimetric Method.—The sample should not be of greater volume than 50 cc. Make alkaline with 20 cc. of ammonia reagent and add exactly 60 cc. of a solution of 8-hydroxyquinoline. (This latter solution should be prepared quantitatively.) Filter and wash with a small amount of weak ammonia. Make the volume of the filtrate up to 150 cc. with distilled water. The depth of color in the filtrate, due to the uncombined 8-hydroxyquinoline, is inversely proportinoal to the amount of magnesium in the sample. This can be compared in a 100-cc. colorimeter, using the 8-hydroxyquinoline solution as a standard. Since 1 cc. of 8-hydroxyquinoline solution is equivalent to 0.0000416 g. of magnesium, the following calculation can be made

$$\left(60 - \frac{3 \times \text{Reading}}{2}\right) \times 0.0000416 \times \frac{1{,}000{,}000}{\text{vol. of sample (cc.)}} = \frac{\text{parts of magnesium}}{\text{per million}}$$

Or if a 50 cc. sample is taken, which does not contain more than 50 parts of magnesium per million, this may be written in the form

$$1.248 \times (40 - \text{Reading}) = \text{parts of magnesium, per million}$$

$$49.92 - (1.248 \times \text{Reading}) = \text{parts of magnesium, per million}$$

If the amount of magnesium is greater than 50 parts per million, a correspondingly smaller sample should be taken and calculation made on the basis of the reduced sample. (The use of a sample containing a greater amount of magnesium than this makes necessary the use of a larger amount of 8-hydroxyquinoline solution, and is not advisable for reasons of economy.)

A range of amounts from 0.0005 to 0.0050 g. of magnesium were run as described above, and the results are shown herewith, as compared to the theoretical.

TABLE III

COMPARISON OF RESULTS

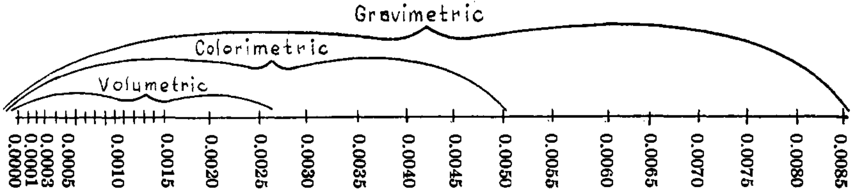
	8-Hydroxyquinoline							
	60 cc. used					120 cc. used		
Mg taken, mg.	0.5	1.0	1.5	2.0	2.5	3.0	4.0	5.0
Reading	28	24	18	10	5	18	9	4
Mg found, mg.	0.7	0.9	1.4	1.8	2.3	3.1	4.3	5.3

Summary

1. Quick determinations of magnesium can be made by precipitating it as the salt of 8-hydroxyquinoline and estimating the magnesium content of the salt either gravimetrically, volumetrically or colorimetrically. In many cases where the saving of time is an important factor and extreme accuracy is secondary, one of these methods may prove useful.

2. The most advantageous method to use depends on the amount of magnesium in the sample. (a) For amounts ranging from 0.0010 g. up to the highest concentrations, the gravimetric method is most accurate. (b) For amounts ranging from a minute trace up to 0.0025 g. the volumetric method is most accurate, and is very quick in comparison with many methods commonly used. (c) For amounts ranging from 0.0005 g. up to high concentrations (if proper aliquots are taken), the colorimetric method is very accurate and is the quickest of the three methods.

3. The following scale will illustrate at a glance the advantageous range of the three methods.



4. None of the other metals commonly found in natural waters will react with 8-hydroxyquinoline, except calcium.

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THE EMISSION SPECTRA OF SOME SIMPLE BENZENE DERIVATIVES

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The main features of the spectra obtained from the vapor of benzene and its simple derivatives under the excitation of the Tesla discharge have been described by McVicker, Marsh and Stewart,[3] who designated them as Tesla luminescence spectra to distinguish them from the fluorescence and absorption spectra. The present investigation was undertaken as an extension of this work; it was hoped on the purely chemical side to develop the suggestion made by them that a means of ascer-

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[1] From a dissertation presented by J. B. Austin to the Graduate School of Yale University, June, 1928, in candidacy for the degree of Doctor of Philosophy.

[2] Commonwealth Fellow 1926–1928.

[3] McVicker, Marsh and Stewart, *J. Chem. Soc.*, **123**, 642, 2147 (1923).