

岡山大学温泉研究所報告

第 13 号

昭和 28 年 12 月 発行

PHOTOMETRIC DETERMINATION OF MAGNESIUM IN NATURAL WATERS.

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Various colorimetric methods for determining magnesium in natural waters have been studied, and the methods using 8-oxyquinolin, ammonium molybdate and titan yellow were studied most frequently¹⁾, following the studies on the interfering ions²⁾. Brilliant yellow³⁾, 1-amino-2-naphthol-6-sulfonic acid⁴⁾ and other new reagents were also used. E. D. T. A. was used, but the determination by using this reagent is not exact.

Present reagent already reported by T. Ashizawa⁵⁾, magneson II, is insoluble in water, soluble in alkali and hardly soluble in ethanol. In the existence of magnesium ion, the color of solution varies from pink-violet (in alkali) and orange (in ethanol) to blue-violet. This variation of color was evaluated photometrically by Shimadzu photoelectric spectrophotometer, and moreover the grades of interference by interfering ions were clarified.

REAGENTS

Magneson II. p-nitroanilin 1.38 g. were heated 80-90°C. with 2-3 ml. of conc. hydrochloric acid and 25 ml. of water, and diluted to 160 ml., and after cooling poured into concentrated solution of 0.9 g. sodium nitrite. This liquid was mixed with 1.4 g. α -naphthol solution in alkali, then acidified by hydrochloric acid. The brownish red crystal deposited was filtered off and washed by hydrochloric acid and distilled water and dried.

Magneson II solution in ethanol (sat. at 5°C.)

5% sodium hydroxide solution.

Magnesium, aluminum, ammonium, calcium and iron compounds are purified as follows :

Magnesium sulfate, aluminum sulfate and manganese sulfate were recrystallized, and ammonium chloride was purified by sublimation. Calcium chloride was dissolved in water and added ammonium oxalate, then the calcium oxalate was varied to calcium oxide by ignition and it was dissolved in hydrochloric acid, and then evaporated to dryness. Ferric chloride was dissolved in dil. hydrochloric acid and hydrogen sulfide was passed through the solution. To the filtrate of this solution, ammonium chloride and ammonium hydroxide were added, and the precipitate was dissolved in hydrochloric acid, then excess of sodium hydroxide was added. The precipitate was dissolved in hydrochloric acid and condensed by evaporation. The crystal of ferric chloride was deposited after cooling.

PROCEDURE

To 10 ml. of sample water, 1 ml. of magnesium II solution are added and the solution is mixed completely. 1 ml. of sodium hydroxide solution is added, and the solutions mixed completely. After few minutes, the absorbancy is determined at 520 $m\mu$.

APPARATUS

Absorbancy measurement were made with Shimadzu photoelectric spectrophotometer against distilled water as a reference blank. 1-cm. cuvettes were used throughout the study.

EXPERIMENTAL

The absorption curves for the mixtures of magnesium, magnesium II and sodium hydroxide and of water, magnesium II and sodium hydroxide are shown in Figure 1.

The maximum difference of absorbancy is found at 520 $m\mu$. The absorbancy of a series of solutions, each containing 0.4 to 20 p.p.m. of magnesium and made up according to the procedure mentioned above, are determined one by one. The result is shown in Figure 2, and the linearity of the curve is obeyed up to 4 p.p.m. of magnesium. When the concentration of magnesium is more than 8 p.p.m., the color of solution fades immediately after the color development.

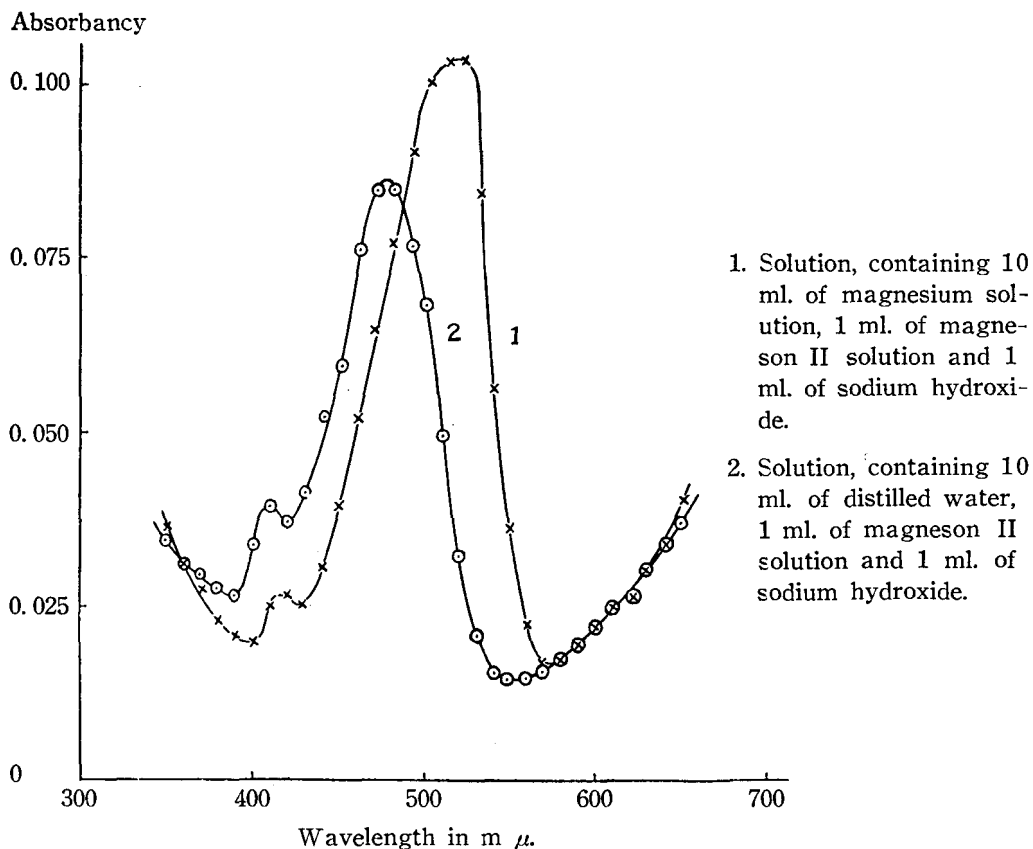


Figure 1. Absorption Spectra.

The effects of calcium, ammonium, ferric, manganese, aluminum, silicious and phosphate ions are shown in Table 1, 2, 3, 4, 5, 6 and 7. According to the results of this study, the presence of less than 1 p. p. m. of calcium, 500 p. p. m. of ammonium, 5 p. p. m. of ferric, 0.1 p. p. m. of manganese, 0.2 p. p. m. of aluminum, 1 p. p. m. of silicious and 0.1 p. p. m. of phosphate ion do not interfere the determination.

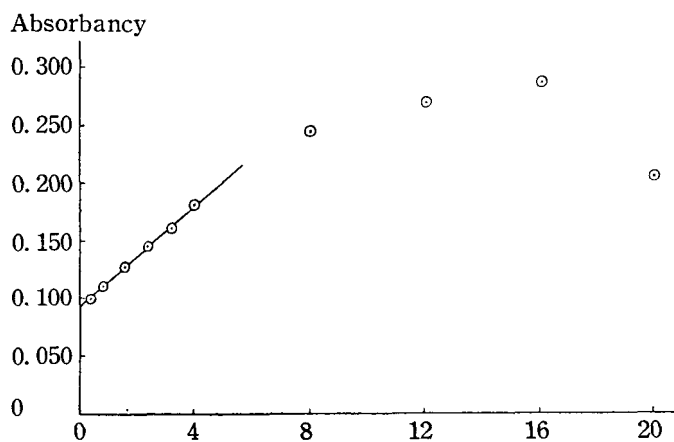


Figure 2. Concentration of Magnesium, p. p. m.

Table 1. Effect of Calcium Ion.

Concentration of calcium ion (p. p. m.)	Absorbancy
80	0.142
60	0.146
40	0.150
20	0.155
10	0.161
5	0.168
1	0.170
0	0.171

Table 2. Effect of Ammonium Ion.

Concentration of ammonium ion (p. p. m.)	Absorbancy
3000	0.032
2100	0.164
900	0.164
500	0.163
300	0.162
100	0.161
65	0.163
39	0.163
13	0.162
0	0.163

Table 3. Effect of Ferric Ion.

Concentration of ferric ion (p. p. m.)	Absorbancy
5	0.162
3	0.163
1	0.164
0	0.162

Table 4. Effect of Manganese Ion.

Concentration of manganese ion (p. p. m.)	Absorbancy
5.5	0.088
3.3	0.098
1.1	0.114
0.66	0.129
0.44	0.135
0.22	0.138
0.11	0.141
0	0.142

Table 5. Effect of Aluminum Ion.

Concentration of aluminum ion (p. p. m.)	Absorbancy
5.4	0.086
3.3	0.103
1.1	0.111
0.88	0.118
0.66	0.120
0.22	0.124
0	0.125

Table 6. Effect of Silicious Ion.

Concentration of silicious ion (p. p. m.)	Absorbancy
50	0.085
30	0.089
20	0.093
10	0.105
5	0.117
3	0.126
1	0.136
0	0.137

In common natural water, calcium is far more than magnesium and more than 500 p. p. m. of ammonium ion interfer, then the elimination of calcium by precipitating with ammonium oxalate is inconvenient. Therefore, to the standard solution compensating solution must be added.

In natural water, silicious ion is more than 1 p. p. m., and in this case, also, compensating solution must be added to the standard solution.

Other interfering ions also may be present in natural water, and in this case the analysis can be done by dilution as far as the magnesium is not diluted to very low concentration.

Table 7. Effect of Phosphate Ion.

Concentration of phosphate ion (p. p. m.)	Absorbancy
4	0.113
3	0.118
1.2	0.121
0.4	0.134
0.2	0.138
0.1	0.142
0	0.143

However, when the dilution is not allowed, compensating solution must be used as the cases of calcium and silicious ions.

The effect of temperature is shown in Table 8., and the high temperature gives the negative interference. The photometry must be accomplished at the temperature near that at which the absorbancy of standard solution was determined.

Temperature (°C.)	Absorbancy	As the absorbancy of the solution is varied by the variation of the amount of magneson II and sodium hydroxide solution added, its amounts should be districtly constant.
7.6	0.135	
20.2	0.134	
44.5	0.123	

ACKNOWLEDGEMENT

The author wishes to express his sinscere thanks to Prof. K. Kimura of Tokyo University for his kind guidance and encouragement, and to T. Ashizawa for the offering of magneson II.

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