

THE DIRECT SPECTROPHOTOMETRIC MICRODETERMINATION OF HIGH-LEVEL MAGNESIUM IN SILICATE MINERALS. A CLAYTON YELLOW PROCEDURE¹

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ABSTRACT

The MgO content of 5–20 mg samples of silicate minerals containing major concentrations of magnesium is determined spectrophotometrically using Clayton Yellow (C.I. 813). The sample is decomposed by heating with hydrofluoric and sulfuric acids. No separations are made. The common rock-forming elements likely to be present in the solution of most silicate minerals do not interfere. Determinations of the MgO content of various silicate minerals using this procedure agree satisfactorily with those determined by macroprocedures.

INTRODUCTION

Many of the samples of silicate minerals received by the analytical laboratories of the U. S. Geological Survey are too small (100–1000 mg) for a complete analysis by classical silicate methods or by other macroprocedures. Semimicro- or micromethods must therefore be used for their analysis.

The author is ascertaining the applicability of various methods for the direct determination (*i.e.*, without separations) of the common rock-forming elements in small samples of silicate minerals. The procedure described herein has been tested and is recommended for the direct determination of high-level magnesium in small samples of silicate minerals.

The "Thiazole Yellow" dyes have been used for a long time for determining colorimetrically small amounts of magnesium (Sandell, 1959, pp. 591–598). Thiazole Yellow, Titan Yellow, and Clayton Yellow are different trade names of the "Thiazole Yellow" dyes which have the same Color Index, C.I. 813 (Sandell, 1959, p. 591). Clayton Yellow (Indicator), C.I. 813, was used in the procedure described below which is based on Shapiro's Thiazole Yellow spectrophotometric procedure (Shapiro, 1959, and Shapiro and Brannock, 1962) for determining low-level magnesium in rocks. Changes were made to adapt the procedure to the analysis of small samples of minerals.

EXPERIMENTAL WORK

Beer's law is obeyed in the concentration range 0.2 ppm (20 micrograms per 100 ml) to 2.0 ppm (200 micrograms per 100 ml) of MgO. This does not include a "spike" of approximately 0.5 ppm (50 micrograms per 100 ml) MgO which is added to all the solutions analyzed including the

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reference solution. Hereafter, the MgO "spike" will not be mentioned, except when necessary, and the reader should understand that the stated concentrations of MgO in the solutions analyzed are 0.5 ppm higher. Absorbance readings obtained in the range 0.01 ppm to 0.1 ppm MgO using duplicate solutions did not agree with each other and did not obey Beer's law.

The concentration of some of the common rock-forming elements, such as iron and manganese, in silicate minerals is often much greater than that in silicate rocks. To make certain that the recommended procedure would be applicable to most of the silicate minerals likely to be encountered, the author investigated the effect of the presence of the common rock-forming elements: calcium, manganese, titanium, phosphorus, ferrous iron and ferric iron. Silicon and fluorine are removed during the preparation of the solution of the mineral and several times the amount of aluminum present is added during the determination of the magnesium. The upper limit of these "foreign" elements used in testing the procedure was in excess of that likely to be found in most silicate minerals. No attempt was made to determine the maximum amount that could be tolerated. The effect of these constituents was determined at three concentrations: 0.5 ppm (50 micrograms per 100 ml), 1.0 ppm (100 micrograms per 100 ml) and 1.5 ppm (150 micrograms per 100 ml) MgO.

The effect of a "foreign" element was studied in the following manner. A series of solutions (8 to 12 in number) containing a constant amount of magnesium, *e.g.*, 50 micrograms of MgO, and varying amounts of the "foreign" element were made. Each series included duplicate solutions containing magnesium but no "foreign" element. The complete series of solutions was analyzed at one time by the recommended procedure and the precision of analysis of each series of determinations was measured by calculating the standard deviation from the mean of the absorbances. At all levels of magnesium concentration where there was no interference by the "foreign" element, the relative standard deviation, expressed as per cent was with two exceptions 3 per cent or less. The exceptions were at the 50 microgram MgO level when manganese was present. The per cent relative standard deviation was 4 and 5.

At the 0.5 ppm MgO (as MgSO_4) level, 5.0 ppm CaO (as CaCl_2), 3.0 ppm MnO (as MnCl_2), 3.3 ppm TiO_2 (as $\text{Ti}(\text{SO}_4)_2$), 0.48 ppm P_2O_6 (as KH_2PO_4), 4.0 ppm CaO plus 0.48 ppm P_2O_5 , 5.0 ppm Fe_2O_3 (as $\text{FeNH}_4(\text{SO}_4)_2$), and 5.0 ppm FeO (as $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$) do not interfere. At the 1.0 ppm MgO level 6.0 ppm CaO, 3.0 ppm MnO, 3.3 ppm TiO_2 , 0.48 ppm P_2O_5 , 4.0 ppm CaO plus 0.48 ppm P_2O_5 , 5.0 ppm Fe_2O_3 , 5.0 ppm FeO, and 0.3 ppm Pt (as H_2PtCl_6) do not interfere. At the 1.5 ppm MgO level, 6.0 ppm CaO, 1.0 ppm MnO, 3.3 ppm TiO_2 , 0.48 ppm P_2O_5 , 5.0 ppm

Fe_2O_3 , and 5.0 ppm FeO do not interfere. Manganese in the range 1.5 to 3.0 ppm MnO interferes giving an increase in absorbance readings beyond acceptable limits. However, standard magnesium solutions containing 0.5 to 1.5 ppm MgO and 2.4 ppm MnO obey Beer's law. Calcium plus phosphorus in the amount as low as 2 ppm CaO plus 0.12 ppm P_2O_5 interfere by forming cloudy solutions. Platinum was tested at the 1.0 ppm MgO level to make certain that any platinum which might dissolve during the decomposition and solution of the mineral would not interfere in the determination.

These observations can be expressed in another way. If the aliquot of solution analyzed for MgO is equivalent to one milligram of sample then 5% MgO can be determined in silicate minerals containing concentrations as great as 50% CaO, 30% MnO, 33% TiO_2 , 4.8% P_2O_5 , 40% CaO plus 4.8% P_2O_5 , 50% Fe_2O_3 , and 50% FeO; 10% MgO can be determined when they contain concentrations as great as 60% CaO, 30% MnO, 33% TiO_2 , 4.8% P_2O_5 , 40% CaO plus 4.8% P_2O_5 , 50% Fe_2O_3 , and 50% FeO; 15% MgO can be determined when they contain concentrations as great as 60% CaO, 10% MnO, 33% TiO_2 , 50% Fe_2O_3 , and 50% FeO. Table 1 presents the data obtained on the effect the "foreign" elements have on the determination and the data on the precision of analysis at the three concentration levels.

Frank Cuttitta, U. S. Geological Survey, determined the MgO content of standard rocks G-1 and W-1 using the recommended procedure and obtained the following results:

Rock	Per cent MgO Found	Per cent MgO Reported by Conventional Procedures
G-1	0.44	Arithmetic Mean=0.40; Adopted limits of acceptability=0.27-0.53; (Stevens and others, 1960, p. 31.)
W-1	6.57 6.52 6.45	Arithmetic Mean=6.58; Adopted limits of acceptability=6.23-6.93; (Stevens and others, 1960, p. 32.)

Table 2 presents values obtained by the recommended microprocedure for six minerals which had been analyzed completely by U. S. Geological Survey chemists; also included are MgO values for seven biotites not previously analyzed. The precision of duplicate determinations is about 3% of the amount present and values obtained by macroprocedures also fall within this range.

TABLE 1. PRECISION OF COLOR DEVELOPMENT IN THE DETERMINATION OF MgO IN THE ABSENCE AND PRESENCE OF FOREIGN SUBSTANCES

Foreign Substance	Micrograms of Foreign Substance	Mean of Absorbance Readings ¹	Standard Deviation of Absorbance	Relative Standard Deviation, %
50 Micrograms (0.5 ppm) MgO ²				
None	None	0.237	0.007	3
CaO	0, 100, 200, 300, 400, and 500	0.236	0.005	2
MnO	0, 40, 60, 80, and 100	0.234	0.009	4
MnO	0, 150, 200, 250, and 300	0.235	0.011	5
TiO ₂	0, 110, 220, and 330	0.244	0.006	2
P ₂ O ₅	0, 12, 24, 36, and 48	0.235	0.005	2
{ CaO+ P ₂ O ₅ }	0, 200, 200, 200, and 200	0.239	0.005	2
{ P ₂ O ₅ CaO+ }	0, 12, 24, 36, and 48			
{ CaO+ P ₂ O ₅ }	0, 400, 400, 400, and 400	0.238	0.003	1
{ P ₂ O ₅ Fe ₂ O ₃ }	0, 12, 24, 36, and 48			
Fe ₂ O ₃	0, 200, 300, 400, and 500	0.243	0.003	1
FeO	0, 200, 300, 400, and 500	0.251	0.006	2
100 Micrograms (1.0 ppm) MgO ²				
None	None	0.494	0.008	2
CaO	0, 200, 400, and 600	0.475	0.005	1
MnO	0, 40, 60, 80, and 100	0.479	0.007	1
MnO	0, 150, 200, 250, and 300	0.505	0.008	2
TiO ₂	0, 110, 220, and 330	0.495	0.007	1
P ₂ O ₅	0, 12, 24, 36, and 48	0.461	0.009	2
{ CaO+ P ₂ O ₅ }	0, 200, 200, 200, and 200	0.481	0.011	2
{ P ₂ O ₅ CaO+ }	0, 12, 24, 36, and 48			
{ CaO+ P ₂ O ₅ }	0, 400, 400, 400, and 400	0.455	0.009	2
{ P ₂ O ₅ Fe ₂ O ₃ }	0, 12, 24, 36, and 48			
Fe ₂ O ₃	0, 200, 300, 400, and 500	0.499	0.004	1
FeO	0, 200, 300, 400, and 500	0.502	0.009	2
Pt	0, 10, 20, and 30	0.489	0.005	1
150 Micrograms (1.5 ppm) MgO ²				
None	None	0.736	0.008	1
CaO	0, 200, 400, and 600	0.684	0.008	1
MnO	0, 40, 60, 80, and 100	0.685	0.015	2
MnO	0, 150, 200, 250, and 300	— ³		

¹ Duplicate solutions at each level of foreign substance were analyzed and the total number of solutions analyzed in each set varied from 8 to 12.

² The volume of solution in which the color was developed was 100 ml. The light path was 5 cm. A "spike" of approximately 50 micrograms of MgO was present.

³ Manganese increased absorbance beyond acceptable limits. See text for additional comment.

TABLE I—(continued)

Foreign Substance	Micrograms of Foreign Substance	Mean of Absorbance Readings ¹	Standard Deviation of Absorbance	Relative Standard Deviation, %
TiO ₂	0, 110, 220, and 330	0.722	0.012	2
P ₂ O ₅	0, 12, 24, 36, and 48	0.692	0.016	2
{ CaO+ P ₂ O ₅ }	0, 600, 600, 600, and 600	— ⁴		
{ CaO+ P ₂ O ₅ }	0, 12, 24, 36, and 48			
{ CaO+ P ₂ O ₅ }	0, 400, 400, 400, and 400	— ⁴		
{ CaO+ P ₂ O ₅ }	0, 12, 24, 36, and 48			
{ CaO+ P ₂ O ₅ }	0, 200, 200, 200, and 200	— ⁴		
{ CaO+ P ₂ O ₅ }	0, 12, 24, 36, and 48			
Fe ₂ O ₃	0, 200, 300, 400, and 500	0.726	0.009	1
FeO	0, 200, 300, 400, and 500	0.722	0.008	1

⁴ Solution was cloudy.

TABLE 2. MgO CONTENT OF VARIOUS SILICATE MINERALS—COMPARISON OF RESULTS OBTAINED BY MICRODETERMINATION AND MACRODETERMINATION

Sample	Mineral	Microdetermination		Macrode- termina- tion	Macrode- termina- tion	Macrode- termina- tion
		Spectrophotometric		Per cent MgO pyro- phosphate gravi- metric	Per cent MgO EDTA titration	Percent MgO x-ray fluores- cence spectrom- etry
		Sample Size mg.	Per cent MgO ¹			
158422	Biotite	19.63, 20.87	11.0, 11.2		11.4	11.5
158933	Biotite	19.77, 17.36	18.3, 17.8		17.9	18.4
158936	Hypersthene	19.98, 18.25	25.8, 25.4		25.6	25.2
158937	Sapphirine	18.17, 20.10	17.4, 17.6		17.8	18.2
I 4052	Pyroxene	21.50, 17.37	9.1, 9.1	9.4		
I 4056	Amphibole	21.29, 18.41	11.4, 11.4	11.9		
159901	Biotite	9.60, 9.57	14.2, 14.4			
159902	Biotite	10.16, 10.22	11.7, 11.9			
159903	Biotite	10.60, 10.66	11.4, 11.3			
159904	Biotite	9.05, 8.77	11.6, 11.5			
159905	Biotite	8.52, 10.64	12.4, 12.5			
159906	Biotite	8.96, 10.39	16.0, 16.4			
159907	Biotite	10.41, 8.38	9.9, 9.9			

¹ Duplicate samples.

DISCUSSION

Slightly different absorbance readings are obtained at different times for the same amount of magnesium at all levels (Table 1). Therefore, it is necessary to analyze standard MgO solutions at the same time the unknown solutions are analyzed. The level of MgO both in standard and unknown solutions should be approximately the same.

The precision is highest at the 1.0 ppm and 1.5 ppm levels. The aliquot of solution taken for analysis should be approximately 100 to 150 micrograms MgO. It should not be much above 150 micrograms. The reliability at all levels will be increased by analyzing 2 samples of each mineral and running replicate aliquots of each solution when sufficient sample is available.

Normally the aliquot of solution taken for analysis will be equivalent to one milligram of sample. If the concentration of MgO is less than 5%, an aliquot of solution equivalent to two milligrams of sample of the silicate minerals most likely to be encountered can be taken without exceeding the maximum amount of "foreign" elements permitted according to Table 1. Very often the composition of the silicate mineral will be such that an aliquot of solution equivalent to more than two milligrams of sample can be taken for analysis. By developing the color in a volume of 50 ml rather than the normal 100 ml, one-half the equivalent sample size can be taken or by keeping the sample size the same a mineral having one-half the concentration of MgO can be analyzed. The mean absorbance of 0.2 ppm (20 micrograms per 100 ml) MgO using the recommended procedure is 0.092, the standard deviation is 0.004, and the per cent relative standard deviation is 4%. It is therefore feasible to determine directly MgO as low as 0.5% on sample sizes as little as two milligrams with acceptable reliability. Where the composition of the mineral permits, concentrations lower than 0.5% can be determined by taking aliquots of solution equivalent to more than two milligrams of sample.

Magnesium in high manganese silicate minerals can be directly determined by this spectrophotometric procedure but cannot be determined directly by the EDTA-Eriochrome Black T procedure (Shapiro and Brannock, 1962, p. 35). A possible application of this spectrophotometric procedure is the direct determination of magnesium in small samples of ilmenite and magnetite.

REAGENTS AND EQUIPMENT

Sulfuric acid, 18 *N*: 500 ml of solution contains 250 ml concentrated H₂SO₄, ACS Reagent.

Sulfuric acid, 9 *N*: 500 ml of solution contains 250 ml of 18 *N* H₂SO₄.

Acid blank solution, approximately 1.2 *N* H₂SO₄: 100 ml contains 13 ml 9 *N* H₂SO₄.

Concentrated HF, ACS Reagent.

Standard MgO solution: Dissolve 6.1g MgSO₄·7H₂O, ACS Reagent, in water and dilute to 1 liter in a volumetric flask. This solution should contain 1 mg MgO per ml and is standardized gravimetrically by a standard pyrophosphate or 8-hydroxyquinolate procedure.

Working standard MgO solution: Concentration = 20 μg MgO per ml. Dilute 10.00 ml of standard MgO solution, 1 mg MgO/ml, to 500 ml.

Complexing solution: Dissolve 16 g KCN in 100 ml of water, add 100 ml triethanolamine (2,2',2''-nitrilotriethanol), and mix, dilute to 250 ml with water and mix well.

NaOH solution, 30 per cent: Dissolve 60 g of NaOH pellets, ACS Reagent, in approximately 50 ml of water in a 250 ml plastic beaker. Dilute to slightly less than 200 ml. Cool and transfer to a plastic bottle and dilute to 200 ml.

Clayton Yellow stock solution, 0.02 per cent: Dissolve 100 mg of dye [Fisher Scientific Co., Clayton Yellow (Indicator) Color Index No. 813, Catalog No. C-357] in 100 ml water. Filter using a fine filter paper and dilute to 500 ml.

Clayton Yellow reagent solution: Add 1 ml of standard MgO solution (1 mg MgO/ml) to 100 ml of Clayton Yellow stock solution and mix. Prepare fresh solution just prior to use.

Mixed reagent solution: Add 100 mg of polyvinyl alcohol to 150 ml of water in a 600 ml beaker. Place on hot-plate and heat gently with constant stirring until the temperature of the solution is 60° C. Heat at 60–70° C. with constant stirring until solution is clear. Add 300 ml of H₂O and mix. Add 5 ml 9 *N* H₂SO₄ and mix. Add 750 mg Al(NO₃)₃·9H₂O, ACS Reagent, and mix. Add 20 g hydroxylamine hydrochloride and mix. Cool. Dilute to 500 ml and filter using a fine filter paper.

Dish, evaporating, platinum, 15 ml.

Stirring rod, Teflon, $\frac{1}{8}$ in. × 2–2 $\frac{3}{16}$ in.

Funnel, filter, plastic, 40 mm wide, 80 mm long, and 7 mm tip.

Spectrophotometer, Beckman, Model B.

Cells, absorption, 5 cm light path.

PREPARATION OF SAMPLE SOLUTION

Weigh by difference 20 mg of silicate mineral (–200 mesh) in a 15 ml platinum evaporating dish. Moisten the sample with a few drops of water. Add dropwise (using a plastic pipet) 1 ml concentrated HF. Mix using a small Teflon stirring rod. The Teflon stirring rod remains in the dish. Digest on a steam bath or in a hot air bath. Cool. Add 2.0 ml 18 *N*

H₂SO₄, mix, and continue digestion. Cool. Add 5 drops concentrated HF and evaporate to the first appearance of SO₃ fumes. (If the mineral contains large amounts of calcium and magnesium, it is necessary to fume longer to complete the decomposition of the fluorides.) Cool. Add 1 ml of water dropwise, mix, and evaporate most of the water. Place the evaporating dish in one-half of a petri dish which is sitting on a hot plate whose surface temperature is approximately 270° C. Evaporate to the first appearance of SO₃ fumes. Cool. Add 1 ml of water dropwise to the dish and mix. Rinse down the inside surface of the dish. Warm on steam bath or in hot air bath to insure complete solution of salts. Add 5 ml of water to the dish. Mix well and transfer (using a small plastic funnel) the solution to a 100 ml volumetric flask. Rinse with water and add to the main solution. Add 9 ml 9 *N* H₂SO₄ to the flask and mix well. Cool to room temperature and dilute to 100 ml. Transfer to a dry plastic bottle. The normality of this solution is approximately 1.2 *N* H₂SO₄. If the final dilution is 50 ml instead of 100 ml, add 2 ml 9 *N* H₂SO₄ to the flask instead of 9 ml 9 *N* H₂SO₄.

Other constituents such as total Fe₂O₃, Al₂O₃, TiO₂, CaO, K₂O, and Na₂O can be determined using portions of this 1.2 *N* H₂SO₄ solution.

PROCEDURE FOR THE DETERMINATION OF MgO

Transfer 5.0 ml of "acid blank" solution to a 100 ml volumetric flask. Transfer 3.00, 4.00, 5.00, 6.00, and 7.00 ml of "working standard" MgO solution to 100 ml volumetric flasks and wash the neck of the flask with water using a plastic wash bottle with a fine nozzle. Add to the flasks containing the standard magnesium solution 5.0 ml of "acid blank" solution. Transfer to duplicate 100 ml volumetric flasks 3.00 to 5.00 ml (containing no more than 150 micrograms MgO) of the approximately 1.2 *N* H₂SO₄ solution of the mineral. Wash the neck of the flask with water. Add to each of the flasks enough "acid blank" so that the volume of sample solution taken plus the added amount of "acid blank" is 5.0 ml. Wash the neck of each flask and mix. Add 5.0 ml of "mixed reagent" solution to each flask. Wash the neck of each flask with water and mix. Add 45 ml of water to each flask and mix. Add 2.0 ml "complexing" solution to each flask (a note of caution—cyanide). Wash the neck of each flask with water and mix. Add to the first of the flasks 5.00 ml (using a transfer pipet) of Clayton Yellow reagent solution. Mix, wash the neck of the flask with water and again mix. Immediately add 5.0 ml 30% NaOH swirling the contents of the flask, mix; wash the neck of the flask with water and again mix. After the NaOH has been added to the second of the series of flasks, the solutions in both flasks are diluted to mark and mixed. The dye and NaOH are added to the next two flasks of the series

and again the second set of two flasks are diluted to mark and mixed. This sequence is followed systematically. Allow the solutions to stand for at least 20 minutes. Determine the absorbance at 545 $m\mu$ relative to the reagent blank in a 5 cm absorption cell.

CALCULATIONS

Calculate, for each of the five standard MgO solutions, the factor "micrograms MgO/absorbance." Calculate the average of the five values and use this average factor in computing the per cent MgO according to the following formula.

$$\text{Per cent MgO} = \frac{\text{Absorbance} \times \text{factor} \times 100}{\text{Micrograms of sample in aliquot}}$$

Notes:

1. When a 10.00 ml aliquot of the 1.2 *N* H₂SO₄ solution of the mineral is used for the magnesium determination, add 5.0 ml 1.2 *N* NaOH to neutralize the 5.0 ml of excess acid. Add to the flasks containing the reference solution and the standard MgO solutions, 5.0 ml 1.2 *N* NaOH and 5.0 ml 1.2 *N* H₂SO₄.

2. When the volume in which the color is developed is 50 ml instead of 100 ml and the aliquot of 1.2 *N* H₂SO₄ solution of the mineral used is 5.00 ml, add 2.5 ml 1.2 *N* NaOH to neutralize one-half of the acid present and then add 2.5 ml "mixed reagent," 20 ml water, 1.0 ml "complexing" solution, 5.00 ml of half-strength Clayton Yellow reagent solution and 5.0 ml 15% NaOH. The flasks holding the reference solution and the standard MgO solutions contain 5.0 ml 1.2 *N* H₂SO₄ and 2.5 ml 1.2 *N* NaOH before the "mixed reagent" is added.

3. When a 10.00 ml aliquot of the 1.2 *N* H₂SO₄ solution of the mineral is used together with a final dilution of 50 ml, add 7.5 ml 1.2 *N* NaOH and then add 2.5 ml "mixed reagent," 10 ml water, 1.0 ml "complexing" solution, 5.00 ml of half-strength Clayton Yellow reagent and 5.0 ml 15% NaOH. The flasks holding the reference solution and the standard MgO solutions contain 10.0 ml 1.2 *N* H₂SO₄ and 7.5 ml 1.2 *N* NaOH before the "mixed reagent" is added.

REFERENCES

- SANDELL, E. B. (1959) *Colorimetric Determination of Traces of Metals*, 3rd ed., Interscience Publishers, Inc., New York.
- SHAPIRO, LEONARD (1959) Rapid photometric determination of low level magnesium in rocks. *Chemist-Analyst*, **48**, 73-4.
- AND W. W. BRANNOCK (1962) Rapid analysis of silicate, carbonate and phosphate rocks. *U. S. Geol. Survey Bull.* **1144-A**.
- STEVENS, R. E. AND OTHERS (1960) Second report on a cooperative investigation of the composition of two silicate rocks. *U. S. Geol. Survey Bull.* **1113**.

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