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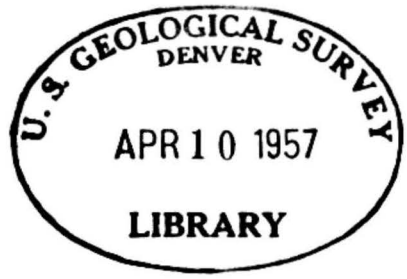

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A FIELD METHOD FOR THE DETERMINATION OF CALCIUM AND MAGNESIUM IN LIMESTONE AND DOLOMITE

by

Leonard Shapiro and W. W. Brannock

The method is an adaptation of a procedure described by Betz and Noll[1/] in 1950. Calcium and magnesium are determined by visual titration using Versene (disodium ethylenediamine tetraacetate) with Murexide (ammonium purpurate) as the indicator for calcium and Eriochrome Black T as the indicator for magnesium.

The analyses need not be made in a chemical laboratory. They can be made wherever a suitable table space and facilities for heating flasks and beakers are available. An electric, gas, or even a gasoline hotplate can be used.

After the technician has made enough practice determinations to become familiar with the method, he can obtain values for CaO and MgO which will deviate only occasionally by more than 1 percentage point, and he will be able to detect magnesium in a limestone containing as little as 0.3 percent MgO.

If it is necessary or desirable to change locations from time to time and make determinations at different sites, the apparatus and reagents can be arranged in a kit for convenient transport and handling.

1/ Betz, J. B., and Noll, C. A., 1950, Total-hardness determination by direct colorimetric titration: Am. Water Works Assoc. Jour., v. 42, p. 437-440.

Samples should be analyzed in batches of 4 to 8 samples to make the best use of time. After an operator has run a sufficient number of analyses to become very familiar with the method, it should require about two hours, exclusive of preparation of reagents and grinding of samples, for the completion of the calcium and magnesium determinations on eight samples.

The method calls for the use of a 20-ml pipet which has been coated with silicone water repellent. This technique eliminates the necessity for rinsing the pipet between aliquots and makes it practicable to increase the flow time of the pipet from about one minute to about ten seconds without significant loss of accuracy.

APPARATUS

10 150-ml beakers

10 Watch glasses for covering 150-ml beakers

10 250-ml erlenmeyer flasks

10 100-ml volumetric flasks, pyrex, Kohlrausch type

1 50-ml graduate

2 10-ml graduates

1 50-ml buret

1 Buret support

1 Water repellent, silicone type, for coating 20-ml pipets, 2 oz.

2 20-ml transfer pipets. Remove portions of the tips with a file or coarse emery paper until the flow rates are about 10 seconds. Apply a coating of water repellent to the inside of the pipets as directed in the instructions supplied by the manufacturer of the repellent. The repellent coating should be renewed from time to time as it becomes ineffective.

2 2-ml serological pipets

1 50-ml polyethylene dropping bottle

1 1000-ml volumetric flask

1 Roll of pH indicator paper, type suitable for indicating pH 7

1 Balance, portable type, suitable for weighing 500 mg $\pm$ 3 mg

1 Hot plate, electric, gas, or gasoline, with a heating surface at least 6 inches square.

1 Beaker tongs

1 Spatula

1 Beaker brush

1 Mortar, Plattner, diamond

1 Mortar and pestle, procelain

2 100-ml polyethylene bottles

3 500-ml polyethylene bottles

6 1000-ml polyethylene bottles

1 Demineralizer for preparation of demineralized water if distilled water is not available.

1 1000-ml stainless-steel beaker or other stainless-steel container of at least 1 quart capacity.

REAGENTS

HCl 1+1, 500 ml. Store in a polyethylene bottle.

NH_4OH 1+1, 500 ml. Store in a polyethylene bottle.

NaOH solution, 20 percent, 1 liter. Make up in a stainless steel container, and when cool, store in a polyethylene bottle.

Buffer solution, 66 g NH_4Cl in a liter of 1+1 NH_4OH. Store in a polyethylene bottle.

Sodium tungstate solution, 20 percent, 500 ml. Store in a polyethylene bottle.

Murexide (ammonium purpurate), powder, at least 1 g.

Murexide solution (indicator for calcium). About 25 mg of powder dissolved in 50 ml of demineralized water. Prepare fresh solution each day.

Eriochrome Black T, powder, at least 1 g.

Eriochrome Black T solution (indicator for magnesium). About 50 mg of the powder dissolved in 100 ml of demineralized water. Do not store the solution more than a few days.

National Bureau of Standards standard sample No. 88, (dolomite). The standard contains 30.5 percent CaO and 21.5 percent MgO.

Standard Versene solution: Weigh 18.00 g of Versene (disodium ethylenediamine tetraacetate) and make up 2 liters of solution with demineralized water. Standardize the solution by running several portions of National Bureau of Standards standard sample No. 88 (dolomite) through the procedure described below.

Obtain the factor for CaO:

$$\frac{30.5}{\text{average of titration volumes for No. 88}} = \text{factor}$$

Obtain the factor for MgO:

$$\frac{21.5}{\text{average of titration volumes for No. 88}} = \text{factor}$$

PROCEDURE

1. Crush a selected chip of each sample to a coarse powder with a Plattner mortar.
2. Reduce 2 or 3 grams of each sample to a fine powder by grinding a portion of the well mixed coarse powder in a porcelain mortar.
3. Weigh 500 mg $\pm$ 3 mg of each of the ground samples and transfer to 100-ml volumetric flasks.
4. Add 5 ml of HCl 1+1 to each flask, cover with watch glasses and heat on a hot plate until the reactions subside, and then boil an additional 1/2 minute.
5. Remove the flasks from the hot plate, to each add about 70 ml of water, a small piece of indicator paper, and NH_4OH 1+1 dropwise until the color of the paper shows the solution to be slightly alkaline.
6. Add water to the 100-ml mark on the flasks and mix.
7. Allow the flasks to stand for at least 5 minutes so that any iron and aluminum hydroxides formed can settle out.
8. Transfer 20 ml of the solution from the top portion of each volumetric flask to a 150-ml beaker, with a pipet. Blow out the last drop of solution from the pipet and do not rinse between aliquots. Ignore small amounts of precipitate which may be carried along. These aliquots will be used for the determination of magnesium.

9. Add about 50 ml of water, 10 ml of buffer solution, and 2 ml of sodium tungstate solution to each beaker. Bring them to a boil on the hot-plate and boil for 1-2 minutes to bring about precipitation of calcium tungstate.
10. Remove the beakers from the hot plate and allow the precipitates to settle. While waiting for the precipitates to settle proceed with the determination of calcium (steps 11-14).
11. Withdraw an additional 20-ml aliquot from the upper portion of each volumetric flask and transfer to 150-ml erlenmeyer flasks. Blow out the last bit of solution for each aliquot and do not rinse between aliquots.
12. Add about 50 ml of demineralized water, 2 ml of NaOH solution and 2 ml of Murexide indicator solution to one of the solutions.
13. Fill the buret with standard Versene solution, adjust to zero and record the reading. Titrate rapidly until the color of the solution shows a pronounced change from red to reddish purple. Then add three-drop increments of Versene until a deep purple color results which does not change with the addition of a three-drop increment of Versene. Record the final buret reading.
14. Repeat steps 12 and 13 for each sample solution in the batch.
15. Carefully decant the liquid (from step 10) into a 250-ml erlenmeyer flask, retaining as much as possible of the precipitate in the beaker. Do not rinse the beaker, yet at the same time transfer all of the liquid to the flask which will flow out of the beaker. Ignore any of the precipitate which is transferred.

16. Add 5 ml of the buffer solution and 2 ml of the indicator solution to the flask.

17. Fill the buret with standard Versene solution, adjust to zero and record the reading. Titrate rapidly until the color of the solution shows a pronounced change from red to purple. Then add three-drop increments of Versene until the color of the solution becomes clear blue and shows no further change upon addition of Versene. Record the final buret reading.

18. Repeat steps 15-17 for each sample solution in the batch.

19. To obtain percent CaO multiply the volume of Versene used in the calcium titration by the CaO factor: volume Versene x CaO factor = percent CaO.

20. To obtain percent MgO multiply the volume of Versene used in the magnesium titration by the MgO factor: volume Versene x MgO factor = percent MgO.