

maize in Matagorda County (p. 124). Mr. Gilbert was not listed in the 1850 census. Later, he moved to San Antonio, where he is probably buried.

GILBERT, Samuel Augustus (1825-68) Born in Zanesville, Ohio; educated as a civil engineer, Mr. Gilbert worked with the U.S. Coast Survey on the triangulation and topography of the Texas Coast from 1855 to 1860, and again in 1867. He died in St. Paul, Minnesota. On the outbreak of the Civil War he became a major of engineers on the staff of General John Q. Foster, U.S.V.; subsequently he commanded a brigade in Kentucky; and in 1865 was brevetted brigadier-general of volunteers. (See *ACAB*, 6, 1889, 682.)

GILBERT, Wyllis S. (d. 1862) In 1860 and 1861 Mr. Gilbert surveyed the topography of the Texas coast for the U.S. Coast Survey. (*U.S. Coast Survey Rept.*, 1860, 92; 1861, 64/5.)

(To be continued)

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A Rapid Volumetric Analysis for Carbonate in Rocks

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ABSTRACT

Rapid, accurate analyses for the CO₂ content of carbonate rocks may be made by allowing a known amount of the rock to react with a measured quantity of standard H₂SO₄ and then determining the amount of acid which remains by back-titration with standard NaOH. The technique is faster and more accurate than the leaching method and, more important, allows the analyst to determine directly the CO₂ content. Very accurate analyses for CO₂ in limestones may be made by potentiometric titration methods, but quite satisfactory results are obtained using phenolphthalein as an indicator.

As is the case with igneous rocks, the classification of carbonate rocks may be based on modal composition as determined by studies of thin-sections or it may be based on chemical composition. The exact mineralogical composition of a rock cannot be determined from a chemical analysis. The weight percent CO₂ is a more meaningful index for the chemical classification of limestones than the percent carbonate mineral or the percent insoluble residue.

Introduction

The most generally-used basis for the classification of impure carbonate rocks is the weight percentage of carbonate minerals in the rock (Pettijohn, 1949, p. 291). This ratio is usually determined by the "leaching method" in which the dried and weighed sample is allowed to react completely with dilute HCl. The sample is then washed free of all soluble compounds, dried, and the residue weighed (Ireland, 1950, p. 1942). As an analytical technique the leaching method has several disadvantages. Errors are large, particularly when the analysis is done by students or semi-skilled assistants. The method is messy and time-consuming. Relatively large quantities of material are needed to gain accuracy. Iron oxides are converted to soluble chlorides and flushed out, thus introducing sizable errors in the analysis of many limestones.

A fast, neat, and accurate method of carbonate analysis is needed. The carbon dioxide-capture method used for high precision analyses (see Hillebrand, 1919, p. 217) is the most accurate technique in use; it is, however, slow and rather difficult, and requires specialized equipment.

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The method described in the present report is nearly as accurate as the gas-capture method, is faster and more accurate than the leaching method, and requires little special equipment.

Description of Technique

The titration method of carbonate analysis is not a new technique, but is seldom used by geologists, although it is faster and more accurate than the more troublesome leaching method. The sample preparation is similar in both methods; however, a simple back-titration gives the correct answer in only a matter of minutes; whereas the leaching method requires several hours before a final measurement can be made.

Standardization techniques.—Standard solutions of both sulfuric acid and sodium hydroxide are required with normalities of 0.40 and 0.45, respectively. It would be wise for the geologist to prepare these two standard solutions in five-gallon carboys. In order to simplify the discussion of the preparation of normal solutions, the unit of weight will be the gram and the unit of volume will be the liter.¹ A solution of approximately 0.40 normality is made by cautiously adding 12 ml. of pure, concentrated H_2SO_4 (d. = 1.84) to 500 ml. of distilled water. Mix thoroughly and then dilute to 1 liter, and mix again. If the standard solution is prepared in a five-gallon carboy, the carboy should be approximately half full before adding 228 ml. of H_2SO_4 . Again mix thoroughly and then fill the five-gallon carboy with distilled water. A solution of approximately 0.45 normality is made by dissolving 19 grams of NaOH in 500 ml. of water and diluting to 1 liter. Using a five-gallon carboy, 361 grams of NaOH would be dissolved in 2.5 gallons of distilled water. This solution should be mixed thoroughly and the carboy should be completely filled with distilled water, and mixed again. The acid is relatively stable and need not be checked against a newly-standardized base more than once a year. However, the basic solution reacts slowly with glass and is affected by CO_2 so that it should be checked once a month. To protect the base from contamination by CO_2 from the atmosphere, a trap containing NaOH or Ascarite should be employed and the solution should be covered at all times. It is imperative that the solutions be standardized to the same pH used in the runs. If a potentiometric method is used, the solutions should be standardized to a pH of 7; however, if phenolphthalein is used as an indicator, the solution must be standardized to the phenolphthalein end point (pK 8.8).

Standardization-runs for both the acid and the base should be in triplicate. The NaOH solution is standardized in the following manner: weigh out about 0.8 grams of potassium acid phthalate and record the

¹Approximately 19 liters are equal to 5 gallons; therefore, the weights of the reagents discussed will be increased by a factor of 19 in order to get the desired normality.

weight to the nearest milligram. Place the acid in a beaker with 150 ml. of distilled water. Add 3 or 4 drops of phenolphthalein (0.1% in ethyl alcohol) and titrate with NaOH to a pink color. If the potentiometric procedure is used, merely titrate to pH 7. The normality is found by use of the following equation:

$$^N\text{NaOH} = \frac{\text{wt. KH phthalate}}{.2042 \times \text{ml. NaOH}}$$

In order to standardize the H_2SO_4 , pipette 25.00 ml. of the acid into a beaker containing about 100 ml. of distilled H_2O . Add 3 to 4 drops of phenolphthalein and titrate with standardized NaOH to a pink color or titrate to pH 7 using the potentiometric method. The following equation is used to calculate the normality of the acid:

$$^{m1}\text{H}_2\text{SO}_4 \times ^N\text{H}_2\text{SO}_4 = ^{m1}\text{NaOH} \times ^N\text{NaOH}$$

Analytical procedure.—Grind the sample until it will pass through a 200-mesh Tyler sieve. Mix the sample well before splitting off about 10 grams. Dry the sample for 4 hours at about 105°C . and weigh out exactly 1 gram for the analysis. To the 1 gram sample, pipette 50 ml. of standard H_2SO_4 then heat to about 90°C . for 20 minutes. At this point indicator paper should be used to check the pH. If the pH is more than 2, add with a pipette 25 ml. more H_2SO_4 and heat to about 90°C . for 10 minutes. This procedure is much the same as the leaching method up to this point; however, the amount of CO_2 in the sample using this method is determined by a back-titration which can be done in a few minutes in the following way. Add distilled water until the beaker is half full. Add 3 to 4 drops of phenolphthalein if no potentiometric equipment is available. It is very important that a glass bead rather than a stop-clock burette be used since there is a deleterious action between NaOH and stop-cock grease. Back-titrate with NaOH using a 50 ml. burette. Stir constantly, preferably with a magnetic stirrer, while back-titrating to pH 7 or the phenolphthalein end point. The amount of NaOH used in the titration is determined by the difference in the readings on the burette before and after the titration.

Computation.—The computation procedure is as follows: (1) Multiply the number of ml. of H_2SO_4 used by the normality of the H_2SO_4 solution. (2) Multiply the number of ml. of NaOH used by the normality of the NaOH. (3) Subtract 2 from 1.

The resulting figure is the number of milli-equivalents of H_2SO_4 which reacted with 1 gram of sample and is equal to the number of milli-equivalents of CO_2 which reacted with the acid. The percentage of the compound in 1 gram of sample reacting with the acid is obtained by multiplying (3) times the milli-equivalent weight of the compound

times 100. Milli-equivalent weights for the most common carbonate compounds are as follows:

CaCO ₃	.0500
CaMg(CO ₃) ₂	.0471
CO ₃	.0300
CO ₂	.0220

It is possible to solve for CO₂ or CO₃ in any carbonate rock; however, a decision as to the nature of the proper cation is needed before the amount of carbonate mineral can be determined. This will be discussed in a later section.

Discussion of Analyses

Analyses of the CO₂ content were made on samples obtained from the Bureau of Standards and on samples of the Austin limestone of north Texas. The latter were also analysed by the leaching method. The analyses were run quickly, but carefully, according to the technique described in the preceding section, in an attempt to approximate the accuracy attainable in routine laboratory procedures.

The first sample was Bureau of Standards number 1a, argillaceous limestone (76.1% CaCO₃ by weight). The mean of eight analyses using the titration method was $32.19 \pm 0.20\%$ CO₂. The mean of eight analyses by a second analyst using different standard solutions was $32.94 \pm 0.10\%$ CO₂. Both of the above sets of analyses used phenolphthalein (pK 8.8) as an indicator. The mean of three analyses in which the end point (pH 7.0) was indicated with a Beckman Zeromatic pH meter was $33.46 \pm 0.03\%$. According to the Bureau of Standards, the mean of five analyses using the gas-capture method was $33.53 \pm 0.05\%$ of CO₂. For this sample the results are statistically similar for the gas-capture method and the titration method using a pH meter. The low values of CO₂ content obtained by use of phenolphthalein indicator probably resulted from the inability of the analyst to see the color change at the end point in the dark mixture of clay, calcium sulphate, and water, as well as from the fact that more accurate determinations of CO₂ content may be made if the end point of the titration is pH 7.0.

Bureau of Standards number 88, dolomite, was analysed by the titration method using phenolphthalein. The mean of 8 analyses was $46.60 \pm 0.04\%$ CO₃. Two analyses using potentiometric titration gave a mean of 46.86% CO₂. The Bureau of Standards reports a value of 47.25% CO₂, from one analysis. The values obtained by titration may be low because of incomplete reaction of CaMg(CO₃)₂ with H₂SO₄.

Another series of analyses on Bureau of Standards samples 1a and 88 indicate that the most accurate results are obtained by titrating to pH of 7.0; however, as the pH is very sensitive to changes in the hydrogen

ion concentration in a near-neutral solution, the error incurred by titrating to a pH of 8 or 9 is relatively small.

Analyses of marls and limestones in which the percent of residue insoluble in HCl had been carefully determined show differences of 4% to 6% in the CaCO_3 content determined by the two methods. In each case the carbonate content as determined by the leach method was the higher of the two. As there is no reason to think that the titration method would show an error in excess of one percent, it was concluded that the leaching method is subject to errors as high as 5% of CaCO_3 .

It is to be expected that the results obtained for a carbonate determination by the hydrochloric acid leach method would be significantly higher than those obtained by the method proposed in this paper. This is so because of the multitude of components that could be put into solution by hydrochloric acid. Most probable among these are oxides of iron, aluminum, manganese, titanium, and silicon. In fact, hydrochloric acid is usually recommended for the preliminary decomposition of carbonate and silicate rocks (Hillebrand and others, 1953, pp. 857 and 964).

By the titration method proposed in this paper, the only components that will contribute to the results are those that will react with dilute sulfuric acid and form an equivalent amount of volatile or insoluble products. Except for carbonates, sulfides are the only compounds that may be expected to occur and react in this fashion. The error caused by the oxides of transition metals that are almost always present in rocks would not be appreciable because by back-titrating to a pH of 7.0 or greater the sulfates formed would be precipitated by an equivalent amount of sodium hydroxide.

Carbonate Analyses and Limestone Classification

Techniques of chemical analysis are intended to give weight-percentages of certain compounds, *e.g.*, gases of simple composition, water, and oxides of metals. A chemical analysis of an igneous rock, for example, is commonly stated in terms of oxides and does not give the weight percent of the various minerals present. In the analysis of carbonate rocks the weight percent of CO_2 is determined, and because CO_2 normally occurs in the carbonate radical, the weight percent CO_3 can be computed accurately. In order to compute the weight percent of carbonate minerals in the rock, it is necessary to know what minerals are present. In calcite, CO_3 accounts for 59.60% of the weight of the mineral, but in dolomite, CO_3 makes up 63.69% of the mineral. Magnesite is 71.16% CO_3 . Let us assume that a certain rock is 85% by weight carbonate mineral. If the mineral is calcite, then CO_3 makes up 51%

of the rock; but if the carbonate is all dolomite, then CO_3 constitutes 55% of the rock by weight.

In the analysis of carbonate rocks the density of the non-carbonate minerals will affect the percent of carbonate by weight. A limestone determined by thin-section analysis to be 60% calcite by volume is about 73% calcite by weight if the non-carbonate is clay (sp. gr. = 1.5) and is about 62% calcite by weight if the non-carbonate is chert (sp. gr. = 2.5). Neither analyses for the percent insoluble residue, nor analyses for the percent CO_3 , can give values of percent carbonate which will correspond to estimates from studies of thin-sections. The classification of carbonate rocks must be based either on the chemical composition expressed in weight percent carbonate radical or on the modal or volume ratios of minerals present as is determined from thin-sections.

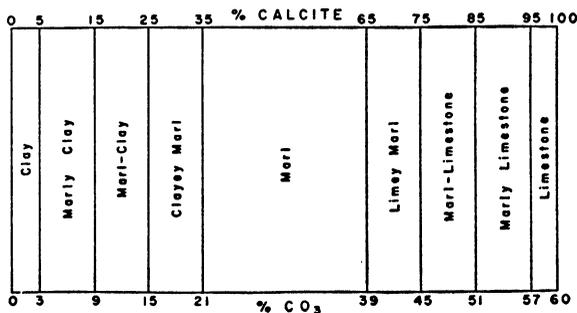


FIG. 1. Classification of clay-lime carbonate mixtures. (After Barth, Correns, & Eskola in Pettijohn, 1949, p. 291).

To prevent confusion in the interpretation of carbonate analyses we suggest that analyses be reported as percent carbonate radical (CO_3) rather than as percent insoluble residue and that chemical classifications of limestones be based on this ratio. In order to describe quantitatively the mineralogy of carbonate rocks, a complete analysis must be made and a normative composition must be computed as is done in studies of igneous rocks (see Barth, 1952, pp. 74-85).

In some limestones, tests for magnesium may indicate that all of the carbonate mineral is calcite. In such a case the following modification of Barth's, Correns' and Eskola's (in Pettijohn, 1949, p. 291) limestone classification chart may be used to name the rocks in terms of the percent CO_3 by weight.

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