NOTES

ON THE ROUTINE ANALYSIS OF CARBONATES IN UNCONSOLIDATED SEDIMENTS

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ABSTRACT

An inexpensive instrument built largely from standard laboratory items serves for rapid gasometric determination of carbonate content in sediments. Results obtained with reagent grade powder samples are in close agreement with theoretical values. Error estimations are given for variations of temperature, pressure, and sample weight.

INTRODUCTION

Most surveys of modern marine sediments include measurements of the carbonate contents. Several methods give accurate results, but for routine analyses speed and ease of operation are important. For these reasons Bien (1952) proposed a gasometric technique after evaluating several others. Subsequently, other authors have elaborated on the volumetric analysis of carbonates, for example Shapiro and Brannock (1962). This note describes a modification of Bien's device and method as developed at the University of Southern California in Los Angeles and Woods Hole Oceanographic Institution. The method is characterized by simple implementation, great economy, and ease of handling.

APPARATUS

The apparatus consists of a gas generating and cooling part and of a manometer (fig. 1 and appendix). Most components are standard laboratory items: a 250 ml leveling bulb (A) filled with mercury connected by flexible tubing to a 100 ml gas buret (B), which is calibrated in 0.1 ml units and has a 3-way stopcock (B1) at the upper end, a Liebig condenser jacket (D) with threaded ends and heat-resistant nuts and washers, and several joints and tubing.

The following are not standard laboratory equipment but can easily be constructed from stock items: (1) A condenser tube (E) one end of which is connected to a joint with an O-ring seal (E1); this joint has to branch off to a ground joint with standard taper (E2). The length of these two joints should be kept as small as possible to minimize the volume of air within the apparatus; (2) several joints with O-ring seal (G), sealed at one end to make sample digestion tubes of about 10 cm length; (3) a few ground joints with standard taper (F), sealed and blown to make small bulbs with a capacity of about 5 ml to hold the acid reagent; the neck of these joints has to be bent 90°; the ground section may be cut obliquely to provide easier flow of the content during the analysis (drip tip).

PROCEDURE

Between 0.2 g and 1.0 g of powdered and dried sediment (higher values for carbonate-poor samples) is weighed into the sample digestion tube, and 5 ml of 2 N hydrochloric acid is poured into the acid bulb. Both vessels are attached to the system. The inside air pressure is brought to equilibrium with the outside air pressure by means of the 3-way stopcock, and the mercury in the manometer is set to a convenient zero mark near the top of the gas buret. With cooling water running through the condenser and the stopcock open to the digestion tube, the mercury in the leveling bulb is lowered about 0.2 ml below its level in the buret. This creates a slight vacuum in the gas generating system and provides a perfect seal for the acid bulb. By slowly turning the bulb, acid is added to the sample and carbon dioxide is generated.

Care should be taken that the mercury in the leveling bulb stays slightly below that in the buret at all times so that the gas pressure inside the system does not exceed the barometric pressure. If the gas pressure does exceed barometric pressure, the acid vessel inserted in the lower part of the condenser acts as a safety valve and may blow out.

Effervescence of the sample ceases after 1 to 2 minutes. The mixture is heated for 1 to 3 minutes to break down the less soluble carbonates and to drive off all the carbon dioxide. The end of the effervescence that results from the heating indicates that the reaction is complete. The digestion tube is then cooled by immersing it in a large beaker containing water at room temperature. As the system cools and the mercury rises in the buret, the leveling bulb is slowly raised.
Within 5 or 6 minutes the system comes to equilibrium, as shown by cessation of the rise of the mercury in the buret. A final adjustment is made with the mercury in the leveling bulb, and the volume gained in the buret is recorded as volume CO₂ observed. A zero point correction is made when applicable. Room temperature is recorded at the time of zero setting and of final reading, and the temperature of the cooling water and the barometric pressure are read and recorded once during the analysis. If desired, the acid-treated residue may be saved for further analysis, such as the determination of organic carbon in an induction furnace.

In routine analyses it is quite practical to set up more than one apparatus. Then the analyst can manipulate one instrument while another is approaching thermal equilibrium. In this fashion it is easy to complete as many as ten analyses per hour.

Calculation

The calculation of the content of carbonate ion is based on the Gas Laws (p·v = R·T), and on the assumption of the reaction:

$$\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$$

The formula for computing the amount of CO₂⁻ can conveniently be written:

$$\% \text{CO}_2^- = \frac{v \cdot (P - M)}{W \cdot (T + I)} \cdot 0.0961$$ (1)

where

- v = observed volume of CO₂ in ml,
- P = barometric pressure in mm Hg,
- M = vapor pressure of water in mm Hg, dependent on lowest temperature in system (this is usually the temperature of the cooling water) read from a table (such as Weast, 1964, p. D-92),
- W = weight of the sample in grams,
- T = room temperature in °C; in order to compensate for variations between the beginning and the end of the analysis the average of the two is entered, and
- I = 273.16 (constant for conversion to absolute temperature scale).

0.0961 is a constant resulting from the conversion of the barometric pressure to c.g.s. units (1 mm Hg = 1.332·10⁻⁴ dyn cm⁻²), the Gas Constant (R = 8.3144·10⁷ erg·degree C⁻¹·mol⁻¹), and the molecular weight of CO₂⁻ (60.01).

In marine sediments the carbonate ion is chiefly combined with that of calcium, because CaCO₃ constitutes more than 90 percent of the total carbonate in most environments (Chave, 1954). Other cations, such as magnesium or strontium may be present, but they produce little effect on the result if the total carbonate content is calculated as calcium carbonate according to the formula:

$$\% \text{CaCO}_3 = \frac{v \cdot (P - M)}{W \cdot (T + I)} \cdot 0.1603$$ (2)

The presentation of the analytical results of calcium carbonate content as weight percent of the dry sample is preferred whenever it appears more meaningful to the geologist to consider the rock or sediment-forming mineral component than the individual ions. However, where it seems desirable to determine the carbonate content separately for calcium, magnesium or other ions, the constant (0.1603) given in formula (2) would change depending on the molecular...
weight, for example 0.1352 for magnesium carbonate. Then the percentage amounts for carbonates are calculated according to the ratios of the corresponding cations found by other means.

If the amount of carbon contained in the measured calcium carbonate is desired, the result of formula (2) simply is multiplied by 0.120. This may serve as a value for "inorganic" carbon as opposed to the organic carbon contents found from combustion of the acid-treated residue of the original sample.

ACCURACY OF THE METHOD

The method was checked by using reagent grade calcium carbonate "Fisher Certified" A.C.S. The analyst was not informed about the problem and handled the samples in the same manner as the regular sediment samples. The results are shown in table 1. It is not suggested that these results are the best the method can produce; however, they represent a series which may serve as a value for "inorganic" carbon as opposed to the organic carbon contents found from combustion of the acid-treated residue of the original sample.

Chief potential sources of errors are (1) the moisture content of the sample; (2) incomplete digestion; and (3) temperature difference between the zero setting and the reading of the CO₂ volume. The first source of error results in inaccurate sample weight; this can be minimized by keeping the exposure to the air (weighing time) of the oven-dried and desiccator-cooled sample as brief as possible. Incomplete digestion, resulting in too low a volume of CO₂, is generally overcome by boiling the sample during acid digestion. The third source of error is closely related to the design of the apparatus. Because the air in the system expands and contracts with temperature changes, it can offset the observed volume gain, which, in the calculation, is assumed to be due only to the amount of carbon dioxide developed. The initial air volume of the apparatus is about 50 ml, and a temperature fluctuation of ±0.5°C causes a volume variation of ±0.09 ml. This approaches the accuracy with which the buret can be read. It also shows why the average room temperature should be used in the calculation, and why volume corrections are needed for large amounts of CO₂.

The initial volume of air and the resulting systematic error are proportional to the size of the system, and the total error is proportional to the volume of gas generated. For most studies of marine sediments it is adequate to report the calcium carbonate content to the nearest one-half of one percent.

Errors in the determination of the percentage of calcium carbonate, due to uncertainty in the variables used in the computation, are demonstrated for a test case in table 2. The assumed values are well within the range of actual data. Several tests were made to evaluate the suitability of different acids for the sample digestion. Hydrochloric and (ortho-) phosphoric acid in 1- and 2 N solutions gave results in close agreement with the theoretical value of the reagent grade powder (100 percent CaCO₃), whereas sulfuric acid of the same concentrations yielded low values (average 96 percent).

Tests with hydrochloric acid on reagent grade calcium carbonate cannot assess the influence of the acid on non-carbonate components of a field sample. Some of these components may interfere with the analysis by generating gas. If such an interference is suspected (as in the presence of iron sulfide) and if sample purification is not possible, one may have to resort to other less rapid methods.

APPENDIX

List of Parts Used in Apparatus for Volumetric Determination of Carbonates

Leveling bulb (A) with side tubulature; capacity 250 ml. (Letters A-G refer to fig. 1.)
Table 2.—Error estimate. Percent calcium carbonate as a function of barometric pressure, cooling water temperature, room temperature, and sample weight

<table>
<thead>
<tr>
<th>Variable</th>
<th>Reading</th>
<th>Range</th>
<th>Error in result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barometric pressure</td>
<td>760.0 mm Hg</td>
<td>±1.0 mm Hg</td>
<td>±0.15%</td>
</tr>
<tr>
<td>Cooling water temp.</td>
<td>15.0°C.</td>
<td>±1.0°C.</td>
<td>±0.12%</td>
</tr>
<tr>
<td>Room temperature</td>
<td>25.0°C.</td>
<td>±1.0°C.</td>
<td>±0.37%</td>
</tr>
<tr>
<td>Weight of sample</td>
<td>0.4000 g</td>
<td>±0.001 g</td>
<td>±0.28%</td>
</tr>
</tbody>
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Total error < ±1.00% if all partial errors in the same direction.

Calculated % CaCO₂ = 30.00

Leveling bulb support, self-locking, with fine adjustment.
Mercury, redistilled, about 2.2 kg.
Gas buret (B) 100 ml capacity, graduated in 0.1 ml subdivisions, 3-way stopcock (B₁) at the top.
Liebig condenser jacket (D) with threaded ends and plastic nuts and washers, 165 mm long, (similar to Kimble #18003).
Condenser tube (E) with blown on Joint with O-ring Seal (E₁), 15 mm i.d. (Kimble #33650) and Ground Joint (E₂) outer member, medium length, #14/20 (Kimble #33564).

Ground Joint (F) inner member, #14/20, with drip tip (Kimble #33562), serves as acid bulb; 3-6 are sufficient.
Joint with O-ring Seal (G), 15 mm i.d., 18 mm o.d., length made to about 10 cm (Kimble #33650), serves as sample digestion tube; two to four dozen.
O-rings to fit joints (Kimble #33652, size 116).
Clamps, same as for ball-and-socket joints, #28/15.
Barometer, thermometer, beaker and bucket for water at room temperature, Bunsen burner, flexible tubing, glass connections or reducer, stand and clamps.

REFERENCES