

## RAPID DETERMINATION OF CALCITE AND DOLOMITE FOR ROUTINE ANALYSIS BY GASOMETRY

M. HETÉNYI and I. VARSÁNYI

### INTRODUCTION

Analysis of calcite and dolomite is a routine work in laboratories dealing with examination of mineral composition of rocks, and problems of dolomitization.

Several methods are well known, which are very different in their rapidity and accuracy according to demands.

The determination of Ca and Mg by complexometry connecting it with the determination of CO<sub>2</sub> offer a possibility to calculate the amounts of calcite and dolomite [MÜLLER, 1967]. Naturally in this case all the Mg is taken as belonging to the dolomite.

According to SMYKATZ—KLOSS cited by MÜLLER the DTA method may be considered more exact for determination of calcite and dolomite than the X-ray diffractometry, however, it gives correct results only in the case of relatively pure carbonate rocks.

A wide-spread method is the X-ray diffractometry. According to TENNANT and BERGER [1957] the ratio of amount of calcite and dolomite is proportional to the ratio of the peak heights  $\frac{d_{cal} 3,03 \text{ \AA}}{d_{doi} 2,896 \text{ \AA}}$  and the relative amounts may be read from a calibration curve. The accuracy of this method is  $\pm 5\%$  in case of from 10 to 90 per cent dolomite content.

Knowing the relative calcite and dolomite content of the samples and determining the CO<sub>2</sub> content by gasometry the absolute amounts of the carbonates may be calculated [VAN MOORT, 1973; MOLNÁR, 1974].

A comparison of the accuracy of determination of calcite and dolomite in sedimentary rocks, by different methods is given by MEZŐSI [1975].

The aim of this work is to find a simple, rapid calcite and dolomite determination, which can be carried out in laboratories without X-ray diffractometer or derivatograph.

### EXPERIMENTAL PART

This method is based on the fact that calcite dissolves rapidly and perfectly in 1:1 HCl at room temperature, but dolomite dissolves after some time and very slowly.

Measurement of CO<sub>2</sub> released treating the sample by 1:1 hydrochloric acid is carried out by gasometry. 1:1 HCl releases CO<sub>2</sub> from carbonates. The volume of CO<sub>2</sub> and the volume of air in the tube is determined at room temperature and atmospheric pressure. The gas mixture is passed into KOH solution several times in order to discharge CO<sub>2</sub>. The volume of the rest of gas is measured

again at room temperature and atmospheric pressure. The difference between the two volume corresponding to the volume of the CO<sub>2</sub> is reduced to standard temperature and pressure on the basis of fundamental gas equation. The weight of CO<sub>2</sub> is calculated in the following way:

$$1 \text{ ml CO}_2 = 0,1976 \text{ g CO}_2 \quad (1)$$

$$\text{CO}_2 \% = \frac{0,1976 V}{A} \quad (2)$$

where V means the reduced volume of CO<sub>2</sub>,

A means the weight of sample.

According to experiments the results are reliable, the maximum deviation from the average value is  $\pm 1$  per cent.

Dolomite, magnesite and calcite from Ratkószuha were used in the experiments. Samples were ground in agate mortar to grain size  $d \leq 60 \mu$ .

According to our experiments 0,1 g calcite dissolves perfectly in 10 ml 1:1 hydrochloric acid within 15 seconds at room temperature, but the dissolution of dolomite does not start within 60 seconds. Therefore, the CO<sub>2</sub> content measured after 30 seconds reaction time at room temperature gives the amount of CO<sub>2</sub> belonging to the calcite content of the sample.

Weighing in another 0,1 g portion of the sample and determining the CO<sub>2</sub> content after 4—5 minutes boiling, the CO<sub>2</sub> content both of the calcite and dolomite was determined. The difference of the two measurements gives the CO<sub>2</sub> of the dolomite present in the sample.

However, a part of the CO<sub>2</sub> released at room temperature is dissolved in the 1:1 hydrochloric acid and this part of the gas can be expelled only after boiling. It was assumed, that the volume of CO<sub>2</sub> dissolved at room temperature and at constant volume of HCl is proportional to the volume of the total CO<sub>2</sub>.

Mixtures were made from pure calcite and clay mineral free of carbonate, the calcite content of the series changed between 10—100 per cent. The volume of CO<sub>2</sub> of separate portions was measured at room temperature and after boiling. Results can be seen in Table 1. CO<sub>2</sub> determined at room temperature and after boiling differ from each other, but they are proportional (*Fig. 1*).

On the curve *Fig. 1* three sections may be distinguished corresponding to samples of 0—30 per cent, 30—80 per cent and 80—100 per cent calcite content, respectively.

TABLE 1

*Calcite content of mixtures made from pure calcite and clay mineral free of carbonate*

Calcite % in mixture	CO <sub>2</sub> %		Calcite %	
	measured at room temperature		measured after boiling	
9,77	1,94	4,39	4,45	10,09
19,91	5,22	11,84	8,80	19,97
30,59	9,73	22,08	13,66	31,00
40,23	12,43	28,22	17,28	39,23
50,54	15,74	35,73	21,88	49,67
60,22	18,72	42,50	26,76	60,75
70,54	21,92	49,77	31,18	70,77
80,44	26,67	60,55	35,59	80,79
90,12	32,39	73,53	40,27	91,41
100,00	34,51	78,34	44,26	100,40

This is in connection with the solution of the  $\text{CO}_2$  in the hydrochloric acid. By the calibration curve given the quantity of  $\text{CO}_2$  belonging to the calcite content of the samples can be determined on the basis of  $\text{CO}_2$  content measured at room temperature.

The method was controlled by measuring the  $\text{CO}_2$  content of mixtures of calcite and dolomite. Results are shown in Table 2. Quantity of calcite and dolomite measured and calculated from calibration curve corresponds to the theoretical values well enough.

Some measurements were carried out in order to study the effect of grain size on the accuracy of this method. Determining the calcite and dolomite content of the calcite-dolomite standards of  $10\text{--}30\ \mu$  and  $30\text{--}50\ \mu$  fractions, it was found, that results were independent of grain size within this range (Table 3.)

If other minerals containing carbonate are present besides calcite and dolomite, it can effect on the results of measurements. If these carbonates dissolve in 1:1 hydrochloric acid at room temperature, the calcite content determined by this method will be higher, and dolomite will be lower than the theoretical value. In the presence

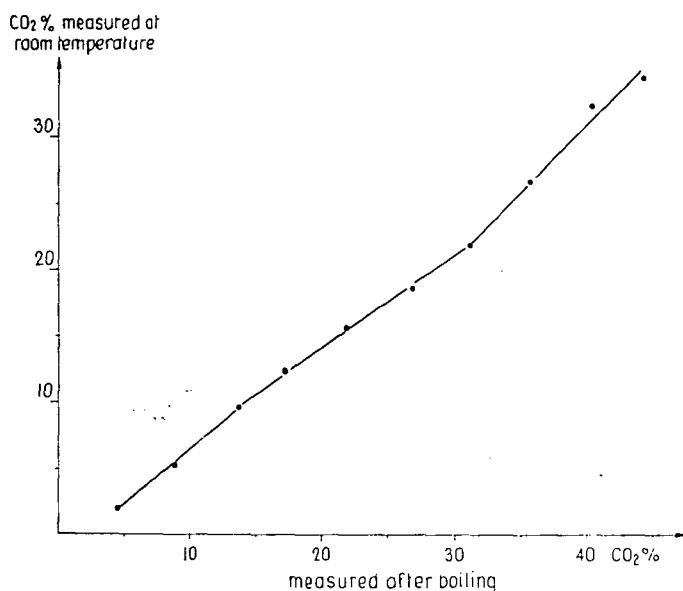


Fig. 1. Calibration curve for determination of calcite content.

TABLE 2

Comparison of the amount of the calcite and dolomite measured and calculated

Calcite/dolomite ratio	CO <sub>2</sub> measured		CO <sub>2</sub> % (calcite)	CO <sub>2</sub> % (dolomite)	Calcite %		Dolomite %	
	at room temperature	after boiling			measured	calculated	measured	calculated
20/80	5,0	45,6	8,6	37,0	19,5	20,3	77,7	77,1
50/50	15,7	44,8	22,3	22,5	50,6	50,1	47,2	46,8
80/20	26,7	45,0	36,0	9,0	81,7	80,0	18,9	18,4

TABLE 3

*Calcite and dolomite content of samples of different grain size*

Grain size	Calcite %		Dolomite %	
	calculated	measured	calculated	measured
10—30 $\mu$	50,2	51,0	49,8	49,0
30—50 $\mu$	50,6	51,1	49,4	48,9

of carbonate compounds soluble only by boiling, the determination of the calcite is exact, but values concerning the dolomite content will be higher including the  $\text{CO}_2$  content both of dolomite and other carbonates.

The behaviour of the magnesite was studied under the conditions applied. It did not dissolve at all at room temperature, and only 20 per cent was dissolved even if it was boiled for 5 minutes.

The amount of calcite of samples containing also magnesite can be determined exactly, but the presence of magnesite results failure in the determination of dolomite content.

In the case of standard samples calcite and dolomite content calculated and measured correspond well, therefore, core samples from the southern part of the Great Hungarian Plain were studied in this way. Results are shown in Table 4.

Determinations of calcite and dolomite content of the same samples were already carried out by X-ray diffractometry combined with gasometric total  $\text{CO}_2$  determination as mentioned previously. Comparison of calcite and dolomite content determined by these two different methods in the same samples is compiled in Table 5.

TABLE 4

*Calcite and dolomite content of core samples from the southern part of the Great Hungarian Plain*

Samples	$\text{CO}_2$ % measured		$\text{CO}_2$ %		Calcite %	Dolomite %
	at room temperature	after boiling	(calcite)	(dolomite)		
Upper Pannonian aleurite 1660 m	2,4	11,7	5,0	6,7	11,3	14,0
Lower Pannonian sandstone 2061 m	1,0	10,9	3,2	7,7	7,3	16,1
Lower Pannonian clay marl 4140 m	2,6	9,1	5,2	3,9	11,8	8,2
Lower Pannonian clay marl 4152 m	1,9	16,7	4,4	4,2	10,0	8,8
Lower Pannonian marlstone 4153 m	9,5	10,5	13,5	3,2	30,6	6,7
Miocene aleurite 4248 m	2,8	8,6	5,6	4,9	12,7	10,3

TABLE 5

*Comparison of calcite and dolomite content of samples measured by different methods*

Samples	Calcite % measured		Dolomite % measured	
	by gasometry	by X-ray diffr.	by gasometry	by X-ray diffr.
Upper Pannonian aleurite 1660 m	11,3	9,5	14,0	15,8
Lower Pannonian sandstone 2061 m	7,3	6,1	16,1	17,1
Lower Pannonian clay marl 4140 m	11,8	12,3	8,2	7,8
Lower Pannonian clay marl 4152 m	10,0	9,9	8,8	8,9
Lower Pannonian marlstone 4153 m	30,6	33,9	6,7	3,7
Miocene aleurite 4248 m	12,7	12,8	10,3	10,2

#### SUMMARY

Determination of calcite and dolomite by gasometry is a rapid, suitable method for routine examinations, it is based on the fact, that 1:1 hydrochloric acid dissolves calcite at room temperature under certain duration, whereas dolomite remains unattacked within the conditions given, and either calcite or dolomite dissolves after 5 minutes boiling.

Measuring the volume of CO<sub>2</sub> of the first portions of the sample at room temperature the quantity of calcite, whereas measuring the CO<sub>2</sub> volume of the second portion after boiling, the quantity of calcite+dolomite can be determined.

Since the CO<sub>2</sub> partly dissolves in the solution at room temperature the CO<sub>2</sub> content have to be corrected by the calibration curve determined experimentally.

Advantage of this method is that it can be carried out with simple equipments, it does not need any special pretreatment, only a grinding to  $d \leq 60 \mu$  grain size.

#### REFERENCES

- MEZŐSI, J. [1975]: Comparison between the X-ray diffractometric quantitative determination methods of calcite and dolomite on the basis of the investigation of Neogene sediments of the Great Plain. *Acta Miner. Petr.*, Szeged, XXII/1, . . . . .
- MOLNÁR, E. [1974]: Possibilities of carbonate content determination of sedimentary rocks. *Acta Miner. Petr.*, Szeged, XXI/2, p. 259—267.
- VAN MOORT, J. C. [1973]: The magnesium and calcium contents of sediments, especially pelites, as function of age and degree of metamorphism. *Chem. Geol.*, 12, p. 1—37.
- MÜLLER, G. [1967]: *Methods in sedimentary petrology*. Stuttgart.

- NÁRAY-SZABÓ, I., PÉTER, T. [1964]: Quantitative determination of the mineral constituents of clays and soils by means of diffractometer. *Földt. Közlöny* 94, p. 444—451.
- SUREAU, J. FR. [1974]: Etude experimentale de la dolomitisation de la calcite. *Bull. Soc. Fr. Mineral Cristallogr.*, 97, 300—312.
- TENNANT, C. B., R. W. BERGER [1957]: X-ray determination of dolomite-calcite ratio of a carbonate rock. *Amer. Mineral.*, 42, p. 23—29.

*Manuscript received, July 10, 1975*

MISS DR. MAGDOLNA HETÉNYI  
MRS. DR. IRÉN VARSÁNYI  
Institute of Mineralogy, Geochemistry  
and Petrography, Attila József University  
H-6701 Szeged, Pf. 428. Hungary