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QUANTITATIVE ESTIMATION OF CALCITE IN LIMESTONES BY DIFFERENTIAL THERMAL ANALYSIS

K. JEHAN, M. A. QAISER and A. H. KHAN*

P.C.S.I.R. Laboratories, Jamrud Road, Peshawar, Pakistan

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A quantitative method is presented for the estimation of calcite in limestones by differential thermal analysis, using calcium hydroxide as an internal standard. The effects of variations due to particle size and impurities such as quartz, iron oxide, organic material, dolomite, magnesite, gypsum and phosphates are discussed.

Quantitative estimation of minerals by differential thermal analysis is influenced by the thermal nature of the sample and changes in the specific heat or thermal diffusivity. The rate of temperature rise is also important; accurate results can be secured only by maintaining a reproducible rate. Berg et al. [1] suggested the use of gypsum as an internal standard in determining polyhalite quantitatively. Grimshaw and Roberts [2] suggested that accurate and reproducible results can be obtained by diluting all samples with some standard, thermally inert material before testing. They found that a mixture of 25 percent sample with 75 percent calcined Al_2O_3 was the most effective. Smykatz-Kloss [3] correlated the temperature of decomposition of pure minerals with the amount of material used in DTA. Jehan, Qaiser and Khan [4] have shown that magnesium hydroxide can be successfully used as an internal standard in the estimation of kaolinite in clays.

The purpose of this paper is to suggest a simple method of estimating calcite in carbonate rocks using calcium hydroxide as an internal standard. The effects of particle size, and impurities such as quartz, iron oxide, organic matter, dolomite, magnesite, gypsum and calcium phosphates have also been studied.

Experimental

Equipment and procedure

Aliquots of about 0.3 g of material (sample and alumina) were placed in the three holes (one containing sample and two containing alumina) of a stainless steel crucible and subjected to a uniform rise in temperature (10°/min) in a vertical furnace with nichrome wires as the heating element [5]. The furnace temperature is controlled manually by a variable transformer and chromel-alumel thermocouples (24 gauge) are used for recording on an automatic Cambridge recorder

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* Present address: P.C.S.I.R. Laboratories, Karachi–39, Pakistan

having a scale between +1 and −1 mV. The recorder driven by an electrical clock marks every twenty seconds on a chart 95 mm wide with a maximum duration of 125 minutes.

Preparation of the samples

Analytical reagent alumina was ignited to 1000°. The material was then cooled and powdered to <150 μ e.s.d.) (equivalent spherical diameter). May & Baker (Dagenham, England) calcium hydroxide was dried at 140° for two hours. The dried material was cooled and kept in an airtight bottle. Precipitated calcium carbonate (calcite), Judex Laboratory reagent (manufactured by the General Chemical & Pharmaceutical Co. Ltd., England), was used for the construction of the calibration curve.

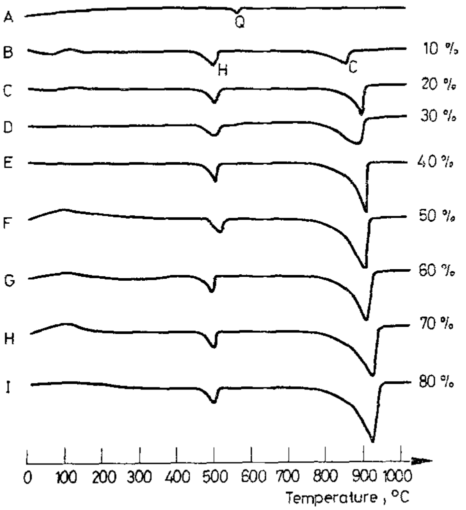

Fig. 1. DTA curves of pure quartz (A), and mixtures of $CaCO_3$, $Ca(OH)_2$ and Al_2O_3 (B, C, D, E, F, G, H, and I). Q, H and C indicate the endothermic peaks of quartz, $Ca(OH)_2$ and $CaCO_3$, respectively. (Not to the original scale)

A series of mixtures of calcium carbonate, calcium hydroxide and alumina were prepared, mixed thoroughly and analyzed thermally.

The DTA curves are presented in Fig. 1 and the results in Table 1. The ratio of the area (measured with a planimeter) of the endothermal peak of calcium carbonate to that of calcium hydroxide is directly proportional to the concentration of calcium carbonate. Many authors [6–12] have described the methods for measuring peak areas. All the methods involve quite arbitrary geometrical procedures. In the present method the peak areas were measured from a base line joining the points of beginning and end of the peak.

Table 1

DTA data of various mixtures

Sample No.	Composition (in weight percent)			Area of $CaCO_3$ endothermic peak, cm^2 a	Area of $Ca(OH)_2$ endothermic peak, cm^2 b	a/b
	$CaCO_3$	$Ca(OH)_2$	Al_2O_3			
B	10	10	80	1.05	0.76	1.38
C	20	10	70	1.90	0.70	2.71
D	30	10	60	3.20	0.80	4.00
E	40	10	50	4.08	0.76	5.37
F	50	10	40	5.36	0.80	6.70
G	60	10	30	5.55	0.70	7.93
H	70	10	20	6.44	0.70	9.20
I	80	10	10	6.98	0.66	10.58

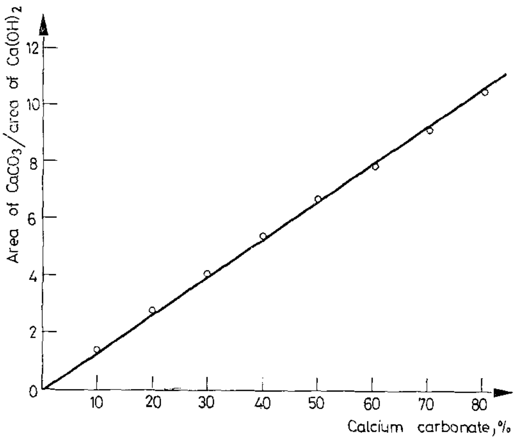

Fig. 2. Area of $CaCO_3$ peak/area of $Ca(OH)_2$ peak plotted against percentage $CaCO_3$. (Not to the original scale)

The optimum amount of internal standard was found to be 10 percent by weight of the whole mixture. Ten percent of inert alumina was normally added to each sample for dilution. Thus, each unknown sample is diluted by 20 percent and the actual amount of calcium carbonate must be obtained by multiplying the amount indicated in the graph (Fig. 2) by a factor of 1.25 (and by 1.11 when alumina is not added).

Reproducibility and tests on known samples

The physical properties of a mineral, together with the amount and degree of compaction in the test cavity, influence the heat measurement considerably. The

Table 2

Repeated quantitative estimation of $CaCO_3$ in KL (Kohat Limestone)

No.	Composition (in weight percent)			Area of $CaCO_3$ endothermic peak, cm² a	Area of $Ca(OH)_2$ endothermic peak, cm² b	a/b	Weight percent $CaCO_3$		Error	Mean error	Percentage error
	KL	$Ca(OH)_2$	Al_2O_3				from calibration curve	by chemical analysis			
1	80	10	10	9.12	0.88	10.4	97.50	97.3	+0.2	+1.08	+1.1
2	80	10	10	9.24	0.88	10.5	98.75		+1.45		
3	80	10	10	9.36	0.88	10.6	99.38		+2.08		
4	80	10	10	8.84	0.84	10.5	98.75		+1.45		
5	80	10	10	8.76	0.84	10.4	97.50		+0.20		

size of the thermocouple beads also affects the areas of the peaks. Great care is normally needed to achieve high reproducibility, but in the present method, using calcium hydroxide as an internal standard, the effects of some of the variables mentioned above are eliminated. The results of the five repeated analyses of Kohat Limestones (KL) containing 97.3 percent $CaCO_3$ are given in Table 2. The average deviation was +1.08, corresponding to an error of 1.1 percent.

Mullaghori Marble (MM), Wah Limestone (WL) and Kohat Limestone (KL) were analyzed chemically and then thermally by the present method. The results are presented in Table 3. Deviations from the actual amounts in the calcite contents of the three samples range between +0.15 and 2.28.

Table 3

Quantitative estimation of $CaCO_3$ in Mullaghori Marble, Wah Limestone and Kohat Limestone

Sample	Composition (in weight percent)			Area of $CaCO_3$ endothermic peak, cm² a	Area of $CaCO_2$ endothermic peak, cm² b	a/b	Weight percent $CaCO_3$		Error
	Sample	$Ca(OH)_2$	Al_2O_3				from calibration curve	by chemical analysis	
MM	80	10	10	9.92	0.94	10.60	99.38	97.1	+2.28
WL	80	10	10	10.96	1.04	10.54	98.75	98.6	+0.15
KL	80	10	10	9.24	0.88	10.50	98.75	97.3	+1.45

Possible sources of error

The particle size of the material and the impurities present influence the quantitative measurements of the heat effects. Some of these factors are discussed below.

(a) *Particle size*

Various investigators have found that over the range 50–300 μ e.s.d. the particle-size effects appear to be unimportant. However, Kulp, Kent and Kerr [13] have shown that below 75 μ e.s.d. the decomposition peak of calcite may be shifted to lower temperatures by as much as 50°. They consider that broad peaks sometimes obtained for calcite samples indicate a wide particle-size range. Gruver [14] has also noted enlargement of peaks of limestone with particle size < 170 μ e.s.d. The Wah Limestone (WL) was crushed and separated into the following size fractions:

(i) <150 μ e.s.d. > 105 μ e.s.d.
(ii) <105 μ e.s.d. > 75 μ e.s.d.
(iii) < 75 μ e.s.d. > 53 μ e.s.d.
(iv) < 53 μ e.s.d.

The results of the particle size investigations are summarized in Table 4. No significant relationship was observed; the maximum percentage error was +1.42.

Table 4

Effect of particle size

Particle size, μ e.s.d.	Composition (in weight percent)			Area of $CaCO_3$ endothermic peak, cm^2 a	Area of $Ca(OH)_2$ endothermic peak, cm^2 b	a/b	Weight percent $CaCO_3$		Error	Percentage error
	WL	$Ca(OH)_2$	Al_2O_3				from calibration curve	by chemical analysis		
<150>105	80	10	10	10.96	1.04	10.54	99.06	98.6	+0.46	+0.47
<105> 75	80	10	10	9.24	0.88	10.50	98.75		+0.15	+0.15
< 75> 53	80	10	10	11.36	1.08	10.52	98.75		+0.15	+0.15
< 53	80	10	10	10.00	0.94	10.64	100.00		+1.40	+1.42

(b) *The effects of various impurities*

(i) *Quartz:* The silica in carbonate rocks occurs as detrital and authigenic quartz, chert and amorphous silica. The shells of silicious organisms such as diatoms, radiolaria and silicious sponges are composed of silica. Thus silica is a common impurity of limestones. A series of mixtures of calcite (av. peak temp. 919°), quartz (av. peak temp. 583°) and alumina, ranging from 10 to 50 percent quartz were analyzed thermally; the results are presented in Table 5. The presence of quartz does not affect the results for calcite significantly and the maximum percentage error found was +3.3 with 50 percent quartz.

(ii) *Iron oxide:* There is a decrease in error with an increase of iron oxide content (Table 5). The reason for this is not clear.

Table 5

Effects of impurities

(i) Effect of quartz:

Sample No.	Composition (in weight percent)				Area of $CaCO_3$ endothermic peak, cm^2 a	Area of $Ca(OH)_2$ endothermic peak, cm^2 b	a/b	Percent $CaCO_3$ from calibration curve	Error	Percentage error
	$CaCO_3$	$Ca(OH)_2$	Al_2O_3	Quartz						
Q-1	70	10	10	10	8.32	0.88	9.45	71.0	+1.0	+1.4
Q-2	60	10	10	20	5.50	0.68	8.09	61.5	+1.5	+2.5
Q-3	50	10	10	30	3.68	0.54	6.81	51.5	+1.5	+3.0
Q-4	40	10	10	40	3.89	0.72	5.40	40.5	+0.5	+1.25
Q-5	30	10	10	50	3.50	0.85	4.10	31.0	+1.0	+3.3
(ii) Effect of Fe_2O_3:										
	$CaCO_3$	$Ca(OH)_2$	Al_2O_3	Fe_2O_3						
F-1	75	10	10	5	7.50	0.72	10.40	78.0	+3.0	+4.00
F-2	70	10	10	10	7.23	0.76	9.51	71.5	+1.5	+2.14
(iii) Effect of organic material:										
	$CaCO_3$	$Ca(OH)_2$	Al_2O_3	Wood						
O-1	79.0	10	10	1.0	6.80	0.64	10.60	79.7	+0.7	+0.89
O-2	77.5	10	10	2.5	8.64	0.64	13.50	>100		
O-3	75.0	10	10	5.0	5.96	0.40	14.90	>100		
O-4*	75.0	10	10	5.0	8.20	0.80	10.25	77.0	+2.0	+2.70
O-5	70.0	10	10	10.0	5.64	0.36	16.00	>100		

(v) Effect of $MgCO_3$:

M-1	70	10	10	10	9.12	1.00	9.12	68.5	− 1.5	−2.14
M-2	60	10	10	20	10.84	1.92	5.65	43.0	−17.0	
M-3*	60	10	10	20	7.60	0.92	8.26	62.0	+ 2.0	+3.3
M-4	50	10	10	30	7.76	2.76	2.81	21.5	−28.5	

(vi) Effect of gypsum:

	$CaCO_3$	$Ca(OH)_2$	Al_2O_3	Gypsum						
G-1	70	10	10	10	6.76	0.72	9.4	70.50	+ 0.50	+0.71
G-2	60	10	10	20	5.60	0.68	8.2	61.50	+ 1.5	+2.50
G-3	50	10	10	30	4.64	0.68	6.8	51.25	+ 1.25	+2.50

(vii) Effect of calcium phosphate:

	$CaCO_3$	$Ca(OH)_2$	Al_2O_3	$Ca_3(PO_4)_2$						
P-1	75	10	10	5	7.70	0.76	10.10	76.0	+ 1.0	+1.33
P-2	70	10	10	10	7.20	0.76	9.50	71.5	+ 1.5	+2.14
P-3	65	10	10	15	6.44	0.74	8.70	65.5	+ 0.5	+0.77
P-4	60	10	10	20	6.08	0.74	8.20	61.5	+ 1.5	+2.50
P-5**	60	10	10	20	5.60	0.68	8.24	62.0	+ 2.0	+3.30

* calcined sample.
** phosphate rock.

(iii) *Organic material:* Organic matter is a common impurity of limestones. It generally consists of hydrocarbons, asphalt and kerogen. As these compounds were not available, the effect of organic matter was studied by mixing wood powder with calcite. There is a gradual rise from the base line (see Fig. 3) with the increase in the percentage of wood. The reading of the area for the calcium hydroxide internal standard becomes uncertain even in the presence of 2.5 percent organic material (see Table 5), and this results in a wrong estimation of the calcite content. Calcite may be estimated safely in the presence of 1 percent organic matter. Samples containing higher amounts of organic matter should be calcined at 650° for an hour. The calcite may then be estimated in the calcined sample by the present method.

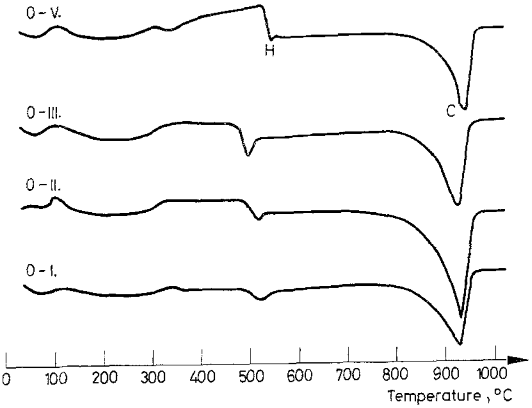

Fig. 3. DTA curves of $CaCO_3$ in the presence of organic material (wood); the curves 0—I, 0—II, 0—III and 0—V contain 1, 2.5, 5 and 10 percent wood, respectively. (Not to the original scale)

(iv) *Dolomite:* Most limestones contain magnesium carbonate in addition to calcite and aragonite. The double carbonate dolomite ($CaCO_3 \cdot MgCO_3$) accounts for most of the magnesium present. A series of mixtures of calcite (av. peak temp. 939°) and dolomite (av. peak temp. of $MgCO_3$ 792°) were analyzed thermally, and the results are presented in Table 6. The apparent increase in the amount of calcite estimated is due to the additive endothermal effect of $CaCO_3$ in dolomite. The estimated $CaCO_3$ content is comparable to the corrected percentage of calcite with a maximum error of +3.98. Thus, in the present method the total $CaCO_3$ (calcite + $CaCO_3$ of dolomite) is estimated.

Attempts were also made to estimate dolomite in limestones by drawing a calibration curve (see Fig. 4, area of $MgCO_3$/area of $Ca(OH)_2$ versus percent dolomite). Unfortunately, the present set-up is not sensitive enough to record the endothermic peak of $MgCO_3$ below 30 percent dolomite. With an amplifier and a suitable recording unit the sensitivity may be increased so that less than 30 percent $MgCO_3$ can be determined.

Table 6

Effect of dolomite:

Sample No.	Composition (in weight percent)				Area of $CaCO_3$ endothermic peak, cm^2 a	Area of $Ca(OH)_2$ endothermic peak, cm^2 b	Area of $MgCO_3$ endothermic peak, of dolomite cm^2 c	a/b	c/b	Per-cent $CaCO_3$ from calibration curve	Corrected percent of $CaCO_3$	Error
	$CaCO_3$	$Ca(OH)_2$	Al_2O_3	Dolomite								
D-1	70	10	10	10	7.60	0.76	—	10.00	—	75.0	75.43	−0.43
D-2	60	10	10	20	7.52	0.76	—	9.89	—	74.5	70.86	+3.64
D-3	50	10	10	30	6.80	0.76	0.12	8.95	0.16	67.2	66.27	+0.91
D-4	40	10	10	40	7.00	0.80	0.60	8.75	0.75	65.7	61.72	+3.98
D-5	30	10	10	50	7.92	1.00	1.08	7.92	1.08	59.5	57.15	+2.35

(v) *Magnesite:* The peak of magnesite ($MgCO_3$ starts at 434° with peak temp. at 650°) interferes with the endothermic peak of the $Ca(OH)_2$ internal standard (peak temp. 500°). Examination of Table 5 reveals that the percentage error in the presence of 10 percent magnesite is -2.14, whereas the effect of 20 percent or more magnesite is conspicuous. The limestone samples containing more than 10 percent magnesite should be calcined at 680° for 1 hour. Such treatment breaks down the $MgCO_3$ structure and the resulting MgO does not interfere with the present method of estimation.

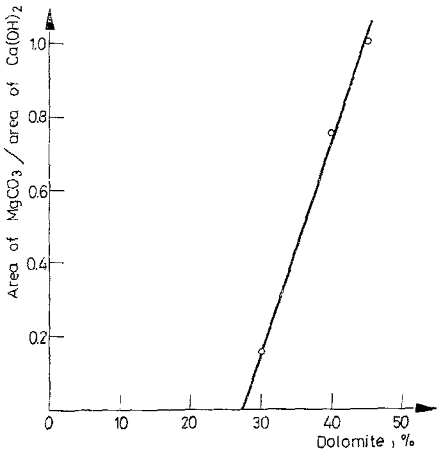

Fig. 4. Area of $MgCO_3$ peak/area of $Ca(OH)_2$ peak plotted against percentage dolomite. (Not to the original scale)

(vi) *Gypsum:* Some limestones may contain gypsum. Sulfate-bearing waters react with limestone with the formation of gypsum. A series of mixtures of calcite, calcium hydroxide, alumina and gypsum were analyzed thermally. The results (see Table 5) indicate that gypsum does not interfere with the estimation of calcite, and the maximum error is $+2.5$ percent.

(vii) *Phosphates:* Phosphates found in limestones are contributed by apatite, by either replaced or originally phosphatic fossils, and by detrital phosphate grains and pebbles. The effect of calcium phosphate on the estimation of calcite was studied by analyzing thermally a series of mixtures (see Table 5). The maximum error was $+2.5$ percent. With Jordanian phosphate the error was slightly higher at $+3.3$ percent.

Conclusions

The ratio of the areas of the endothermic peaks of calcite and calcium hydroxide plotted against concentration gives a sensibly linear relationship, thus allowing quantitative estimation of calcite. Variations in the results due to particle size, quartz, iron oxide, gypsum and phosphates are not significant. However, the presence of organic matter, dolomite and magnesite can interfere with the quantitative estimation.

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Résumé — On propose une méthode de dosage par ATD de la calcite dans les roches calcaires en utilisant l'hydroxyde de calcium comme étalon interne. On discute l'influence de la taille des particles et de la nature des impuretés: quartz, oxyde de fer, corps organiques, gypse, dolomite, magnésite et phosphates.

Zusammenfassung — Es wurde eine quantitative Methode zur Ermittlung von Kalzit im Kalkstein durch Differentialthermoanalyse unter Anwendung von Kalziumhydroxyd als inneren Standard vorgestellt. Der Einfluß von durch unterschiedliche Teilchengröße und Verunreinigungen, wie Quarz, Eisenoxyd, organische Stoffe, Dolomit, Magnesit, Gips und Phosphat hervorgerufenen Veränderungen wurde erörtert.

Резюме — Описан количественный метод определения кальцита, находящегося в карбидах методом дифференциального термического анализа с использованием гидроокиси кальция в качестве внутреннего стандарта. Обсуждены принципы отклонений, к которым относятся размер зерна и такие загрязнения как кварц, окись железа, органические вещества, доломит, магнезит, гипс и фосфаты.