Journal of Thermal Analysis, Vol. 8 (1975) 501—509

QUANTITATIVE ESTIMATION OF MAGNESITE BY DIFFERENTIAL THERMAL ANALYSIS

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(Received December 6, 1974)

A method for quantitative estimation of magnesite in magnesite-rich rocks by differential thermal analysis, using magnesium hydroxide as internal standard, is presented. The effects of variations due to particle size and impurities are discussed.

Earlier, Jehan et al. [1, 2] reported the quantitative estimation of kaolinite in clays and calcite in limestones by DTA. The present communication deals with the estimation of magnesite ($MgCO_3$) in magnesite-rich rocks, magnesium hydroxide being used as internal standard. The effects of particle size, and impurities such as quartz, iron oxide, organic matter, dolomite, calcite, serpentine, talc and chlorite, 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 [3]. The furnace temperature is controlled manually by a variable transformer and chromel—alumel thermocouples (25 gauge) are used for recording temperatures. The differential temperature is recorded on an automatic Cambridge recorder, 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 mixtures:

Analytical grade reagent magnesium oxide was soaked in water overnight, and then dried in an oven at 140°. The dried material was powdered to $<150\ \mu$ e.s.d. (equivalent spherical diameter) and kept in an air-tight bottle.

Aluminium oxide (chromatographic grade, The British Drug House Ltd., England) was ignited to 1000°. This material was then cooled and powdered to

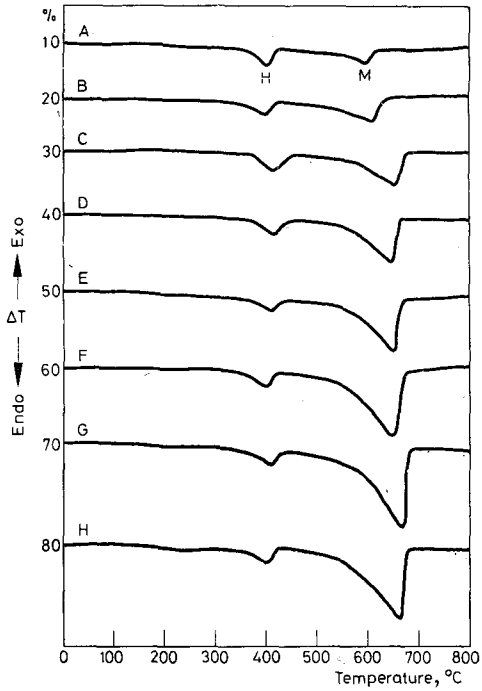

Fig. 1. DTA curves of mixtures of $MgCO_3$, $Mg(OH)_2$ and Al_2O_3 (A, B, C, D, E, F, G and H). H and M indicate the endothermic peaks of $Mg(OH)_2$ and $MgCO_3$ respectively. (Not to the original scale.)

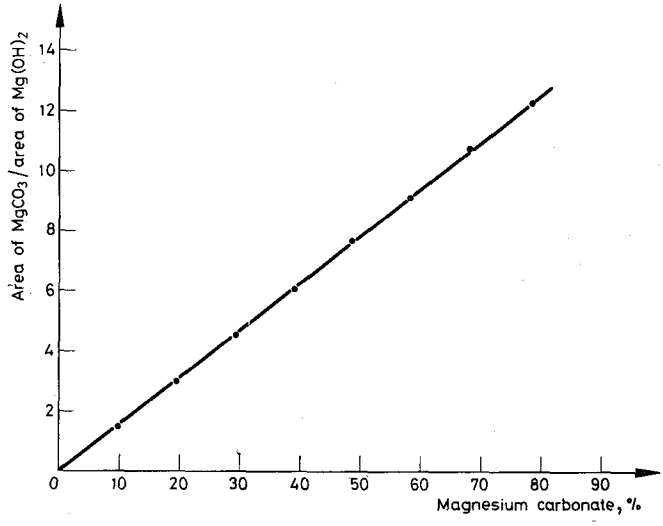

Fig. 2. Area of $MgCO_3$ peak/area of $Mg(OH)_2$ peak plotted against percentage $MgCO_3$. (Not to the original scale.)

$<150\ \mu$ e.s.d. Nasai magnesite (Baluchistan) containing 97.50 per cent $MgCO_3$ was used for the construction of the working curve. Attempts to use analytical grade $MgCO_3$ (E. Merck AG, Darmstadt, & May and Baker Ltd., Dagenham, England) did not work due to the unsatisfactory nature of the endothermic peak. A series of mixtures of Nasai magnesite, magnesium hydroxide and alumina were prepared and analyzed thermally. The various DTA curves are given in Fig. 1, and the results are summarized in Table 1. The ratio of the area of the endothermic peak of magnesite to the area of the peak of magnesium hydroxide is seen to be closely proportional to the concentration of magnesite (Fig. 2).

Table 1

DTA data of various mixtures

Sample No.	Composition, in weight per cent			Area of $MgCO_3$ endothermic peak cm^2 a	Area of $Mg(OH)_2$ endothermic peak cm^2 b	a/b
	Sample = ($MgCO_3$)	$Mg(OH)_2$	Al_2O_3			
A	10 = (9.75)	10	80	1.00	0.68	1.47
B	20 = (19.50)	10	70	2.04	0.68	3.00
C	30 = (29.25)	10	60	3.28	0.72	4.56
D	40 = (39.0)	10	50	4.72	0.78	6.05
E	50 = (48.7)	10	40	6.00	0.78	7.69
F	60 = (58 5)	10	30	7.68	0.84	9.14
G	70 = (68.25)	10	20	9.06	0.84	10.78
H	80 = (78.0)	10	10	9.80	0.80	12.25

The optimum amount of internal standard was found to be 10 per cent of the whole mixture. Addition of 10% inert alumina improved the sharpness of the magnesia peak. Thus, each unknown sample is diluted by a factor of $(100-20)/100$, and the actual amount of magnesite must be obtained by multiplying the amount indicated from the graph (Fig. 2) by a factor of $100/80 = 1.25$.

Reproducibility and testing of known samples:

The physical properties of the minerals, the amount and the degree of compaction in the test cavity and the size of the thermocouple beads greatly influence the peak areas. Great care is needed to achieve high reproducibility. However, in the present method, using magnesium hydroxide as internal standard in the estimation of magnesite, the effects of some of the above variables are eliminated. The results of five repeat analyses of Nasai magnesite are given in Table 2. The average deviation in the per cent magnesite ($MgCO_3$) was -0.17, and the percentage error being -0.18.

A sample of magnesite from Sommergraben Kraubath, Styria, containing 92.1% $MgCO_3$ was analyzed thermally by the present method and found to contain 90.6%

Table 2

Repeated quantitative estimation of $MgCO_3$ in Nasai Magnesite

No.	Composition, in weight per cent			Area of $MgCO_3$ endothermic peak cm^2 a	Area of $Mg(OH)_2$ endothermic peak cm^2 b	a/b	Weight per cent $MgCO_3$		Mean error	Percentage error
	Sample	$Mg(OH)_2$	Al_2O_3				from calibration curve	by chemical analysis		
1.	80	10	10	9.96	0.82	12.15	97.25	97.50	−0.17	−0.18
2.	80	10	10	10.08	0.84	12.00	96.30			
3.	80	10	10	9.80	0.80	12.25	98.10			
4.	80	10	10	8.72	0.72	12.10	97.10			
5.	80	10	10	8.56	0.70	12.23	97.90			

Table 3

Quantitative estimation of $MgCO_3$ in Magnesite

Sample	Composition in weight per cent			Area of $MgCO_3$ endothermic peak cm^2 a	Area of $Mg(OH)_2$ endothermic peak cm^2 b	a/b	Weight per cent $MgCO_3$		Error	Percentage error
	Sample	$Mg(OH)_2$	Al_2O_3				from calibration curve	by chemical analysis		
Sommergraben kraubath styria	80	10	10	8.6	0.76	11.3	90.6	92	−1.5	−1.6

Table 4

Effect of particle size in Magnesite from Nasai

Particle size μ e.s.d.	Composition, in weight per cent			Area of $MgCO_3$ endothermic peak cm^2 a	Area of $Mg(OH)_2$ endothermic peak cm^2 b	a/b	Weight percent $MgCO_3$		Error	Percentage error
	Sample	$Mg(OH)_2$	Al_2O_3				from calibration curve	by chemical analysis		
< 150 > 105	80	10	10	10.08	0.84	12.0	96.3	97.5	−1.2	−1.24
< 105 > 75	80	10	10	8.96	0.76	11.8	94.6		−2.9	−3
< 75 > 53	80	10	10	8.96	0.76	11.8	94.6		−2.9	−3
< 53	80	10	10	9.44	0.80	11.8	94.6		−2.9	−3

Table 5

Effect of impurities

(i) *Effect of quartz*

Sample No.	Composition, in weight per cent				Area of $MgCO_3$ endothermic peak cm^2 *a*	Area of $Mg(OH)_2$ endothermic peak cm^2 *b*	*a*/*b*	Per cent $MgCO_3$ from calibration curve	Error	Percentage error
	Sample = ($MgCO_3$)	$Mg(OH)_2$	Al_2O_3	Quartz						
Q-1	70 = (68.25)	10	10	10	10.73	1.00	10.73	68.5	+0.25	+0.4
Q-2	60 = (58.50)	10	10	20	8.64	0.94	9.20	59.0	+0.50	+0.9
Q-3	50 = (48.70)	10	10	30	6.96	0.92	7.57	48.7	0	0
Q-4	40 = (39.00)	10	10	40	5.50	0.88	6.25	40.0	+1.00	+2.6
Q-5	30 = (29.25)	10	10	50	2.44	0.52	4.70	30.0	+0.75	+2.5

(ii) *Effect of* Fe_2O_3

	Sample = ($MgCO_3$)	$Mg(OH)_2$	Al_2O_3	Fe_2O_3						
F-1	70 = (68.25)	10	10	10	10.64	0.92	11.57	73.7	+ 5.45	+ 8
F-2	60 = (58.5)	10	10	20	10.84	0.92	11.78	75.5	+17.00	+29

(iii) *Effect of organic material*

	Sample = ($MgCO_3$)	$(Mg(OH)_2$	Al_2O_3	Wood						
O-1	77.5 = (75.56)	10	10	2.5	11.60	1.08	10.74	68.5	− 7.06	− 9.3
O-2	75.0 = (73.12)	10	10	5.0	12.24	1.20	10.20	65.5	− 7.62	−10.4
O-3	70.0 = (68.25)	10	10	10	11.20	1.24	9.03	58.0	−10.25	−15.2

(iv)a. *Effect of* $CaCO_3$ *(Chemical Grade)*

	Sample = ($MgCO_3$)	$Mg(OH)_2$	Al_2O_3	$CaCO_3$						
C-1	70 = (68.25)	10	10	10	8.44	0.78	10.55	69.5	+ 1.25	+ 1.8
C-2	60 = (58.50)	10	10	20	7.52	0.80	9.40	60.3	+ 1.80	+ 3.0
C-3	50 = (48.70)	10	10	30	5.96	0.78	7.45	49.0	+ 0.30	+ 0.6

(iv)b. *Effect of Dolomite (Ghundai Tarako, Swat)*

	Sample = $(MgCO_3)$	$Mg(OH_2)$	Al_2O_3	Dolomite						
D-1	70 = (68.25)	10	10	10	9.08	0.84	10.80	69.3	+ 1.05	+ 1.5
D-2	60 = (58.50)	10	10	20	8.23	0.88	9.35	60.0	+ 1.50	+ 2.6
D-3	50 = (48.70)	10	10	30	5.68	0.72	7.88	50.5	+ 1.30	+ 2.7

(v) *Effect of Serpentine (Musa Mena, Malakand)*

	Sample = $(MgCO_3)$	$Mg(OH)_2$	Al_2O_3	Serpentine						
S-1	70 = (68.25)	10	10	20	8.28	0.80	10.35	66.3	− 1.95	− 2.8
S-2	60 = (58.50)	10	10	20	6.05	0.70	8.64	55.5	− 3.00	− 5.1
S-3	50 = (48.70)	10	10	30	5.48	0.80	6.82	44.0	− 4.70	− 9.6

(vi) *Effect of (Talc Sherwan, Hazara)*

	Sample = $Mg(CO_3)$	$Mg(OH)_2$	Al_2O_3	Talc						
T-1	60 = (58.50)	10	10	20	4.60	0.50	9.2	59	+ 0.5	+ 0.9

(vii) *Effect of Chlorite (Narangisar, Malakand)*

	Sample = $(MgCO_3)$	$Mg(OH)_2$	Al_2O_3	Chlorite,						
Ch-1	70 = (68.25)	10	10	10	8.60	0.82	10.5	67.05	− 0.75	− 1.1
Ch-2	60 = (58.50)	10	10	20	7.60	0.82	9.3	59.50	+ 1.00	+ 1.7
Ch-3	50 = (48.70)	10	10	30	6.56	0.80	8.2	52.60	+ 3.90	+ 8.0
Ch-4	40 = (39.00)	10	10	40	6.08	0.82	7.4	47.50	+ 8.50	+21.8

$MgCO_3$ (Table 3). Thus, the deviation in the magnesite content is -1.5, corresponding to a percentage error of -1.6.

Possible sources of error:

Quantitative measurement of heat effects is always influenced by the particle size of the mineral and the impurities present. The effects of these are discussed below:

(a) Particle size

Nasai magnesite was crushed and separated into the following size fractions:

i) <150 μm e.s.d. $>$ 105 μm e.s.d.
ii) <105 μm e.s.d. $>$ 75 μm e.s.d.
iii) $<$ 75 μm e.s.d. $>$ 53 μm e.s.d.
iv) $<$ 53 μm e.s.d.

The results of particle size investigations are summarized in Table 4. The peak ratios did not change significantly, with the percentage error varying between -1.2 and -3. Studies with particle sizes below 40 μm may prove interesting.

(b) The effects of various impurities

i) Silica minerals: Magnesite formed by the weathering of ultrabasic rocks is often enriched with opal ($SiO_2 \cdot nH_2O$). The water content in opal is generally from 1 to 10%, but rarely as much as 34%. On heating, opales lose most of their water below 250°. As opal samples were not available, quartz was used, assuming that the effects of quartz would be similar to those of opal at higher temperatures. A series of mixtures of quartz, magnesite, alumina and magnesium hydroxide were analyzed thermally; the results are given in Table 5. The percentage error varies between nil and $+2.6$. The lower values are due to the through mixing of each mixture.

ii) Iron oxides: The effect of iron oxides in the quantitative estimation of magnesite is very marked. The presence of 10 and 20% iron oxides produces percentage errors of $+8$ and $+29$, respectively (Table 5). It seems that there is an apparent increase in the area of the magnesite endotherm with the increase in the iron oxide percentage.

iii) Organic matter: Sedimentary magnesite may sometimes contain organic matter. The percentage error increases with the increase of the organic matter content (Table 5). Even in the presence of 2.5% organic matter the percentage error is -9.3.

iv) Calcite and dolomite: Calcite and dolomite are very often associated with magnesite. A series of mixtures of these carbonate rocks, alumina and magnesium hydroxide were analyzed by DTA, and the results are shown in Table 5. The effects

of calcite and dolomite are not significant and the percentage error varies from +0.6 to +3.7.

v) Serpentinite: $Mg_6(Si_4O_{10})(OH)_6$: In some places magnesite occurs with serpentinite. The presence of serpentine in magnesite affects the estimation of magnesite to a considerable extent (Table 5). The amount estimated is lower than the actual amount; the percentage error increases with increasing amount of serpentinite.

vi) Talc: The presence of talc in magnesite rock does not affect the estimation of the magnesite content (Table 5).

vii) Chlorite: The endotherm of chlorite (peak temperature 670°) interferes with the $MgCO_3$ endotherm. Samples containing up to 20% chlorite can safely be estimated by the present method. Higher amounts of chlorite give high results.

Conclusion

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

References

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RÉSUMÉ — On présente une méthode d'analyse thermique différentielle pour l'estimation quantitative de la magnésite dans des roches riches en magnésite, en utilisant l'hydroxyde de magnésium comme étalon interne. On discute l'effet des écarts dus à la taille des particules et aux impuretés.

ZUSAMMENFASSUNG — Eine differentialthermoanalytische Methode zur quantitativen Abschätzung von Magnesit in magnesitreichen Felsen durch Magnesiumhydroxid als inneren Standards wird beschrieben. Die infolge verschiedener Teilchengrößen und Verunreinigungen auftretenden Schwankungen werden erörtert.

Резюме — Представлен метод количественного определения магнезита в рудах с богатым содержанием магнезита с помощью дифференциального термического анализа. В качестве внутреннего стандарта использовали гидроокись магния. Обсуждено влияние изменений, обусловленных размером частиц и примесями.