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QUANTITATIVE ESTIMATION OF DIASPORE BY DIFFERENTIAL THERMAL ANALYSIS

Nisar Ahmad, Mumtaz Hasnain, M.A. Qaiser and Ainul Hasan Khan*

PCSIR Laboratories, Peshawar

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A quantitative method is presented for the estimation of diaspore in different clays by differential thermal analysis using magnesium hydroxide as an internal standard. The effects of variations due to impurities such as quartz, iron oxide, calcite, dolomite, titanium oxide, kaolin and boehmite are discussed.

INTRODUCTION

Several authors have used quantitative differential thermal analysis as a rapid, inexpensive and accurate method for the determination of the amount of a particular mineral in mixture. Speil[1] and Kerr and Kulp[2] showed on theoretical grounds that the area of any particular peak on a DTA curve is propotional to the heat evolved by the total mass of the reacting substance. Based on this principle Jehan, Qaiser and Khan[3-6] have developed methods of estimation of Kaolinite in clays, calcite in limestones, magnesite in magnesite-rich rocks and gypsum in gypsiferous rock. As diaspore is an important constituent of bauxite, a simple and quick method of estimating diaspore in different bauxitic clays by DTA is reported in the present paper using $Mg(OH)_2$ as an internal standard. A small amount of ignited alumina is also added to improve the sharpness of the peak. The effects of quartz, iron oxide, calcite, dolomite, TiO_2, kaolinite and boehmite have also been studied.

EXPERIMENTAL

Equipment and Procedure. Samples of about 1gm of material (sample and alumina) were placed in two medium size ceramic crucibles, one containing sample, and the other containing alumina, and subjected to uniform rise in temperature (10°C/min). in a vertical furnace with nichrome wire as heating element. The furnace temperature was controlled manually by a variable transformer, and chromel-alumel thermocouples (25 guage) were used for recording temperatures. The differential temperature was recorded on a automatic recorder (Potentiometric Flatbed Recorder) (SERVOGORS)), having a recording width 20 cms.

Preparation of Mixtures. Analytical reagent grade alumina was ignited to 1000°C. This material was cooled and powdered to 150 e.s.d. (equiverent spherical diameter) and kept in an airtight bottle. BDH $Mg(OH)_2$ was used as internal standard. Diaspore containing 74.6% alumina was used for the construction of the working curve. A series of mixtures of diaspore, $Mg(OH)_2$ and alumina were prepared, mixed throughly and analysed thermally. The

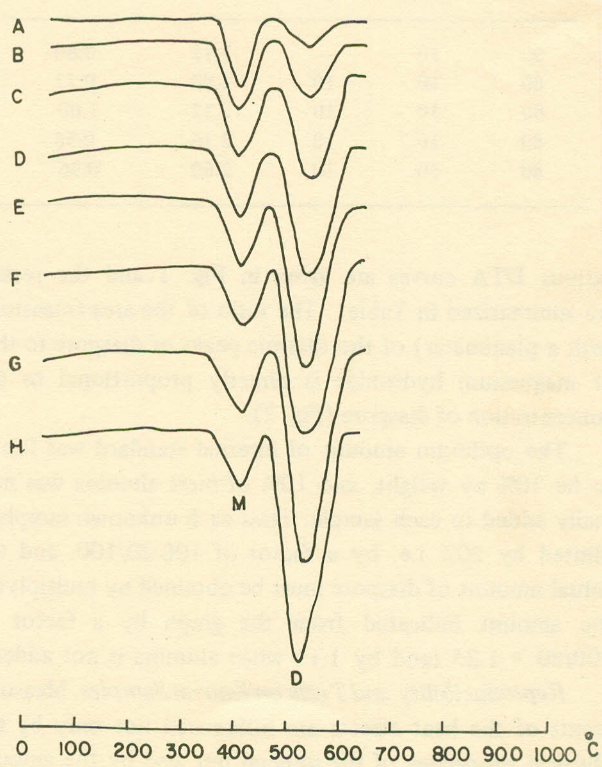

Fig. 1. The various DTA curves of mixtures of diaspore, $Mg(OH)_2$ and Al_2O_3, (A-H), M and D indicate the endothermic respectively (Not to the original scale).

*Present Address: PCSIR, Press Centre, 2nd Floor, Shahrah-e-Kamal Ataturk, Karachi.

Table 1. DTA data of various mixtures. (Quantitative estimation of diaspore by DTA)

Sample No.	Composition wt% Sample diaspore	$Mg(OH)_2$	Al_2O_3	Area of diaspore endothermic peak (cm^2) (a)	Area of $Mg(OH)_2$ endothermic peak (cm^2) (b)	(a/b)
A	10 = (8.77)	10	80	0.48	0.88	0.55
B	20 = (17.54)	10	70	1.00	0.84	1.19
C	30 = (26.31)	10	60	1.68	0.92	1.84
D	40 = (35.08)	10	50	2.32	0.92	2.50
E	50 = (43.80)	10	40	3.00	0.96	3.12
F	60 = (52.62)	10	30	3.60	1.04	3.46
G	70 = (61.39)	10	20	4.80	1.08	4.44
H	80 = (70.16)	10	10	4.68	0.92	5.08

Table 2. Repeat quantitative estimation of diaspore

Composition (wt%) Sample STRB 6-5	$Mg(OH)_2$	Al_2O_3	Area of diaspore endothermic peak (cm^2) (a)	Area of $Mg(OH)_2$ endothermic peak (cm^2) (b)	Ratio a/b	Wt% from calibration curve	Actual amount of diaspore	Diaspore by chemical analysis	Error	Mean error	Error %
90	10	–	2.12	0.80	2.65	37.5	37.5x1.1=41.25	41.48	- 0.23	-2.056	- 4.9
80	10	10	1.80	0.72	2.50	35.0	35x1.25=43.75		+ 1.27		
80	10	10	2.12	1.00	2.12	30.0	30x1.25=37.50		- 3.98		
80	10	10	2.16	0.96	2.25	31.5	31.5x1.25=39.37		- 2.11		
80	10	10	2.00	0.96	2.08	29.0	29x1.25=36.25		- 5.23		

various DTA curves are given in Fig. 1 and the results are summarized in Table1. The ratio of the area (measured with a planimeter) of the thermic peaks of diaspore to that of magnesium hydroxide is directly proportional to the concentration of diaspore (Fig. 2).

The optimum amount of internal standard was found to be 10% by weight, and 10% of inert alumina was normally added to each sample. Thus each unknown sample is diluted by 20% i.e. by a factor of 100-20/100, and the actual amount of diaspore must be obtained by multiplying the amount indicated from the graph by a factor of 100/80 = 1.25 (and by 1.11 when alumina is not added).

Reproducibility and Tests on Known Samples. Measurements of the heat effects are influenced not only by the physical properties of the mineral but also by the amount and degree of campation in the test cavity. The size of the beads of the thermocouples and rate of rise of temperature also affect the areas of the peaks. Normally, great care is needed to achieve high reproducibility, but in the present methods using magnesium hydroxide as an internal standard, the effect of some of the variables mentioned above are eliminated.

The results of the five repeat analysis of STRB-6-5 (the sample provided by PUNJMIN containing diaspore and Kaolin) are given in Table 2. The deviation ranges between –5.23 to + 1.27 and the mean percentage is 5.02 (Table 2). The samples STRB-6(I,II,III provided by Punjmin) were also analysed by DTA. The estimated diaspore from working curve is close to the amount of diaspore analysed chemically (Table 3).

Possible Sources of Error. The impurities present influence the measurement of heat effect. Some of these factors are disscussed below:

Quartz. Quartz is a common impurity. A series of mixtures of diaspore, $Mg(OH)_2$, Al_2O_3 with quartz ranging from 10 to 50% wrere thermally analysed. The results are presented in Table 4. Pure quartz produces a small endothermic peak overlapped by the peak of diaspore. The presence of quartz does not affect the results significantly. The percentage error varies between -3.8 to + 7.5

Iron Oxide. diaspore containing upto 10% Iron oxide

Table 3. Calculated mineral composition of three Punjmin clay samples.

Chemical composition	STRB-6-I	STRB-6-II	STRB-6-III
Al_2O_3	76.95	78.92	77.51
SiO_2	3.50	3.20	6.36
Fe_2O_3	1.19	Trace	Trace
TiO_2	0.87	0.82	0.85
CaO	–	–	–
MgO	–	0.45	0.20
Na_2O	1.01	0.04	0.40
K_2O	1.55	0.05	0.05
LOI	14.56	14.70	14.95
% calculated Diaspore	90.42	92.73	91.08
% Diaspore by DTA	92.08	92.13	92.0

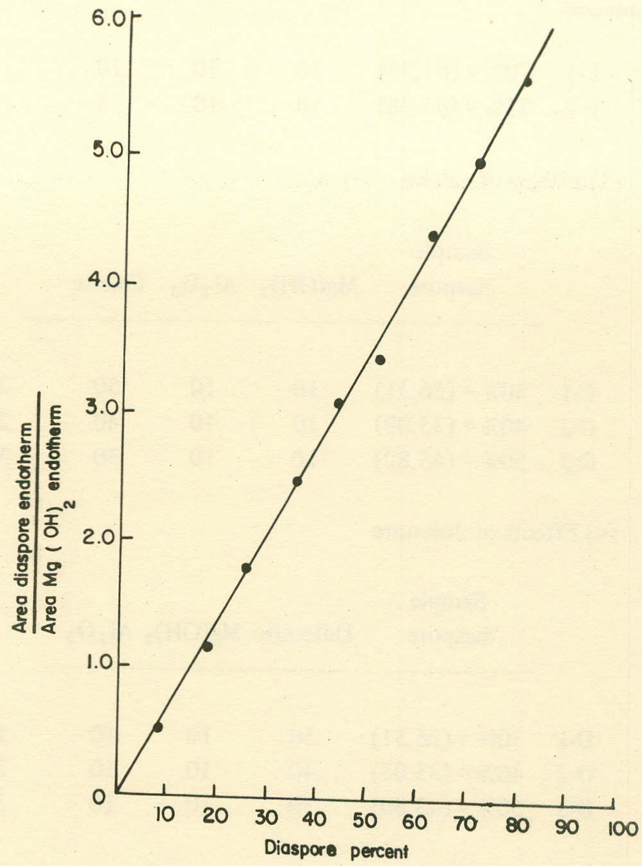

Fig. 2. Area of diaspore endotherm / area of Mg $(OH)_2$ endotherm plotted against percentag diaspore (Not to the original scale)

Table 4. Effect of impurities

Sample	Composition wt%				Area of diaspore 2nd endothermic peak (cm^2) (a)	Area of $Mg(OH)_2$ peak (b)	Ist ratio a/b	Diaspore from calibration curve (%)	Error	Error (%)
(1) Effect of Quartz										
	Sample diaspore	$Mg(OH)_2$	Al_2O_3	Quartz						
Q-1	30% = (26.31)	10	10	50	1.80	1.00	1.80	25.50	- 0.81	- 3.80
Q-2	40% = (35.08)	10	10	40	2.80	1.12	2.50	35.00	- 0.80	- 0.22
Q-3	50% =(43.80)	10	10	30	3.40	1.08	3.14	44.00	+ 0.20	+ 0.45
Q-4	60% = (52.62)	10	10	20	3.96	1.00	3.96	55.50	+ 2.88	+ 5.20
Q-5	70% = (61.39)	10	10	10	4.52	0.96	4.70	66.00	+ 4.61	+ 7.50
(2) Effect of Fe_2O_3										
	Sample diaspore	$Mg(OH)_2$	Al_2O_3	Quartz						

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F-1	70% = (61.39)	10	10	10	5	1.08	4.63	64.5	+ 2.61	+ 4.2
F-2	75% = (65.78)	10	10	5	5	1.00	5.00	69.5	+ 4.00	+ 5.7

(3) Effects of calcite

	Sample diaspore	$Mg(OH)_2$	Al_2O_3	Calcite						
C-1	30% = (26.31)	10	10	50	2.40	1.08	1.88	26.5	+ 0.19	+ 0.72
C-2	40% = (35.08)	10	10	40	2.56	1.00	2.52	36.0	+ 0.92	+ 2.60
C-3	50% = (43.80)	10	10	30	3.20	1.00	3.20	45.0	+ 1.20	+ 2.70

(4) Effects of dolomite

	Sample diaspore	Dolomite	$Mg(OH)_2$	Al_2O_3						
D-1	30% = (26.31)	50	10	10	1.88	0.96	1.95	27.5	+ 1.19	+ 4.4
D-2	40% = (35.08)	40	10	10	2.60	1.08	2.40	34.0	- 1.08	- 3.1
D-3	50% = (43.80)	30	10	10	3.32	1.00	3.36	46.5	+ 2.27	+ 6.16

(5) Effects of TiO_2

	Sample diaspore	TiO_2	$Mg(OH)_2$	Al_2O_3						
T-1	75% = (65.77)	5	10	10	5.08	1.04	4.92	69.0	+ 3.23	+ 4.91

can be safely determined by the present method. The error is not more than + 5.7%.

Calcite and Dolomite, Calcite and dolomite often occur as an impurity in diaspore. The effect of these minerals upto 50% are not significant, and the % error is very low.

TiO_2 Diaspore containing upto 5% of TiO_2 can be safely determined by the present methods (+5% error). Thus the effect of presence of TiO_2 is not significant.

Boehmite. Diaspore is difficult to be estimated quantitively if mixed with boehmite as the peak area overlaps.

CONCLUSIONS

The ratio of areas of the endothermic peaks of diaspore (525°C) plotted against concentration gives a sensible linear relationship, thus allowing quantitive estimation of diaspore. Variations in the results due to quartz, iron oxide, calcite, dolomite and TiO_2 are not significant. However the presence of boehmite interfere with the quantitative estimation.

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