

QUANTITATIVE ESTIMATION OF KAOLINITE IN CLAYS BY DIFFERENTIAL THERMAL ANALYSIS

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A quantitative method of estimating the kaolinite content in clays by differential thermal analysis, using magnesium hydroxide as an internal standard, is presented. The effects of variations due to particle size, and impurities such as quartz, iron oxides, hydrated alumina minerals and organic material are discussed.

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 a mixture. The kaolinite content of a clay sample has been estimated from the area of the endothermic peak at 575°C. Speil¹ and Kerr and Kulp² showed on theoretical grounds that the area of any particular peak on a DTA curve is proportional to the heat evolved by the total mass of the reacting substance. However, Speil, Berkelhamer, Pask and Davies³ found variations of some 30% in the heats of transformation of kaolinite from various origins. Grim⁴ has shown that variations in size and degree of crystallinity of particles of kaolinite are reflected in variations in the intensities of thermal reactions of the mineral. Carthew⁵ has also studied the effects of the degree of crystallinity and particle size distribution of kaolinite on the endothermic peak of the DTA curve. He has shown that the ratio of the area to the width at half the amplitude of the endothermic peak increases with the "slope ratio", and his empirical relationship provides a method of quantitatively estimating the proportions of kaolinite of various particle sizes and degree of crystallinity.

In the present paper, authors suggest a simple method of estimating the amount of kaolinite present in clays by using magnesium hydroxide as an internal standard. A small amount of ignited alumina (inert) is also added to improve the sharpness of the peak. The effects of particle size, and the interference due to the presence of quartz, iron oxides, hydrated alumina minerals and organic materials are also 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°C/min) in a vertical furnace having

nichrome wires as the heating element.⁶ The furnace temperature is controlled manually by a variable transformer, and chromel-alumel thermocouples (25 gauge) are used for measuring the temperatures. The differential temperature is recorded on an automatic Cambridge recorder, having a scale extending from +1 mv to -1 mv. The recorder, driven by an electrical clock marked every twenty seconds on a chart 95 mm wide with a maximum duration of 125 min.

Preparation of the Mixture.—A.R. grade magnesium oxide was soaked in water overnight, then dried in an oven at 140°C. The dried material was powdered to -100 mesh and kept in an air-tight bottle.

A.R. grade alumina was ignited to 1000°C. The material was then cooled and powdered to -100 mesh.

BDH kaolin was used for the construction of the working curve. A series of mixtures of kaolinite, 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 kaolinite to the area of the peak of magnesium hydroxide is seen to be closely proportional to the concentration of kaolinite (Fig. 2).

The optimum amount of internal standard was worked out to be 10 percent by weight of the whole mixture. The endothermic peak of magnesium hydroxide at this concentration was observed to be broad, but the addition of 10% inert alumina was found to improve the sharpness of the peak. Thus, each unknown sample is diluted by a factor of (100-20)/100, and the actual amount of kaolinite must be obtained by multiplying the amount indicated from the graph (Fig. 2) by a factor of 100/80=1.25.

Reproducibility and Tests on Known Samples.—Measurements of the heat effects are influenced

TABLE I.—DTA DATA OF VARIOUS MIXTURES.

Sample No.	Composition			Peak area of $Mg(OH)_2$ cm^2 (a)	Peak area of kaolin cm^2 (b)	b/a
	%Kaolin	% $Mg(OH)_2$	% Al_2O_3			
B	10	10	80	0.72	0.44	0.61
C	20	10	70	0.84	1.16	1.40
D	30	10	60	0.72	1.56	2.17
E	40	10	50	0.72	2.12	2.94
F	50	10	40	0.72	2.60	3.61
G	60	10	30	0.72	3.20	4.44
H	70	10	20	0.72	3.80	5.28
I	80	10	10	0.55	3.32	6.04

Kaolin—BDH, Poole, England; Al_2O_3 —Reference sample; $Mg(OH)_2$ —Internal standard.

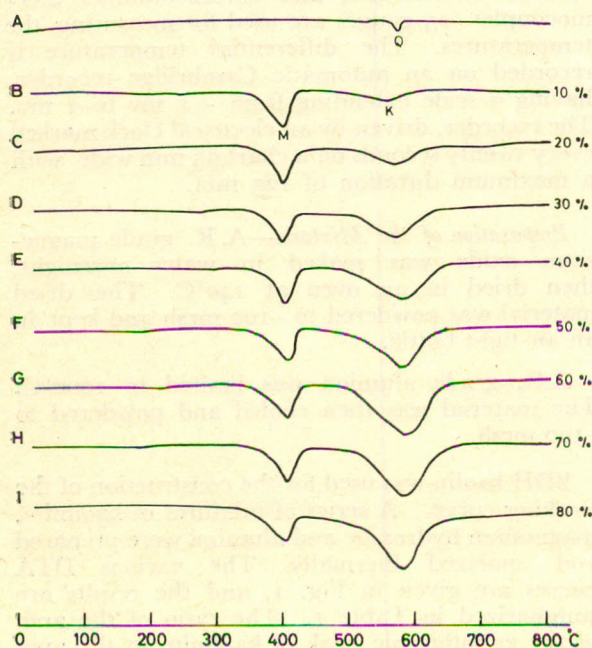


Fig. 1.—DTA curves of pure quartz (A), and mixtures of kaolin, $Mg(OH)_2$ and Al_2O_3 (B,C,D,F,E,G, H and I). Q, M and K show the endotherms of quartz, $Mg(OH)_2$ and kaolin respectively. (Not to the original scale).

not only by the physical properties of the mineral, but also by the amount and degree of compaction in the test cavity. The size of the thermocouple beads also influences the areas of the peaks. Normally, great care is needed to achieve high reproducibility, but in the present method, using magnesium hydroxide as an internal standard, the effects of some of the variables mentioned above are nullified. The results of five repeat analyses of Bagh clays (KLN 9) are given in Table 2. The average deviation in % of Kaolin was +3.4, corresponding to an error of 4.3% of the quantity determined.

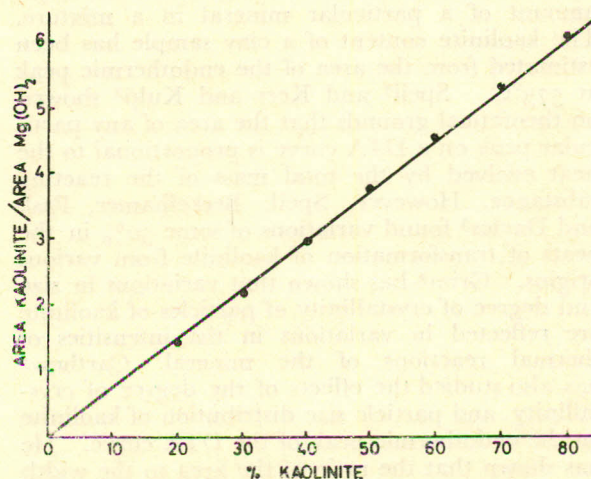


Fig. 2.—Area kaolinite/Area $Mg(OH)_2$ plotted against kaolinite.

Four samples of Bagh clays reported earlier⁷ were thermally analyzed by the present method. The normative compositions calculated from chemical analyses are presented in Table 3 and the results of the thermal analyses in Table 4. Deviations in the kaolinite contents of the four samples from the theoretical amounts range between +1.42 to +5.77, giving an average deviation of +3.8.

Possible Sources of Error.—Quantitative measurements of heat effects are always influenced by the particle size of the material and any impurities present. The effects of these factors are discussed below:

Particle Size.—The Bagh clay KLN₇ was crushed and separated into the following size fractions:

- | | | |
|-------|-------------------|---------------|
| (i) | —100 to +150 mesh | B.S.S. Sieve. |
| (ii) | —150 to +200 | do |
| (iii) | —200 to +300 | do |
| (iv) | —300 | do |

No attempt was made to separate particle smaller than —300 mesh sieve. The results of the particle size investigations are summarized in Table 5, in general the peak ratios increase with decrease in particle size. The maximum percentage error was about +3.2.

The Effects of Various Impurities.—(i) *Quartz:* Quartz is a common impurity in clay minerals. A series of mixtures of BDH kaolin and quartz ranging from 10 to 50% quartz, were thermally analyzed, and the results are presented in Table 6. Pure quartz produces a small endothermic peak (see Fig. 1) at about 573°C, which overlaps the endothermic peak of kaolinite. The presence of 10% or less of quartz in kaolinite does not affect

the estimation of the kaolinite content, but higher percentages of quartz ($\leq 20\%$) would increase the apparent percent kaolinite by 1 to 1.5.

(ii) *Iron Oxides:* The effect of iron oxides in the quantitative estimation of kaolinite is quite large, the presence of 5% iron oxide lowering the estimation of kaolinite by 7.0 (Table 6). Some of the iron oxide and kaolinite may react to form a third compound, thus reducing the apparent concentration of kaolinite in the mixture.

(iii) *Hydrated Alumina Minerals:* Diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) are usually found with kaolinite. The peaks for these minerals overlap the endothermic peak of kaolinite

TABLE 2.—REPEAT ANALYSES OF BAGH CLAYS (KLN 9).

Composition			Peak area of $\text{Mg}(\text{OH})_2$ cm^2 (a)	Peak area of kaolin cm^2 (b)	b/a	% kaolin from working curve	Theoretical %	Error of average	% error
%KLN9 + % $\text{Mg}(\text{OH})_2$ + % Al_2O_3									
80	10	10	0.68	3.36	4.94	82.5	79.38	+3.4	4.3
80	10	10	0.68	3.41	5.01	83.75	—	—	—
80	10	10	0.68	3.41	5.01	83.75	—	—	—
80	10	10	0.68	3.40	5.00	83.12	—	—	—
80	10	10	0.70	3.36	4.80	80.62	—	—	—

TABLE 3.—CALCULATED MINERAL COMPOSITION OF BAGH CLAYS.

Mineral	KLN7	KLN8	KLN9	KLN10	KLN11	KLN12
Quartz	—	2.51	—	2.16	—	—
Muscovite	1.27	3.81	2.03	1.61	1.69	1.61
Paragonite	1.30	3.32	4.06	1.11	1.60	1.97
Chlorite	1.85	3.67	4.74	1.57	0.99	—
Kaolinite	87.20	59.85	79.38	65.20	50.55	80.0
Diaspore	3.67	—	0.15	—	36.95	10.85
Corundum	—	—	3.41	—	3.36	1.74
Haematite	1.89	23.86	1.41	18.75	0.84	1.51
Limonite	—	—	—	6.72	—	—
Apatite	0.33	0.16	0.26	0.05	0.27	—
Rutile or Anatase	1.85	1.54	3.71	1.38	3.17	2.09
MnO	trace	trace	trace	0.22	trace	trace
H ₂ O	0.61	1.34	1.45	1.14	0.77	0.79
	99.97	100.06	100.60	99.91	100.19	100.56

TABLE 4.—QUANTITATIVE ESTIMATION OF KAOLIN IN BAGH CLAYS.

Compositions			Peak area of $\text{Mg}(\text{OH})_2$ cm^2 (a)	Peak area of kaolin cm^2 (b)	b/a	% kaolin from working curve	Theoretical %	Error
% Bagh Clays + % $\text{Mg}(\text{OH})_2$ + % Al_2O_3								
KLN7-80	10	10	0.72	3.92	5.44	90.0	87.20	+2.80
KLN8-80	10	10	0.84	3.24	3.86	65.62	59.85	+5.77
KLN9-80	10	10	0.60	3.04	5.07	84.62	79.38	+5.24
KLN10-80	10	10	0.52	2.02	3.90	66.62	65.20	+1.42

TABLE 5.—EFFECT OF PARTICLE SIZE OF THE SAMPLE ON THE PEAK AREAS OF DTA CURVE.

Particle Size (mesh)	Compositions			Peak area of Mg(OH) ₂ cm ² (a)	Peak area of kaolin cm ² (b)	b/a	% kaolin from working curve	Theoretical %	Error	% Error
	%KLN7 + %Mg(OH) ₂ + %Al ₂ O ₃									
—100 to +150	80	10	10	0.92	4.84	5.26	87.5	87.2	+0.3	
—150 to +200	80	10	10	0.40	2.12	5.30	88.1	87.2	+0.9	
—200 to +300	80	10	10	0.84	4.48	5.33	88.4	87.2	+1.2	
—300	80	10	10	0.72	3.92	5.44	90.00	87.2	+2.8	3.21

TABLE 6.—EFFECTS OF IMPURITIES.

(a) Effect of Quartz.

Composition				Peak area of Mg(OH) ₂ cm ² (a)	Peak area of kaolin cm ² (b)	b/a	%Kaolin from working curve	Theoretical %	Error
% Kaolin + %Mg(OH) ₂ + %Al ₂ O ₃ + %Quartz									
70	10	10	10	0.66	3.44	5.21	69.5		— 0.5
60	10	10	20	0.88	4.00	4.54	61.0		+ 1.0
50	10	10	30	1.00	3.76	3.76	51.5		+ 1.5
40	10	10	40	0.92	2.80	3.04	41.5		+ 1.5
30	10	10	50	0.72	1.60	2.22	31.5		+ 1.5

(b) Effect of Fe₂O₃

% Kaolin	+ %Mg (OH) ₂	+ %Al ₂ O ₃	+ %Fe ₂ O ₃	Peak area of Mg(OH) ₂ cm ² (a)	Peak area of kaolin cm ² (b)	b/a	%Kaolin from working curve	Theoretical %	Error
75	10	10	5						
70	10	10	10	0.72	3.36	4.66	62.8		— 7.2

(c) Effects of Hydrated Alumina Minerals.

% Bagh Clays	+ %Mg(OH) ₂	+ %Al ₂ O ₃	Peak area of Mg(OH) ₂ cm ² (a)	Peak area of kaolin cm ² (b)	b/a	%Kaolin from working curve	Theoretical %	Error
KLN 11-80	10	10						
KLN12-80	10	10	0.60	2.80	4.67	78.50	80.00	— 1.50

(d) Effects of Organic Material.

% Kaolin	+ %Mg (OH) ₂	+ %Al ₂ O ₃	+ %Wood	Peak area of Mg(OH) ₂ cm ² (a)	Peak area of kaolin cm ² (b)	b/a	%Kaolin from working curve	Theoretical %	Error
70	10	10	10						
75	10	10	5	0.80	3.28	4.10	54.5		—20.5
77.5	10	10	2.5	0.96	4.60	4.80	80.4		+ 2.9

(Fig. 3), thus creating a difficulty in the accurate measurement of the kaolinite endotherm. Complicated mathematical calculations may sometimes be needed for complete resolution. The results of the thermal analysis of the two samples KLN-11 and KLN-12 (Table VI) are interesting. The kaolinite content of KLN-12 (containing 10.85% diasporite) estimated by the present method is comparable with that of the normative content. The presence of higher percentages of diasporite (36.95%) in KLN-11 (Fig. 3) makes the measurement of the kaolinite endotherm totally unsatisfactory: the percentage of kaolinite estimated is 10.75%, whereas its known normative percentage is 50.55.

In certain clays, gibbsite (Al₂O₃·3H₂O) may also be present. The gibbsite endotherm lies

between 258° and 360°C, but the endotherm of the internal standard, magnesium hydroxide starts at 363°C, and so gibbsite does not significantly interfere with the quantitative estimation of the kaolinite.

(iv) *Organic Material*: Fireclays and ball clays often contain some organic matter, but because of the low cation-exchange capacity of kaolinite, the quantity of organic cations sorbed is small. The effect of organic matter was studied by mixing wood powder with the BDH kaolin. There is a great shift in the base line when the wood content exceeds 2.5% (Fig. 4). A quantitative estimation of kaolinite in the presence of higher amounts of organic matter is thus suspect; even the presence of 2.5% of wood gives slightly high kaolinite content (Table VI).

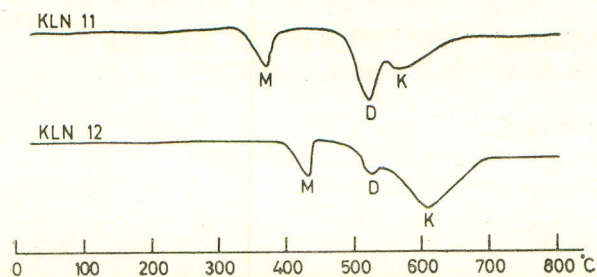


Fig. 3.—DTA curves of KLN 11 and KLN 12. M, D and K show endotherms of $Mg(OH)_2$, diaspore and kaolin respectively. (Not to the original scale).

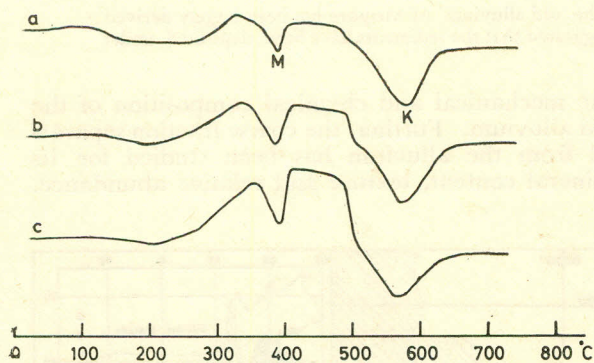


Fig. 4.—DTA curves of kaolin in presence of organic material (wood); the curves a, b and c contain 2.5, 5 and 10% wood respectively. (Not to the original scale)

Conclusions

The ratio of the areas of the kaolinite endotherm and the magnesium hydroxide endotherm, plotted against concentration gives a sensibly linear relationship, thus allowing quantitative estimation of the clay mineral. Variations in the results due to the particle size of the clay minerals, and the presence of quartz are not significant. However, the presence of large amounts of iron oxides, diaspore (or boehmite) or organic matter can interfere in the quantitative estimation.

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