

## THE QUANTITATIVE ESTIMATION OF KAOLINITE BY DIFFERENTIAL THERMAL ANALYSIS

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### ABSTRACT

The effect of variations in the amount, particle size, and degree of crystallinity of kaolinite on the area and shape of the endothermic peak at about 600° C. in the differential thermal curve of this mineral has been investigated. An empirical relationship has been established between the slope ratio of the peak and the ratio of the area to the width of the peak at half its amplitude and provides a method of quantitatively estimating kaolinite, regardless of its particle size distribution and degree of crystallinity.

### INTRODUCTION

In the examination of clays by the differential thermal method of analysis, the kaolinite content of a sample has often been estimated from the area of the endothermic peak at about 600° C. on the differential thermal curve. This has been justified by the theoretical work of Speil (1944) and Kerr and Kulp (1948) who have shown that the area of a peak on a differential thermal curve is proportional to the mass of the reacting substance. However, these theories do not take into account the effect of the degree of crystallinity and particle size of a substance upon the heat of reaction. The theoretical work of Shearer (1949) suggests that changes in particle size in the colloid range would have little influence on the heat of reaction, but Speil (1944) has found that the area of the endothermic peak at about 600° C. on the differential thermal curve of kaolinite decreases with decreasing particle size of the kaolinite. Grim (1947) has found that variations in size and perfection of crystallinity of particles of kaolinite appear to be reflected in variations in the intensity of the thermal reactions of the mineral. Also, Cole and Carthew (1953), in determining the kaolinite content of some clays, were not able to obtain agreement between estimates from differential thermal curves and those from chemical analyses without assuming that kaolinites of different degrees of crystallinity and/or particle size distribution have different heats of dehydration.

The effect of the degree of crystallinity and particle size distribution of kaolinite on the endothermic peak of the differential thermal curve has therefore been investigated and a method is proposed for quantitatively estimating kaolinite, regardless of these factors.

### EQUIPMENT AND PROCEDURE

The method of differential thermal analysis has been described in detail by Norton (1939), Grim and Rowland (1942) and others. The dif-

ferential thermal analysis equipment used in this investigation is that described by Carthew and Cole (1953) except that the sample block is now of 24-12 W (chromium-tungsten) heat-resistant steel, which does not scale or deform as did the 18-8 stainless steel previously used.

The procedure for packing the sample into the block was modified to ensure that the sample was uniformly distributed through the sample cavity. The sample was first packed into a hole of similar size to the sample cavity in a separate steel block, and, if necessary, calcined alumina was added to produce the usual tightness of packing obtained with finger tamping. The sample and calcined alumina were then removed from the hole and intimately mixed before being packed into the sample cavity. The rate of heating was  $10^{\circ}$  C. per minute.

#### THE EFFECT OF VARIOUS FACTORS ON THE DIFFERENTIAL THERMAL CURVE OF KAOLINITE

In this paper, kaolinite refers only to the mineral of that name and does not include the minerals "fireclay" and halloysite. The differential thermal curve of kaolinite shows a large endothermic peak at about  $620^{\circ}$  C. and an intense exothermic one at about  $980^{\circ}$  C. The endothermic reaction is the loss of (OH) from the kaolinite structure and the exothermic reaction is the crystallization of  $\gamma$ -alumina from the amorphous product of the decomposition of the kaolinite. In addition to these two peaks, the differential thermal curve of very well crystallized kaolinite shows a slight endothermic dip immediately before the exothermic peak. This reaction is the breakdown of the meta-kaolin structure which remains after the dehydration of the kaolinite.

##### (1) Amount

To study the effect of varying amounts of kaolinite on the endothermic peak at about  $620^{\circ}$  C., differential thermal curves were prepared (Fig. 1) from different weights of a fairly pure kaolinite (checked by  $x$ -ray examination) from Gordon, Victoria. This kaolinite is well crystallized, as shown by its differential thermal curve (*A*, Fig. 1).

The areas of the endothermic peaks of the differential thermal curves were measured by planimeter and are set out in Table 1. From Fig. 2 it can be seen that the relation between the area of the peak and the weight of kaolinite is not strictly linear. This departure from linearity is due to the variation of the thermal conductivity of the material in the sample cavity with different weights of kaolinite.

The shape of the endothermic peak was determined by measuring the ratio of the slope of the low temperature to the high temperature sides of the peak (the slope ratio) and the width of the peak at half its amplitude

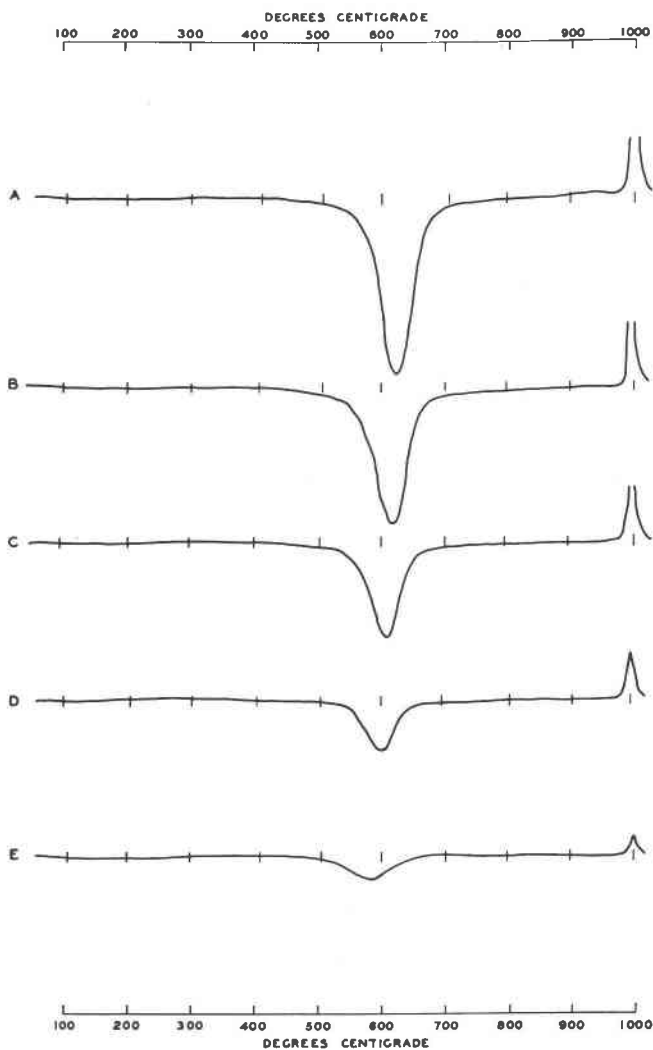


FIG. 1. Differential thermal curves of various weights of kaolinite. A, 0.8g; B, 0.65g; C, 0.5g; D, 0.3g; E, 0.15g.

(henceforth referred to as the width of the peak). The slope ratio was measured by the method of Bramao *et al.* (1952), the slope of the sides being taken as that of the tangents to the sides from the deepest point of the peak. The slope ratios and widths of the endothermic peaks of the curves shown in Fig. 1 are listed in Table 1, except for curve E in which the peak was too shallow for accurate measurement. The slope ratio ap-

TABLE 1. CHARACTERISTICS OF THE ENDOTHERMIC PEAK FOR VARIOUS WEIGHTS OF GORDON KAOLINITE

Weight	Area of Peak	Slope Ratio	Width of Peak	Ratio $A/W$
0.8g.	11.9 sq. cm.	1.18	1.46 cm.	8.15
0.65	9.35	1.24	1.41	6.63
0.5	6.3	1.24	1.29	4.88
0.3	3.15	1.22	1.20	2.63
0.15	1.5	—	—	—

pears to be independent of the amount of kaolinite, whereas the width of the peak decreases with the amount.

### (2) Particle Size

To examine the effect of variations in particle size on the endothermic peak, the kaolinite from Gordon, Victoria, was separated into various size fractions by sedimentation methods, including the use of a Sharples supercentrifuge. Fractions in which the equivalent diameters of the particles were  $> 2$ , 2-1, 1-0.5, 0.5-0.25, and 0.25-0.1 microns were obtained and differential thermal curves were prepared from 0.8 g. of each fraction.

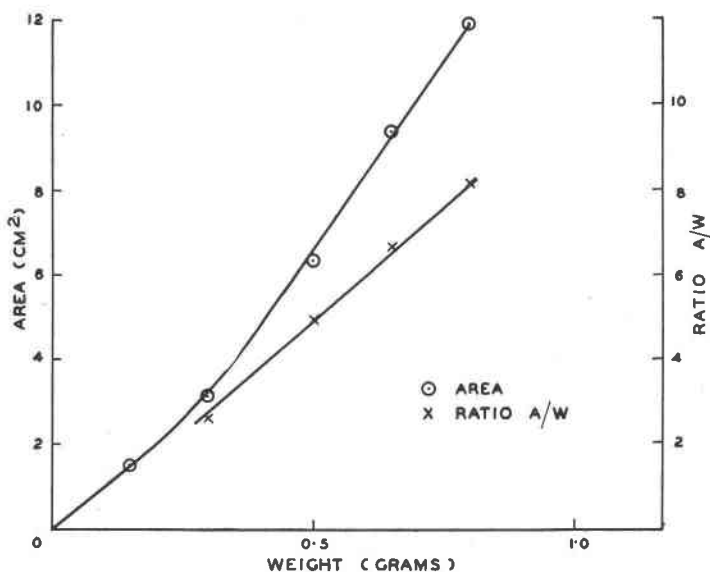


FIG. 2. Relation of the area and the ratio  $A/W$  of the endothermic peak to the weight of kaolinite.

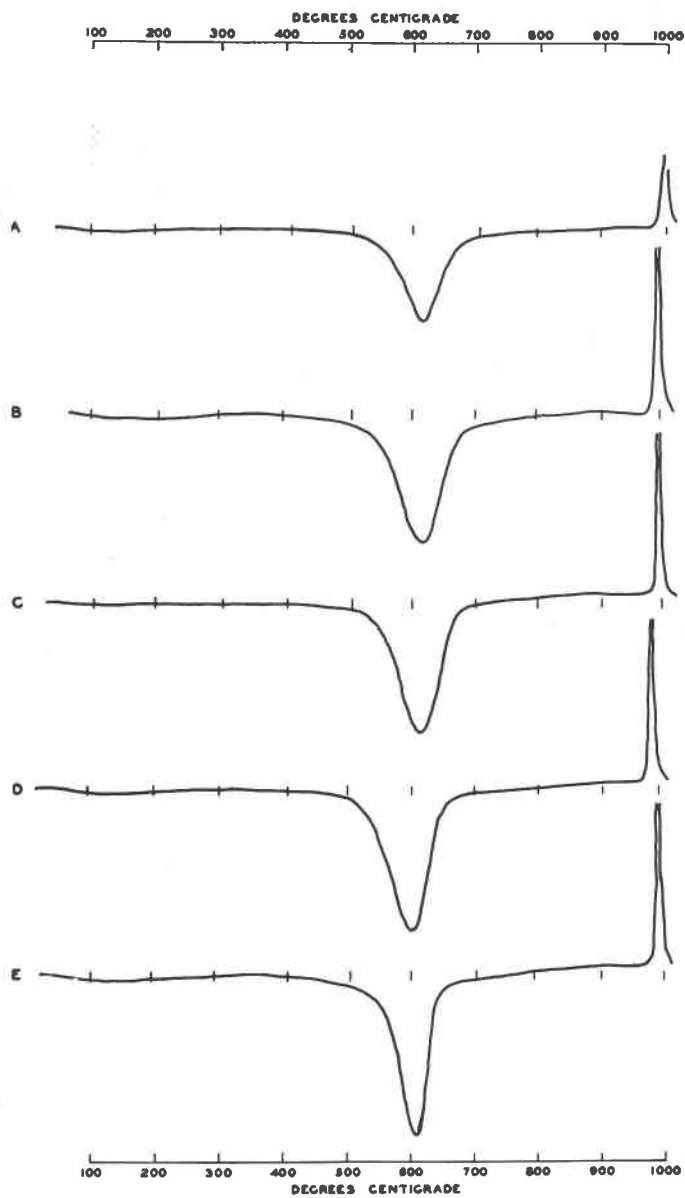


FIG. 3. Differential thermal curves of various particle size fractions of kaolinite.  
A, >2 $\mu$ ; B, 2-1 $\mu$ ; C, 1-0.5 $\mu$ ; D, 0.5-0.25 $\mu$ ; E, 0.25-0.1 $\mu$ .

TABLE 2. CHARACTERISTICS OF THE ENDOTHERMIC PEAK FOR VARIOUS PARTICLE SIZE FRACTIONS OF GORDON KAOLINITE

Fraction	Area of Peak	Slope Ratio	Width of Peak	Ratio $A/W$
>2 microns	8.3 sq. cm.	1.25	1.28 cm.	6.48
2-1	11.8	1.25	1.82	6.48
1-0.5	11.9	1.36	1.79	6.65
0.5-0.25	12.4	1.52	1.61	7.70
0.25-0.1	11.5	1.88	1.35	8.52

The kaolinite in every fraction is well crystallized, as can be seen from the differential thermal curves in Fig. 3.

The areas of the endothermic peaks are given in Table 2, and, except for the >2 micron fraction, are very similar. This is contrary to the results of Speil (1944) who has found that the area of the endothermic peak decreases with the particle size of kaolinite. However, Spiel obtained his particle size fractions by a grinding process, which could reduce the degree of crystallinity of the kaolinite. This supposition is supported by the differential thermal curves of his fine particle size fractions. The area of the peak given by the >2 micron fraction cannot be explained by the presence of impurities, as *x*-ray examination of this fraction has revealed less than 5 per cent quartz as the only impurity.

The slope ratios and widths of the endothermic peaks are listed in Table 2, from which it can be seen that the slope ratio increases as the particle size of the kaolinite decreases whereas the width of the peak, except for the >2 micron fraction, decreases with particle size. This increase in asymmetry of the peak with decreasing particle size has been observed by previous workers. The explanation given by Bramao *et al.* (1952) is that the smaller the particle size of a sample, the greater the number of reaction centres or nuclei formed and the less the amount of kaolinite dehydrated per nucleus. Accordingly, the amount of kaolinite dehydrated by the time the maximum differential temperature is reached (i.e. at the deepest point of the peak) varies inversely with the particle size. Consequently, the return of the differential temperature to zero is faster for the smaller particle size sample, as less kaolinite remains to be dehydrated.

### (3) Degree of Crystallinity

In this investigation, the term "degree of crystallinity" refers to the perfection of the crystal organization of the kaolinite and not to the size of the crystal.

TABLE 3. CHARACTERISTICS OF THE ENDOTHERMIC PEAK FOR THE 2-1 MICRON FRACTIONS OF DIFFERENT KAOLINITES

Locality	Area of Peak	Slope Ratio	Width of Peak	Ratio $A/W$
Gordon, Vic.	11.9 sq. cm.	1.25	1.81 cm.	6.57
S. Aust.	11.0	1.49	1.48	7.43
Langley, S.C., U.S.A.	10.6	1.52	1.34	7.91
Surges Bay, Tas.	10.1	1.56	1.25	8.08
Engadine, N.S.W.	9.7	1.85	1.17	8.29

The effect of variations in the degree of crystallinity of kaolinite on the endothermic peak was studied from samples of five kaolinites from different localities (see Table 3). In order to avoid any effect on the endothermic peaks due to different particle size distributions of these samples, the same particle size fraction of each sample was studied. The 2-1 micron fraction was chosen because the slope ratio varied least in this range of particle size. This fraction was separated from each sample by sedimentation methods and 0.8 g. of it used to prepare a differential thermal curve. The fraction of each sample consisted of fairly pure kaolinite (checked by  $x$ -ray examination).

The differential thermal curves are shown in Fig. 4 and the areas of the endothermic peaks are given in Table 3. The degree of crystallinity of the kaolinite decreases with the area of the endothermic peak. Previous workers have found that the sharpness of the exothermic peak decreases with the degree of crystallinity of kaolinite, and this effect may be seen in the differential thermal curve of the sample from Engadine (*E*, Fig. 4). This curve also shows an endothermic peak at about 130° C., which is characteristic of poorly crystallized kaolinite and is due to the loss of adsorbed water.

The slope ratios and widths of the endothermic peaks are given in Table 3, the slope ratio increasing as the degree of crystallinity of kaolinite decreases, whilst the width of the peak decreases with the degree of crystallinity. This change in the shape of the peak is very similar to that found with decreasing particle size and may be explained in a similar manner. It is probable that more reaction centres or nuclei are formed in poorly crystallized than in well crystallized kaolinite.

#### THE QUANTITATIVE ESTIMATION OF KAOLINITE

In the quantitative estimation of kaolinite from the endothermic peak of the differential thermal curve, the degree of crystallinity of the kaolinite must be taken into account. This cannot be assessed from the

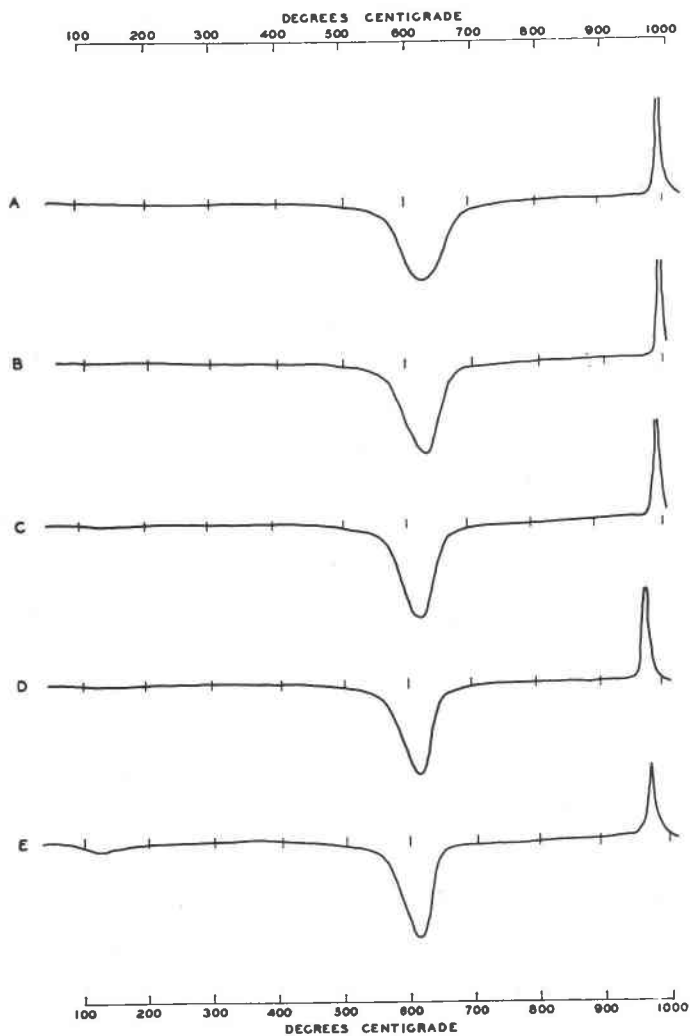


FIG. 4. Differential thermal curves of the 2-1 micron fractions of different kaolinites.  
A, Gordon; B, S. Aust.; C, Langley; D, Surges Bay; E, Engadine.

shape of the endothermic peak as the shape is affected also by the particle size distribution of the sample. Furthermore, an empirical relationship between the area of the peak and a characteristic of the shape (such as the slope ratio) is not possible, as the shape of the peak varies with the particle size distribution of kaolinite whilst the area remains constant.



The ratio of the area to the width of the endothermic peak (henceforth referred to as the ratio  $A/W$ ) has been found to be roughly proportional to the weight of kaolinite (see Fig. 2). From Tables 2 and 3, it is seen that the ratio  $A/W$  increases as both the particle size and the degree of crystallinity decrease. Since the slope ratio of the peak also has been shown to increase as the particle size and the degree of crystallinity decrease, the relationship between the slope ratio and the ratio  $A/W$  was investigated. The ratio  $A/W$  was plotted against the slope ratio for the various particle size fractions and also for the 2-1 micron fractions of the different kaolinites. It was found that one straight line could be drawn through both sets of points (Fig. 5) i.e. the relationship between the ratio  $A/W$  and the slope ratio for variations in the particle size of kaolinite is the same as that for variations in the degree of crystallinity. Thus the endothermic peak from 0.8 g. of any kaolinite, regardless of particle size distribution and degree of crystallinity, gives a point on this curve.

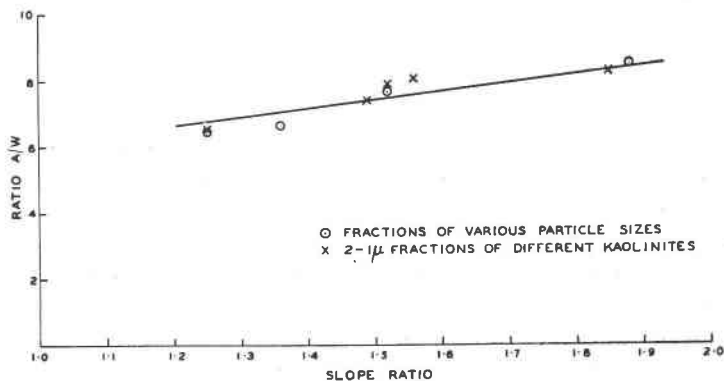


FIG. 5. Relation between the ratio  $A/W$  and the slope ratio of the endothermic peak of kaolinite.

Since the ratio  $A/W$  has been found to be roughly proportional to the weight of kaolinite, the empirical relationship of Fig. 5 may be used to estimate the kaolinite content of a clay. A differential thermal curve is prepared from 0.8 g. of the clay, the slope ratio of the endothermic peak is measured and the corresponding ratio  $A/W$  is read from Fig. 5. The weight of kaolinite in the sample is given by:

$$\frac{\text{Ratio } A/W \text{ (measured from peak)}}{\text{Ratio } A/W \text{ (read from Fig. 5)}} \times 0.8 \text{ grams.} \quad (1)$$

Estimations by this method of the kaolinite content of clays agree well with those from chemical analyses for both poorly and well crystallized kaolinites. In Table 4 estimations of the kaolinite content of some clays

based on chemical, *x*-ray and differential thermal evidence (Cole and Carthew 1953) are compared with estimations by the new method and also with estimations based on the area of the endothermic peak without regard to the degree of crystallinity of the kaolinite.

TABLE 4. ESTIMATIONS OF THE KAOLINITE CONTENT OF SIX CLAYS BY VARIOUS METHODS

Locality of Clay	From Chemical, <i>x</i> -ray and Thermal Evidence*	Using Expression (1)	From Area of Endothermic Peak
St. Helens, Tas. (1)	75%	80%	62%
St. Helens, Tas. (2)	55	59	38
Sth. Mt. Cameron, Tas.	75	76	64
Surges Bay, Tas.	65	61	45
Dover, Tas. (1)	65	64	47
Dover, Tas. (2)	30	32	21

\* Cole and Carthew 1953.

#### CONCLUSIONS

The area of the endothermic peak on the differential thermal curve of kaolinite does not give a strictly linear relationship with the weight of the material when calcined alumina is used as a thermally inert material in the sample.

Variations below 2 microns in the particle size of kaolinite appear to have little effect on the heat of dehydration, which decreases with the degree of crystallinity of kaolinite.

The slope ratio of the endothermic peak is independent of the amount of kaolinite, but increases as both the particle size and the degree of crystallinity of kaolinite decrease.

The ratio of the area to the width at half the amplitude of the endothermic peak is practically proportional to the weight of kaolinite and increases as both the particle size and the degree of crystallinity of kaolinite decrease.

The ratio of the area to the width at half the amplitude of the endothermic peak increases with the slope ratio and this empirical relationship provides a method of quantitatively estimating kaolinite of any particle size distribution and degree of crystallinity.

#### ACKNOWLEDGMENT

The author wishes to thank Dr. W. F. Cole of this Division for suggesting the problem and for helpful advice during the work.

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*Manuscript received Feb. 16, 1954*