QUANTITATIVE ANALYSIS OF ENDELLITE, HALLOYSITE AND KAOLINITE BY DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

A determination of the relative amounts of endellite versus kaolinite and/or halloysite in a sample is obtained by the differential thermal analysis technique. When a sample containing a mixture of these clay minerals is saturated with ethylene glycol and a differential thermal curve obtained, the kaolinite and/or halloysite gives the usual endothermal reaction at approximately 575° C., whereas the endellite-ethylene glycol complex results in a new endothermal peak at 500° C. Standard reference curves for a series of mixtures of the endellite complex and kaolinite (or halloysite) were obtained and a graph made utilizing the ratios of the two peak heights to give a quantitative measure of the minerals. Values obtained were within 3% of the weighed amount of the given clay in the standard mixtures. Three dissimilar differential thermal analysis units were used to test the method and the effect of impurities on the curves was evaluated.

INTRODUCTION

In the investigation of clays containing the members of the kaolin group—endellite, halloysite, and kaolinite, it has been possible only to estimate the amounts of the three similar varieties by the usual techniques of clay mineral analysis. A partial solution to the problem of obtaining a quantitative mineralogical analysis is offered by a differential thermal technique which gives the amount of endellite versus halloysite and/or kaolinite in a sample.

As Bradley (1946) and MacEwan (1948) have shown, various polar organic liquids will replace the interlayer water in endellite. When differential thermal analyses were run on certain of these endellite-organic liquid complexes, such as endellite with ethylene glycol, di- and tri-ethylene glycol, and glycerine, the endothermal peak usually occurring at approximately 575° C. was lowered to 500° C. Since this did not happen with kaolinite or halloysite, which do not form the complex, it became evident that this phenomenon might be used as the basis of a method for determining the amount of endellite versus kaolinite and/or halloysite in a sample.

OBTAINING STANDARD REFERENCE PATTERNS

Endellite from the Dragon Mine, Eureka, Utah, and ethylene glycol were used to form the complex by shaking the clay (aggregate size between 80 and 200 mesh) in an excess of the glycol for five minutes. The suspension was centrifuged at 3,000 rpm and the liquid decanted. Excess ethylene glycol was removed by working the complex on retentive filter

paper. Halloysite produced by dehydrating the endellite at 110° C. was treated in exactly the same manner so that proportional weights of halloysite and endellite-glycol complex were obtained. (Placing the halloysite and endellite complex in a controlled atmosphere might give better standard mixtures, but the stability of the complexes has not yet been worked out and there is the possibility of some of the endellite changing to halloysite. This remains, however, as a possible future refinement of the method.) Ethylene glycol was added to the weighed mixture which was then worked into the consistency of a thick paste and run on the differential thermal unit.

The apparatus used for obtaining the patterns shown in Fig. 1 is similar to that described by Kerr and Kulp (1948). The sample holder is a nickel block with a $\frac{1}{4}''$ dia.$\times \frac{3}{8}''$ hole to contain the sample and covered with a nickel lid. Calcined alumina is used as reference material. The sample block is placed on top of a vertically mounted muffle tube over which a furnace is lowered. The rate of heating is 10° C./min. and the differential thermal effect is recorded on an automatically recording Leeds and Northrup Speedomax potentiometer using a sensitivity scale on the preamplifier providing a full-scale deflection of 0.6 millivolts for chromel-alumel thermocouples on the Speedomax chart. The chart moves at a rate of 6 inches/hr. to give a temperature interval of 100° C./inch.

A series of twenty-one mixtures at 5% intervals was prepared and run, and the curves in Fig. 1 are the endothermal doublets obtained for the standard mixtures. The endothermal peak at 500° C. represents the structural water leaving the endellite complex while the 575° C. peak represents structural water leaving the halloysite. There is a drift to the exothermal side due to the smaller specific heat capacity of the sample than of the standard, so the base line is drawn as in Fig. 3.

Kaolinite from Langley, South Carolina, was substituted for halloysite and mixtures of kaolinite and the endellite complex were also run on the *DTA* unit. Since it was found that kaolinite gave the same peak intensity as halloysite, this method gives the relative amounts of endellite versus halloysite and/or kaolinite in a sample. Where all three minerals are present in a sample other techniques must be used to obtain the proportion of kaolinite and halloysite. Recent base-exchange capacity determinations have suggested a method of quantitatively determining the amounts of kaolinite versus halloysite and/or endellite in mixtures. In special cases where the kaolinite occurs as coarser vermicular crystals, either point counts can be made of the thin sections (Chayes, 1949), or the kaolinite crystals may be fractioned off leaving the fine fractions consisting only of halloysite and endellite.
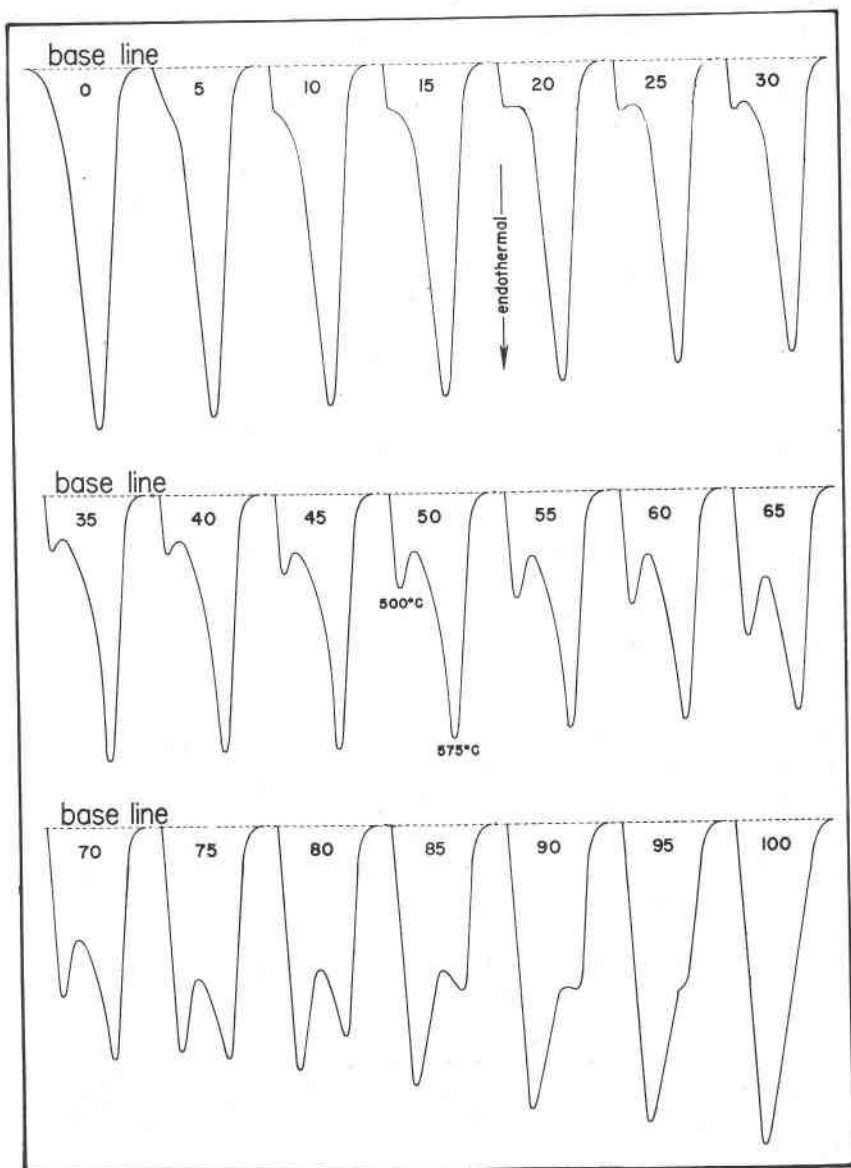
FIG. 1. Differential thermal patterns of standard mixtures containing endellite and halloysite. Percentages are given for content of endellite.

The patterns in Fig. 1 are used for direct comparison with those obtained from unknown mixtures and are especially useful in the low and high percentage mixtures.

GRAPHICAL SOLUTION

For the mixtures between 20% and 80% of one component, it is preferable to use the graph shown in Fig. 2. Here the ratio of the height of the 500° C. peak from base line (E) to the height of the 575° C. peak (H) is plotted along the logarithmic ordinate and the percentage of endellite
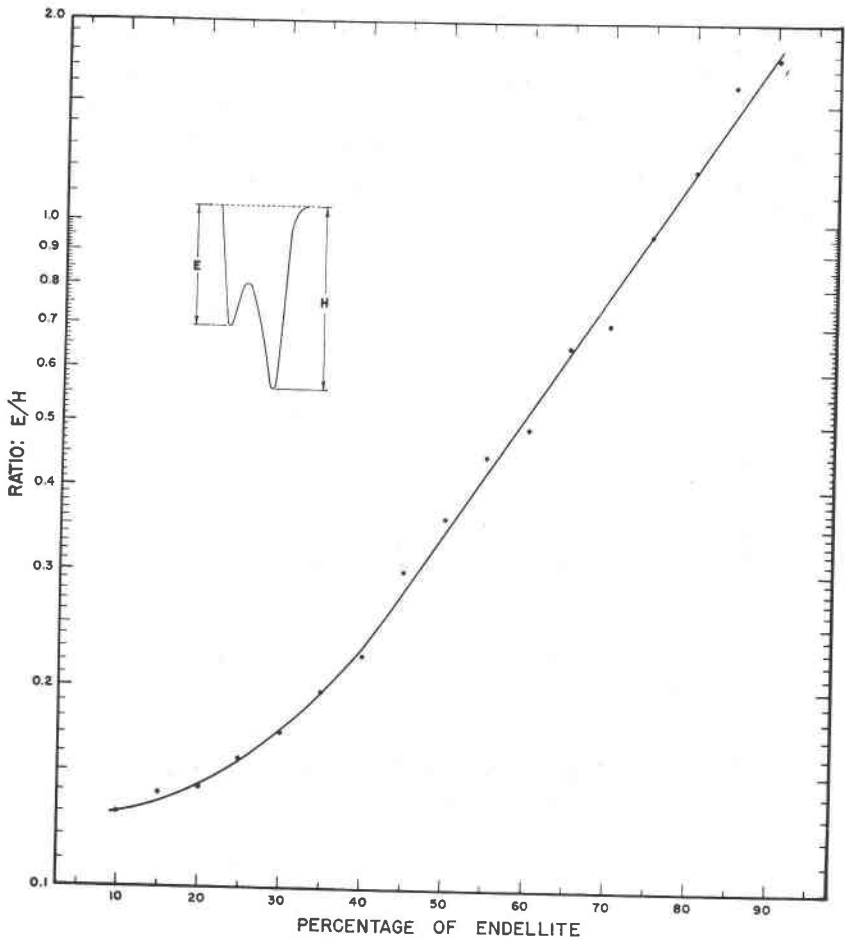

FIG. 2. Graphical solution for obtaining the percentage of endellite in a mixture with halloysite and/or kaolinite.

in the mixture along the abscissa. The ratios as obtained from the standard patterns are as follows:

% Endellite	Ratio: E/H	% Endellite	Ratio: E/H
10	.130	55	.450
15	.138	60	.496
20	.142	65	.660
25	.157	70	.720
30	.172	75	.980
35	.198	80	1.16
40	.226	85	1.60
45	.302	90	1.78

For manually recording potentiometers, where a continuous pattern is not obtained, the graphical solution, which necessitates only the measurement of maximum peak heights, is superior to direct comparison with the reference curves. The over-all accuracy of both methods using our apparatus is $\pm 3\%$ and might be improved by refinement of technique in preparing the standards. It is essential that the base line be established as in Fig. 3. An exothermal peak occurs just before the 500° peak but the return of the 575° peak is to base line.
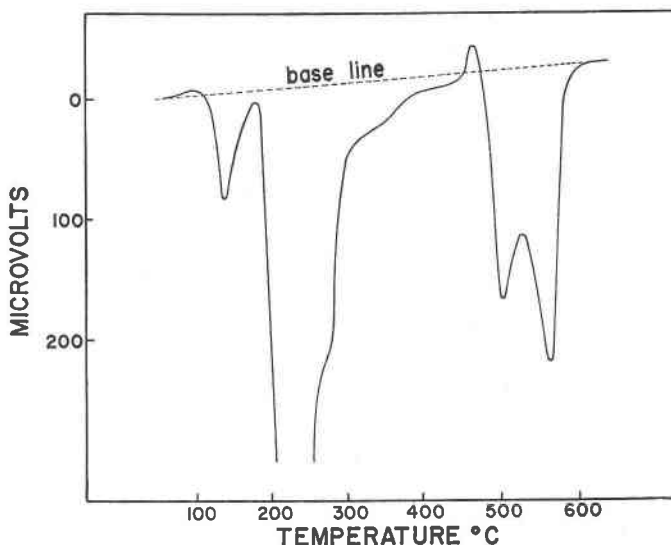

Fig. 3. Differential thermal analysis pattern of a mixture containing 72% endellite-ethylene glycol complex and 28% halloysite.

Preparation of Unknown for Analysis

The unknown sample should be mulled in water so the clay aggregate will wet sieve through 80 mesh and be caught on 200 mesh. The

clay-water suspension is centrifuged in 15 ml. tubes and the clear water decanted. A large excess of ethylene glycol is added to the wet clay and the tube vigorously shaken for five minutes. This is centrifuged at 3,000 rpm for about fifteen minutes and the clear ethylene glycol decanted. The resulting clay-glycol suspension is of the right consistency for differential thermal analysis. (If no centrifuge is available the excess glycol may be removed by working the mixture on filter paper.) If the clay aggregate size is below ten microns, the suspension after centrifugation is not sufficiently compact and the ethylene glycol must be evaporated in an oven until the suspension has the proper consistency.

Effect of Impurities

Since samples to be analyzed for content of the kaolin minerals usually contain other minerals, the effect of impurities on the curves was studied. A mixed layer dioctahedral 2:1 clay, an expanded dioctahedral 2:1 clay, quartz and mica were selected as minerals commonly associated with kaolinite and halloysite, and mixtures of these with the endellite complex were run on the differential thermal analysis unit.

The mixed layer clay was a K-bentonite from Oak Hall, Pennsylvania, containing 20% expanded and 80% non-expanded layers (Weaver and Bates, 1952). A mixture of 25% of this material and 75% endellite complex yielded a curve (Fig. 4a) which is similar to that obtained for 95% endellite and 5% halloysite. A mixture of 50% mixed layer clay and 50% endellite complex gave curve 4b which is similar to 90% endellite and 10% halloysite. A mixture of 50% mixed layer clay, 25% endellite complex, and 25% halloysite gave a curve similar to 42% endellite and 58% halloysite. 10% mixed layer clay in the mixture had no evident effect on the shape of the curve.

The expanded 2:1 clay (montmorillonite from Polkville, Mississippi) had no effect on the curves except to decrease the peak heights.

Vein quartz from Washington, D. C. gave a sharp peak at 573.5° C. which was used as the temperature reference. When ground to 200 mesh and mixed with the endellite complex the quartz had the same effect as the mixed layer clay in causing the halloysite peak to be present to a degree equal to about one-fifth the amount of impurity present in the sample. Curves of a series of quartz-endellite complex mixtures are shown in Fig. 4c, d, e.

Muscovite ground to 200 mesh had the same effect on the curves as the mixed layer clay and quartz.

The effect of impurities, as shown by these curves, is to dampen the peak intensities and produce an erroneous halloysite or kaolinite peak which in magnitude is approximately equal to one-fifth of the amount of impurity present. Less than 10% of impurity in the sample will only
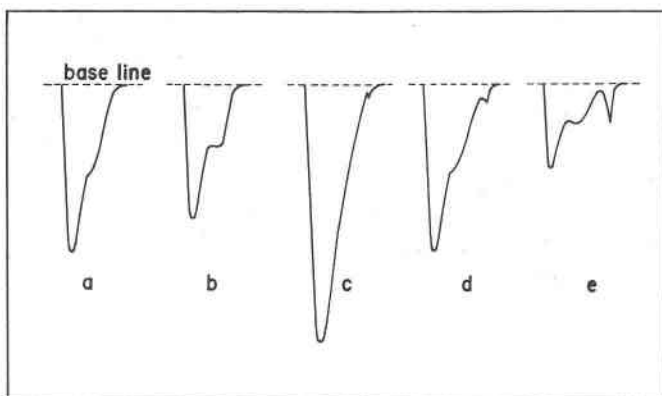
Fig. 4

a. 25% illite and 75% endellite-ethylene glycol complex.
b. 50% illite and 50% endellite-ethylene glycol complex.
c. 10% quartz and 90% endellite-ethylene glycol complex.
d. 25% quartz and 75% endellite-ethylene glycol complex.
e. 50% quartz and 50% endellite-ethylene glycol complex.

cause dampening. Because of its ability to retain the glycol, the expanded 2:1 clay is the only commonly associated mineral which in amounts greater than 10% has no effect on the shape of the curve. The erroneous halloysite or kaolinite peak is produced in the case of the other impurities presumably because there is insufficient glycol retained in the mixture and a small amount of the endellite changes to halloysite. This will also happen if a cover is not placed over the sample, or if the amount of sample is too small or not of the correct consistency.

ANALYSIS ON OTHER DIFFERENTIAL THERMAL ANALYSIS UNITS

To test the application of the method using dissimilar differential thermal analysis units, samples were run on Mr. R. M. Gruver's apparatus in the Division of Ceramics and on Dr. C. D. Jeffries' unit in the Department of Agronomy. These units are described in the respective papers by these authors. Mr. Gruver's unit consists of a horizontally mounted furnace and sample holders which are 1.3 ml. platinum crucibles with covers. The rate of heating is automatically controlled and the differential thermal effects automatically recorded on a Brown potentiometer. Dr. Jeffries uses a large nickel block with cover which holds a two gram sample and is placed in a horizontally mounted furnace. The heating rate is maintained by manually increasing the Variac setting while the temperature and differential thermal effect are measured by reading deflections on a Rubicon 3400H galvanometer.

The two units produced curves which gave values to within ±5% of

those obtained on our unit and which were also sensitive to a minimum of 5% of one component. Greater accuracy could be obtained by running a series of standard mixtures on each unit. It seems apparent that almost any type of apparatus may be used providing the following procedures are observed:

1. Not less than 0.6 ml. of sample should be used.
2. The sample should have the consistency of a thick paste.
3. A lid should cover the sample.
4. Rate of heating should approximate 10° C./min.

SUMMARY

A differential thermal analysis technique is suggested for quantitative analysis of the relative amounts of endellite versus halloysite and/or kaolinite in a sample. The endellite-ethylene glycol complex was found to have an endothermal peak at 500° C. as contrasted with the usual halloysite and kaolinite peak at about 575° C. A series of mixtures of endellite complex and halloysite and of endellite complex and kaolinite were run. A graphical solution is also presented utilizing ratios of the peak heights. The effect of four common impurities has been evaluated and the method has been tested on two other differential thermal units.

ACKNOWLEDGMENTS

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Manuscript received July 5, 1952.