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REPORT OF INVESTIGATIONS—NO. 96

DIFFERENTIAL THERMAL ANALYSIS OF CLAYS AND SHALES, A CONTROL AND PROSPECTING METHOD

BY
R. E. GRIM AND R. A. ROWLAND

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URBANA, ILLINOIS
1944

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This report is a Contribution of the Petrography Division.

March 1, 1944

DIFFERENTIAL THERMAL ANALYSIS OF CLAYS AND SHALES, A CONTROL AND PROSPECTING METHOD*

By

R. E. Grim and R. A. Rowland

Abstract

The differential thermal method, by determining the thermal reactions undergone by a clay or shale, is a rapid means of identifying the mineral components of such materials, and because the properties of clays and shales depend largely on their mineral composition, it is at the same time a rapid method of evaluating the properties of such materials.

Differential thermal analyses are presented for the pure forms and synthetic mixtures of the common components of clays and shales, namely, kaolinite, halloysite, illite, montmorillonite, quartz, gibbsite, boehmite, diaspore, dolomite, calcite, gypsum, organic material, pyrite, marcasite, goethite, and limonite.

Differential thermal analyses are presented also for a variety of well-known types of clays, and on the basis of the thermal data for the pure components, the mineral composition is indicated. The correlation of mineral composition of clays and shales (as reflected in the differential thermal curves) with the ceramic properties is discussed as a basis for using this thermal method for indicating the properties of such materials.

Finally, differential thermal analyses are presented for sequences of samples from the pits of several operating clay products plants in order to illustrate the way in which the method can be applied in prospecting and in plant control.

I. Introduction

STUDENTS of clay materials are now generally agreed that clays and shales are composed essentially of extremely minute crystalline particles of one or more members of a small group of minerals known as the clay minerals.[1] The important clay minerals are primarily hydrous aluminum and/or iron silicate compounds, and when heated to the fusion point they are subject to a series of thermal reactions which accompany the loss of water and changes in crystal structure. The intensity of the thermal reactions and the temperatures at which they take place are not the same for all clay minerals because each contains different amounts of water which is lost at different temperatures and because all clay minerals do not undergo the same changes in crystal structure on heating.

A determination of the thermal reactions of a clay therefore provides data for the identification of its mineral composition.

The differential thermal analytical procedure consists of heating the material at a constant rate up to 1000°C., or as close to fusion as is possible experimentally, and recording, by suitable devices, the intensity of the endothermic and exothermic effects and the temperatures at which they take place.

The properties of clays and shales depend to a large extent on their clay-mineral composition.[2] It is usually possible, therefore, to predict certain properties of clays and shales from a determination of their clay-mineral content. The differential thermal procedure yields analytical data for the determination of the mineral composition of a clay in less than two hours. It is, therefore, a rapid method of getting important data regarding the properties of a clay or shale. The speed of the method should make it valuable in plant practice, for example, in detecting variations in the ceramic properties of clays that look alike in the outcrop before they can cause trouble in the manufacturing process. In the past,

*Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 20, 1943 (Structural Clay Products Division). Received January 10, 1944.

[1]R. E. Grim, Modern Concepts of Clay Materials, *Jour. Geol.*, vol. 50, No. 3, pp. 225–75 (1942); *Ceram. Abs.*, vol. 21, No. 8, p. 177, 1942; *Illinois State Geol. Survey Rept. Investigations*, No. 80, 50 pp., 1942.

[2]R. E. Grim, Relation of Composition to Properties of Clay, *Jour. Amer. Ceram. Soc.*, vol. 22, No. 5, pp. 141–51 (1939); *Illinois State Geol. Survey, Information Circ.*, No. 45, 11 pp. (1939).

the only rapid methods available required expensive equipment and highly skilled manipulation.

There are some ceramic properties, such as fired color, that are not revealed by the differential thermal method. Where such properties are important, the method is not adequate for plant control or prospecting. The study of a large number of samples has shown, however, that in most cases the significant variations that occur in the particular clays used in an operation are indicated by this method. It will be shown also that the use of the method in a plant must follow preliminary work that correlates the differential curve characteristics and the ceramic properties of the particular clays to be used. After such a correlation has been established, the procedure becomes routine, and quantitative results may be obtained.

The present paper records differential thermal analyses for the clay-mineral and nonclay-mineral components of clays as well as natural and synthetic mixtures of these minerals. It records also thermal analyses for a variety of clay materials and attempts to show how such analyses may be used practically to evaluate the properties of clays.
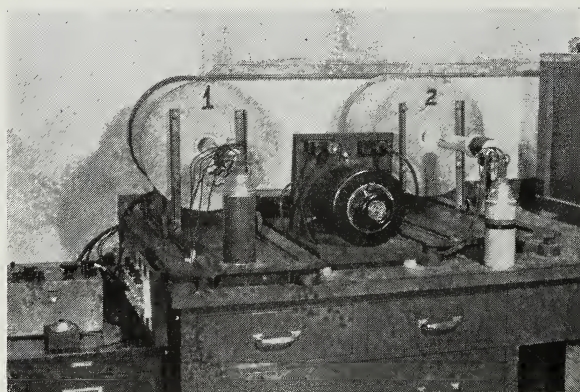

Fig. 1.—Thermal furnace setup showing two furnaces with auto-transformer and potentiometer that can be switched to either furnace.

II. Apparatus and Analytical Procedure

The differential thermal analyses presented herein were made in a furnace consisting of a horizontal tube of Alundum, 12 in. long and 2 in. inside diameter, wound in the middle with 46 ft. of coiled Kanthal A wire and surrounded with 4 in. of refractory insulating brick. A heating rate of approximately 10°C. per minute was obtained by placing a motor-driven autotransformer in the line (Figs. 1 and 2).

The specimen holder was a nickel block 1 in. square and $\frac{5}{8}$ in. deep with four holes each $\frac{1}{4}$ in. in diameter and $\frac{3}{8}$ in. deep, mounted on an Alundum cylinder that fitted inside the furnace tube. The sample was placed in one of the holes of the specimen holder, and calcined aluminum oxide (which undergoes no thermal reaction up to 1000°C.) was placed in the other three holes. A platinum-platinum 10% rhodium thermocouple with the junction in one of the masses of aluminum oxide was attached to a reflecting galvanometer, and the furnace temperature was recorded photographically. A similar thermocouple was placed in another of the masses of aluminum oxide and attached to a potentiometer. The readings from the potentiometer were flashed onto the photographic record in order to evaluate the curve recording the furnace temperature.

A double-junction differential thermocouple, consisting of two platinum leads joined by platinum 10% rhodium wire, was placed with one junction in the sample and the other in the remaining mass of aluminum oxide. When the
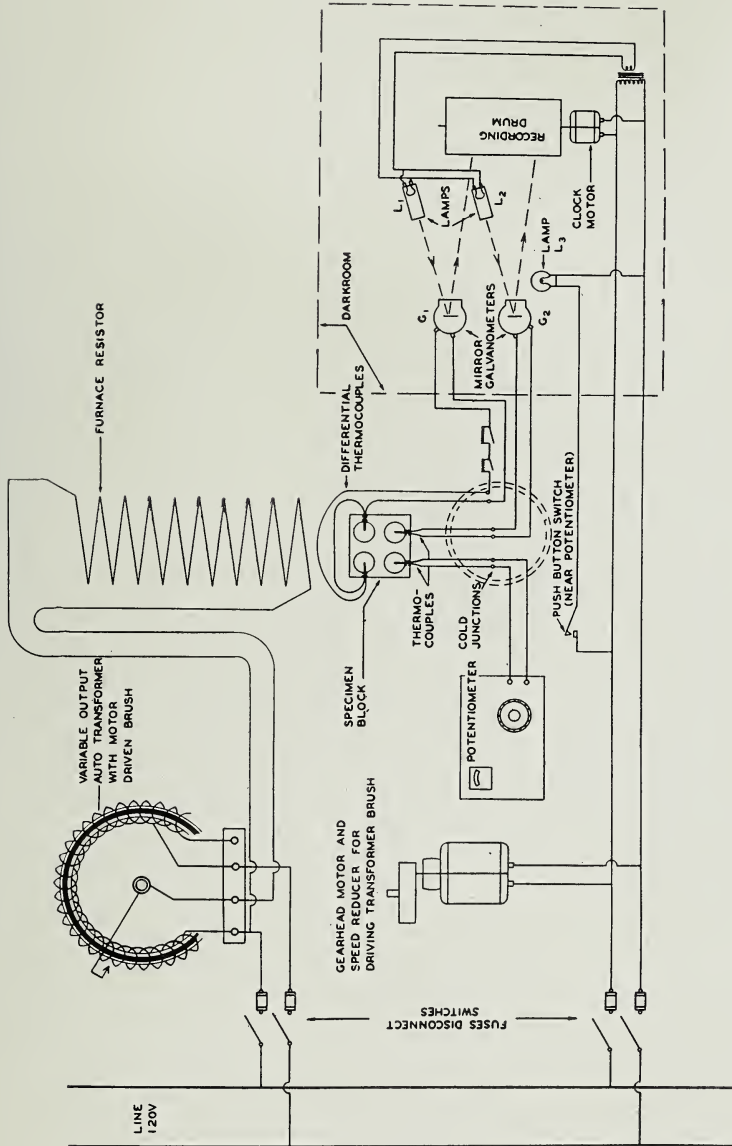
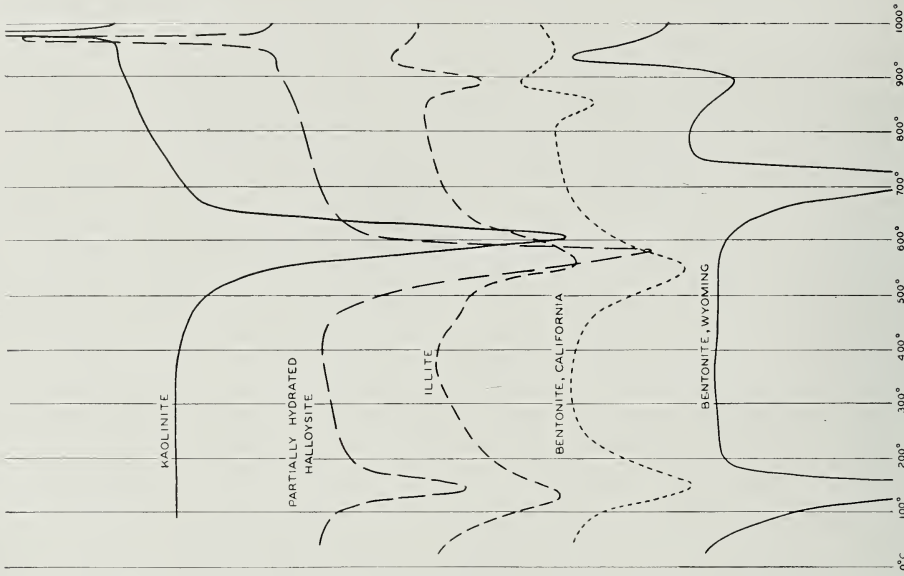Fig. 2.—Wiring diagram of differential thermal analysis furnace setup.

Fig. 4.—Typical clay minerals and clays; kaolinite and hydrated halloysite, scale B; illite and bentonites, scale A (scales on Fig. 3).
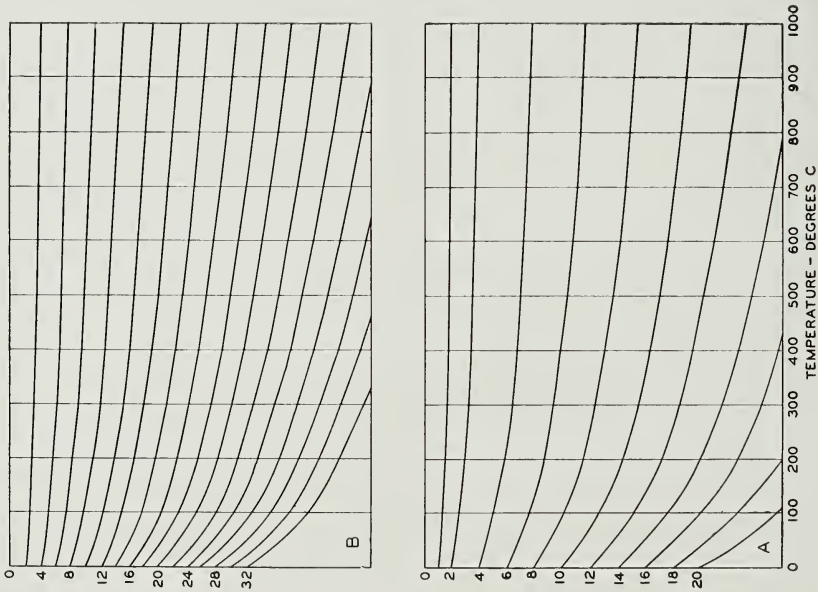
Fig. 3.—Vertical scales for Figs. 4 to 14; these scales indicate temperature differences in degrees as recorded by peaks of thermal curves; scale A = 100 ohms series resistance; scale B = 200 ohms series resistance.

temperature of the sample was greater or less than that of the aluminum oxide because of a thermal reaction, a potential difference was set up in the thermocouple. The differential thermocouple was attached to a second reflecting galvanometer and the temperature differences were recorded photographically on the same sheet used to record the furnace temperature.

By varying the series resistance in the differential thermocouple circuit, different vertical exaggerations can be obtained for the same temperature difference. Resistances up to 400 ohms were used, and on the diagrams (Figs. 4 to 17) scale A represents 100 ohms and scale B represents 200 ohms series resistance. Varying the resistance is important because the magnitude of the thermal reactions is very different for different minerals. A vertical scale designed for the thermal reactions of kaolinite may thus fail to show the thermal reactions of the micas because the intensity of the mica thermal reactions is about one tenth that of kaolinite.

In Figs. 4 to 17, the differential curves are presented so that the endothermic effects (heat taken up) are represented by deflections downward and exothermic effects (heat given off) by deflection upward. In Fig. 3, the vertical scales used in most of the present work are given. The scales were constructed by measuring the swing of the galvanometer for known temperature differences. By applying the scales to the figures, the temperature differences represented by the peaks of each curve can be estimated. The initial endothermic peak for the partially hydrated halloysite, for example, represents a temperature difference of about 14°C., that is, the temperature of the hydrated halloysite lagged about 14°C. behind that of the furnace to produce this deflection of the curve. The temperature difference represented by the peaks can be estimated only because the reactions usually start gradually, making it necessary to select an arbitrary base line of no temperature difference. The galvanometer, moreover, does not always return exactly to the neutral point at the end of a thermal reaction. No attempt has been made to draw a horizontal base line of no temperature difference because it would imply a degree of accuracy that the curves do not possess.

The atmosphere in the furnace during the analyses of all samples was oxidizing.

Each sample was ground to pass a 60-mesh sieve. Great care was taken to pack each one the same way in the specimen holder and to keep the positions of the thermocouple junctions constant. The weight of the sample was determined for each run.

The apparatus used in the present work was constructed in the laboratories of the Illinois State Geological Survey. It would, of course, be possible to set up an automatic temperature control for the furnace heating rate and an automatic device to record the furnace temperature and the temperature of the clay specimen. Such automatic apparatus might be desirable for equipment to be used in actual plant practice.

Experience has shown that the portion of the thermal curves below about 200°C. is not always precise, whereas the curves above this temperature can be duplicated in minute detail. Because the thermal reactions that take place below about 200°C. are frequently the result of adsorbed water, this part of the curve can be made more exact by drying the samples and then subjecting them to a constant humidity.[3] This procedure cannot be used for many natural clays where an irreversible moisture loss may take place on drying, and for plant control work, it would be unnecessary in most instances.

[3] R. E. Grim and R. A. Rowland, Differential Thermal Analyses of Clay Minerals and Other Hydrous Materials, *Illinois State Geol. Survey Rept. Investigations*, No. 85, 34 pp., 1942; *Amer. Mineralogist*, vol. 27, No. 11, pp. 746–61; No. 12, pp. 801–18, 1942; *Ceram. Abs.*, vol. 22, No. 6, p. 107, 1943.
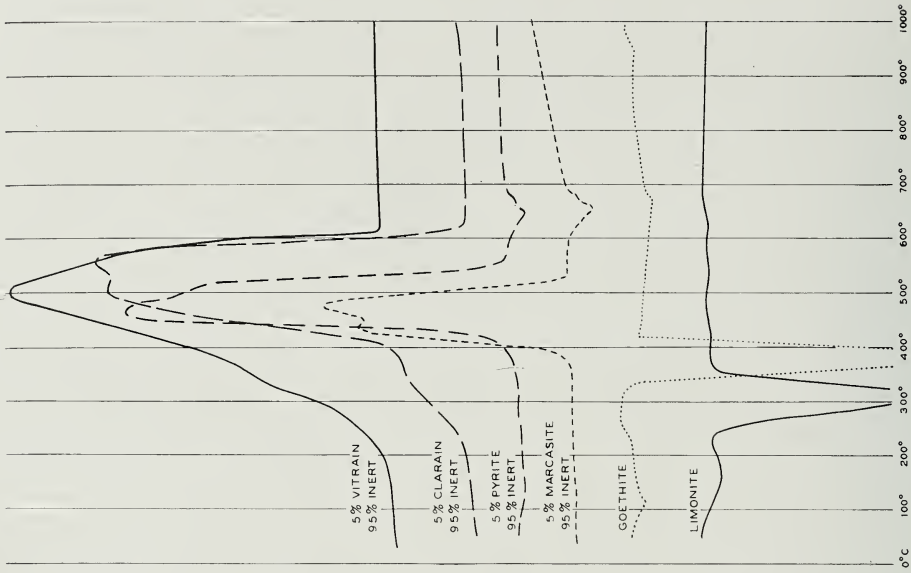
Fig. 6.—Organic materials and minerals found in some clays; clarain, vitrain, and limonite, scale B; marcasite, pyrite, and goethite, scale A (scales on Fig. 3).
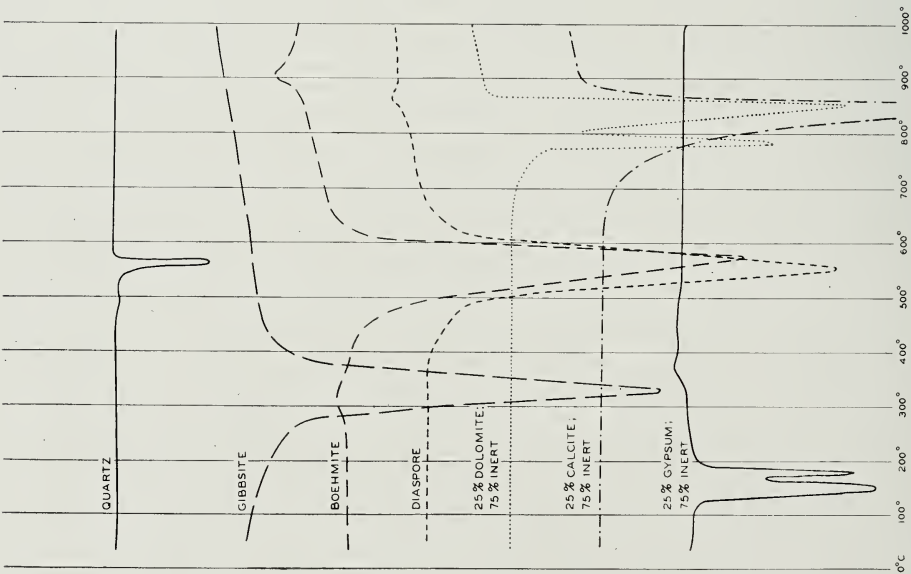
Fig. 5.—Minerals found in some clays; gibbsite, boehmite, and diaspore, scale B; quartz, calcite, dolomite, and gypsum, scale A (scales on Fig. 3).

III. Differential Thermal Analyses of Common Clay-Mineral and Nonclay-Mineral Components of Clays and Shales

The literature[4] contains numerous differential thermal analyses of various clay minerals,[5] and consequently only brief mention is made here of analyses of the more important types. Differential thermal curves for only a few of the common nonclay minerals found in clays have been presented before.

Kaolinite (Fig. 4) shows an intense endothermic reaction between about 550° and 650°C., a slight exothermic effect between about 650° and 950°C., and a very sharp exothermic reaction between 960° and 990°C.

Hydrated halloysite (Fig. 4) exhibits a thermal curve like that of kaolinite except that the thermal reactions appear to take place at slightly lower temperatures. There is also an additional endothermic reaction between about 100° and 200°C. Hydrated halloysite changes irreversibly to halloysite at a low temperature (60°C.) with a loss of $2H_2O$ and the disappearance of the initial endothermic peak.

Illite clay minerals (Fig. 4) show endothermic reactions between about 50° and 250°C., 500° and 650°C., and 850° and 925°C. They show also an exothermic reaction between about 925° and 980°C. The thermal reactions are of relatively slight intensity and may not be detected in apparatus set up for kaolinites. The final endothermic and exothermic reactions are subject to considerable variation from one illite to another, occasionally being so slight that they are scarcely detectable.

Montmorillonite clay minerals (Fig. 4), like the illites, show three endothermic reactions and a final exothermic reaction. Most montmorillonites provide curves differing from those of illites by showing

the second endothermic reaction to be more intense and taking place at a temperature about 100° higher, that is, ±700°C., and by more intense final endothermic and exothermic reactions. Some clay minerals that appear to belong to the montmorillonite group provide thermal curves (California bentonite, Fig. 4) that cannot yet be distinguished from those for the illites. The available data suggest that the latter minerals are iron-rich and perhaps should be designated as nontronites.

Quartz (Fig. 5) shows a sharp endothermic reaction of very low intensity at about 565°C., corresponding to the transformation from α to β form. It is usually impossible to detect a thermal reaction corresponding to the quartz-to-tridymite transformation at about 870°C.

Gypsum (Fig. 5) shows a double endothermic reaction between about 130° and 185°C. The first part of the double reaction is the larger and corresponds to the loss of $1\frac{1}{2}$ H_2O with the change to the hemihydrate. The second part of the peak results from the loss of $\frac{1}{2}$ H_2O with the development of anhydrite. The gypsum curves show also a faint exothermic reaction at about 370° of unknown significance.

Gibbsite (Fig. 5) produces a single strong thermal reaction, endothermic between about 275° and 375°C.

Diaspore (Fig. 5) shows a strong endothermic reaction between 500° and 600°C. and a very faint exothermic reaction at about 865°C.

Boehmite (Fig. 5) yields a curve quite similar to that of diaspore. There is a suggestion that the thermal reactions take place at slightly higher temperatures in boehmite, but this point cannot be considered as established.

Calcite (Fig. 5) shows an intense endothermic reaction, beginning at about 700°C. and ending abruptly at about 860°C. The galvanometer attached to the difference thermocouple frequently swings a short distance past the neutral point at the end of the carbonate endothermic reaction. As a consequence, a false suggestion of an exothermic reaction appears on the thermal curve of samples containing calcite.

[4](a) F. H. Norton, Critical Study of Differential Thermal Method for Identification of Clay Minerals, *Jour. Amer. Ceram. Soc.*, vol. 22, No. 2, pp. 54–63 (1939).
(b) Jean Orcel, Differential Thermal Analysis for Determination of Constituents of Clays, Laterites, and Bauxites, *Congr. Internat. Mines, Met. Geol. Appl.*, 7e *Session, Paris, 1935, Geol.*, I, 359–73; *Ceram. Abs.*, vol. 16, No. 7 p. 218, 1937.
(c) See also footnote 3.
[5]For discussion of the changes in the clay minerals causing the thermal reactions, see R. E. Grim and W. F. Bradley, Investigation of Effect of Heat on Clay Minerals, Illite and Montmorillonite, *Jour. Amer. Ceram. Soc.*, vol. 23, No. 8, pp. 242–48, 1940; *Illinois State Geol. Survey Rept. Investigations*, No. 66, 13 pp., 1940; see also footnote 3.

FIG. 8.—Synthetic mixtures of components of some clays, scale A (scale on Fig. 3).
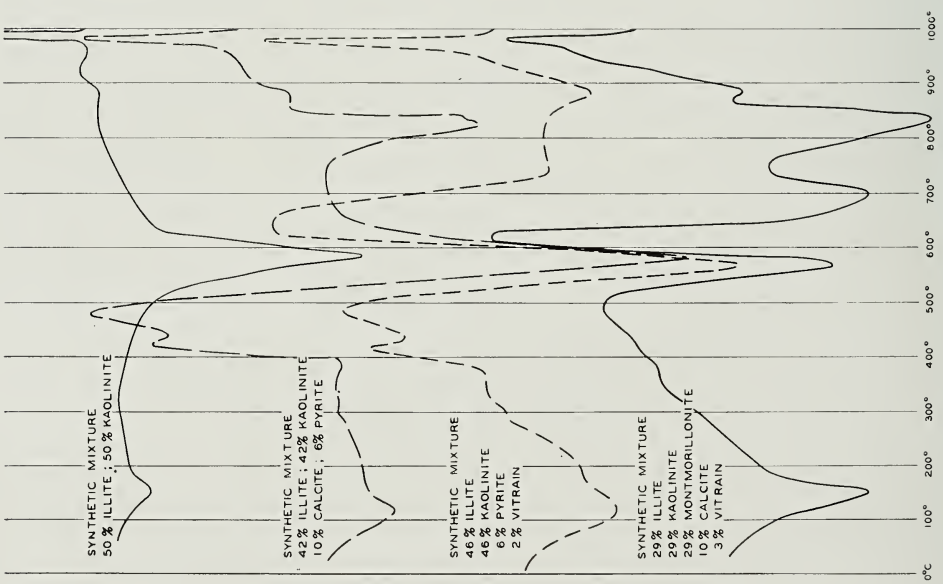
SYNTHETIC MIXTURE
50 % ILLITE
50 % MONTMORILLONITE

SYNTHETIC MIXTURE
49 % ILLITE
49 % KAOLINITE
2 % VITRAIN

SYNTHETIC MIXTURE
41 % ILLITE
41 % KAOLINITE
10 % CALCITE
6 % PYRITE
2 % VITRAIN

SYNTHETIC MIXTURE
44 % ILLITE
44 % KAOLINITE
10 % CALCITE
2 % VITRAIN

FIG. 7.—Synthetic mixtures of components of some clays; scale A, except 50% kaolinite; 50% illite mixture scale B (scales on Fig. 3).

SYNTHETIC MIXTURE
50 % ILLITE ; 50 % KAOLINITE

SYNTHETIC MIXTURE
42 % ILLITE ; 42% KAOLINITE
10 % CALCITE ; 6% PYRITE

SYNTHETIC MIXTURE
46 % ILLITE
46 % KAOLINITE
6 % PYRITE
2 % VITRAIN

SYNTHETIC MIXTURE
29% ILLITE
29% KAOLINITE
29% MONTMORILLONITE
10% CALCITE
3% VITRAIN

Dolomite (Fig. 5) shows a double endothermic reaction between about 775° and 860°C. The final part of the reaction yields a peak at about the same temperature as that given by calcite.

Clarain and *vitrain* (Fig. 6), which are important components of coal, provide intense exothermic effects beginning at about 200°C. and ending near 600°C. The difference in detail shown by the curves may not be significant so that it cannot yet be concluded that this thermal method distinguishes between the components of coal.

Pyrite and *marcasite* (Fig. 6) show intense exothermic reactions between about 400° and 550°C. plus a slight endothermic reaction between 600° and 700°C. The curves suggest that the exothermic reaction of pyrite extends to a slightly higher temperature than that of marcasite.

Limonite and *goethite* (Fig. 6) samples investigated gave endothermic reactions between 250° and 350°C. and between 340° and 425°C., respectively. The specific hydrates of ferric iron have not been well characterized, and the data herein presented are significant only in indicating the temperature range in which characteristic endothermic reactions take place.

IV. Differential Thermal Analyses of Prepared Mixtures of Clay Minerals and Nonclay Minerals

The thermal curve for the mixture of equal parts of kaolinite and illite (Fig. 7) is dominated by the thermal reactions of kaolinite because the thermal reactions of this mineral are much more intense. The presence of illite is indicated by the initial endothermic reaction and the slight endothermic and exothermic effects preceding the final kaolinite exothermic reaction. The second endothermic reaction of illite takes place at about the same temperature as the kaolinite endothermic reaction and is therefore concealed.

The montmorillonite and illite are indicated clearly in the thermal curve of a mixture of equal amounts of these minerals (Fig. 8) by the endothermic reactions at about 550° and 700°C., respectively. It must be emphasized that such a clear differentiation does not exist for all mixtures of these two groups of clay minerals because the second endothermic reaction of some clay minerals that seem to belong to the montmorillonite group takes place at about the same temperature as that of illite.

The differential thermal curves for the prepared mixtures of clay minerals and nonclay minerals (Figs. 7 and 8) show the possibilities of this method of determining the components of clay as well as its limitations. On the basis of these curves and a large number of additional unpublished differential thermal analyses, the following general statements seem warranted.

The initial endothermal peak is indicative of a clay mineral other than kaolinite, usually either an illite or montmorillonite inasmuch as these are common clay-mineral groups. If the reaction is sharp, that is, takes place within narrow temperature limits, a montmorillonite rather than an illite is suggested.

Organic materials give intense exothermic reactions beginning at about 200°C. and continuing until the furnace has reached 650° to 700°C. The reactions are so intense that the endothermic reactions taking place in this temperature interval of all the clay minerals except kaolinite and halloysite are apt to be concealed.

Marcasite and pyrite give intense exothermic reactions in about the same temperature range as organic material. The reaction begins at a higher temperature for the sulfides, which sometimes serves to differentiate them from organic material.

Under the conditions of making differential thermal analyses, the reactions take place in an interval of time during which the temperature of the furance increases. In cases where the reactions take considerable time, the temperature of the peak of the reaction will vary, depending on the amount of the mineral causing the reaction. Thus, in the case of organic compounds, the temperature of the peak may vary several hundred degrees, depending on the amount of the material in the sample analyzed. The temperature at which the reaction starts in any case is significant rather than the temperature at the peak or at the conclusion of the reaction.
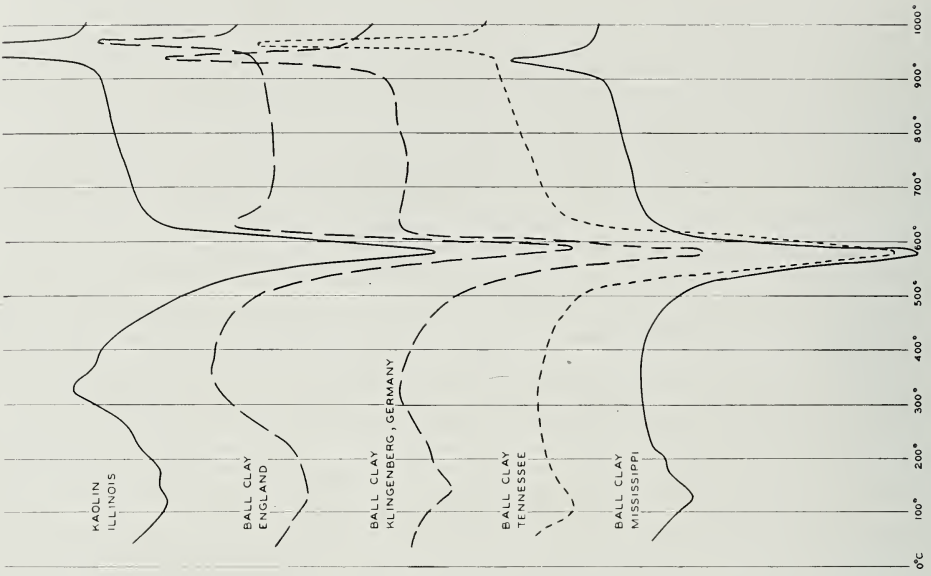
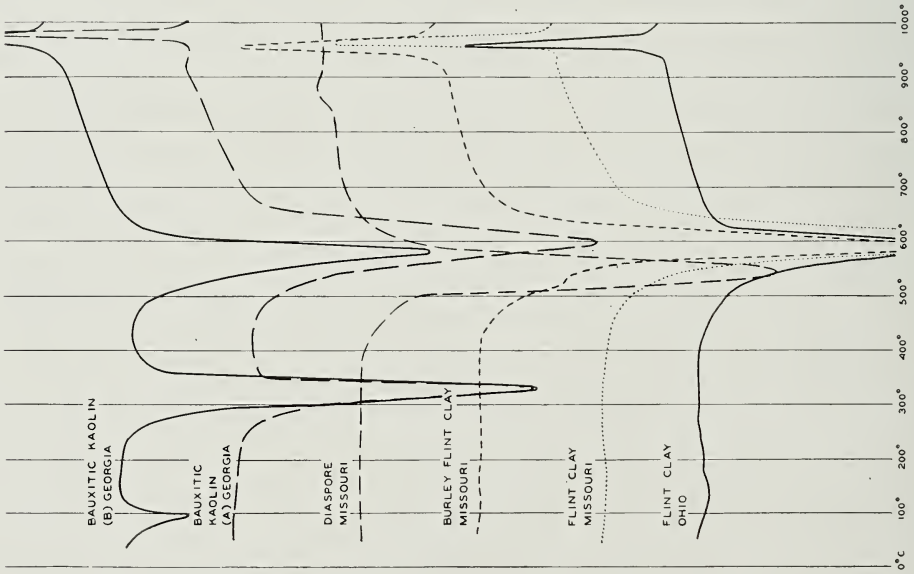FIG. 10.—Natural clays, scale B (scale on Fig. 3).

FIG. 9.—Natural clays, scale B (scale on Fig. 3).

In cases where intense reactions end abruptly, the recording galvanometer shows a tendency to swing past the neutral point, and the resulting curve will suggest a reaction that has not taken place. For example, in the second curve from the top in Fig. 8, an endothermic reaction is suggested at about 675°C., whereas the sample contained nothing to give a reaction at this temperature.

The reaction for the carbonates is quite distinctive because it takes place in a temperature interval (800° to 850°C.) in which most other clay components show no reaction. Calcite in quantities as small as 5% can be closely estimated.

The final exothermic reaction of kaolinite is sharp, intense, and diagnostic of this clay mineral.

The final endothermic and exothermic reactions of illite and montmorillonite can usually be seen. These reactions are variable, however, and the variations seem to increase in mixtures; as a consequence, they must be used with caution.

V. DIFFERENTIAL THERMAL ANALYSES
   FOR CLAYS OF VARIOUS TYPES

The differential thermal analyses shown in Figs. 9 to 12 were selected from several hundred analyses of a large variety of clays. They are presented to indicate the clay-mineral composition of well-known types of clay and to illustrate the possibilities of the differential thermal method in obtaining such data.

Bauxitic kaolin (*A*), *Georgia* (Fig. 9) provides a thermal curve indicating that it is composed of kaolinite and gibbsite with the former considerably more abundant. The endothermic reaction at about 325°C. indicates gibbsite, and the other thermal reactions are those of kaolinite.

Bauxitic kaolin (*B*), *Georgia* (Fig. 9) provides a thermal curve like that of the foregoing sample except that the size of the gibbsite reaction is larger than that of the kaolinite, thereby indicating a relatively larger amount of gibbsite in this sample. The bauxitic kaolin (B) also shows a slight endothermic reaction at about 100°C., and the endothermic reaction at about 600°C. is at a slightly lower temperature than in the bauxitic kaolin (A). These latter characteristics suggest that (B) is actually composed of

halloysite rather than kaolinite or that the kaolinite is poorly crystalline.

Diaspore clay, Missouri (Fig. 9) gives a thermal curve with an intense endothermic reaction at about 540°C., indicating the presence of the mineral diaspore.

Burley flint clay, Missouri (Fig. 9) gives a thermal curve that shows the intense endothermic reaction at about 600° C. and the exothermic reaction at about 960°C. characteristic of kaolinite. A small amount of diaspore is indicated by the distinct hump at about 540°C.

Flint clay, Missouri (Fig. 9) supplies a thermal curve suggesting that kaolinite is the only component; this curve, however, provides no explanation for the flintlike properties.

Flint clay, Ohio (Fig. 9) gives a thermal curve also showing the thermal reactions of kaolinite. The intensity of the reactions, however, is smaller than would be expected if well-crystallized kaolinite made up the entire clay. This flint clay, on the basis of the thermal analysis, apparently contains either a component which shows no thermal reactions in additions to the kaolinite or the kaolinite itself has caused reactions of low intensity. Other analytical data (microscopic and chemical) suggest that kaolinite is the dominant component, and the latter interpretation seems to be the logical one. A considerable body of evidence has been accumulated showing that the intensity of the thermal reactions of the clay minerals generally is reduced as the crystallinity becomes less perfect.

Ball clays, Tennessee, Mississippi, England, and Germany (Fig. 10) exhibit thermal curves which indicate by the endothermic reactions at about 600°C. and the exothermic reactions between 900° and 1000°C. that kaolinite is an important component. The initial endothermic peaks indicate that some other clay mineral is also present, and the character of the peaks suggests that it is an illite (X-ray diffraction data check the presence of illite). The English and German ball clays show exothermic reactions beginning about 200°C. and ending about 650°C. that are the result of the burning of organic material. The curves for the other dull clays suggest only a trace of organic material.

FIG. 12.—Natural clays; slip clay and fuller's earth, scale A; other clays, scale B (scales on Fig. 3).

FIG. 11.—Natural clays, scale B (scale on Fig. 3).

It must be emphasized that the foregoing statements regarding the ball-clay samples do not apply to all ball clays.[6] There are American ball clays, for example, with considerable organic material. The thermal curves, moreover, do not indicate another factor that is vital in the composition of ball clays, namely, that the illite component must be very low in iron.

[6]C. G. Harman and C. W. Parmelee, Testing and Classification of Ball Clays: Thermal History, *Bull. Amer. Ceram. Soc.*, vol. 21, No. 11, pp. 283–86, 1942.

The thermal curves for the ball clays show the additional fact that in natural clays composed of illite and kaolinite the second endothermic and final endothermic and exothermic reactions of the illite may be completely obliterated.

Kaolin, Illinois (Fig. 10) provides a curve with thermal reactions indicating the presence of kaolinite. The kaolinite thermal reactions are of sufficient intensity to account for the entire composition of the clay, but there is an initial endothermic reaction somewhat similar to those that have been interpreted as indicating an illite. X-ray diffraction analysis shows no illite in this sample, and another interpretation must be found. The kaolinite making up the clay is extremely fine grained and poorly crystalline which probably accounts for this thermal feature.

Soft and hard kaolin, Georgia (Fig. 11) provide perfect kaolinite thermal curves. The faint initial endothermic reactions of the hard kaolin probably mean some imperfection in the crystallinity of the kaolinite.

Plastic kaolin, Georgia (Fig. 11) gives a thermal curve that is characteristic of kaolinite with additional endothermic reactions at about 700°C. and between 100° and 200°C. The endothermic reaction at 700°C. suggests the presence of montmorillonite. Montmorillonite would account for the initial endothermic reaction and also explain the plastic properties of this kaolin.

Sagger clay, Tennessee (Fig. 11) shows a thermal curve similar to those of some of the ball clays. Traces of iron adequate to cause variations in firing color would, of course, not be indicated by the thermal procedure.

Glasspot clay, Germany (Fig. 12) gives thermal reactions indicating the presence of kaolinite. The faint initial broad endothermic reaction suggests a small amount of an illite. The reactions shown by the thermal curve are not intense enough to account for all the components in the sample, and a microscopic analysis has shown that about 50% of the clay is composed of very fine quartz.

Wad clay, Tennessee (Fig. 11) shows a thermal curve about like that of the glasspot clay except that the first exothermic reaction is larger, indicating relatively more organic material.

Fire clay, Ohio (Fig. 12) is from a clay deposit used extensively in making steel ladle brick. The endothermic reaction at about 575°C. and the final exothermic reaction indicate the kaolinite type of clay mineral. The initial broad endothermic reaction cannot be explained satisfactorily although it is known from other analytical evidence that the sample contains a considerable amount of an illite. The sharp exothermic reaction between 400° and 500°C. indicates pyrite. The sample contains a considerable amount of quartz, which accounts for the relatively low intensity of the thermal reactions.

Plastic fire clay, Missouri (Fig. 12) exhibits a thermal curve indicating kaolinite and a smaller amount of an illite.

Slip clay, New York (Fig. 12) contains carbonate as shown by the endothermic reaction at about 850°C. and pyrite and organic material as indicated by the exothermic reactions between about 300° and 500°C. Quartz is indicated by the distinct break in the curve at 575°C. The intensity of the thermal reaction for pure quartz is very slight so that a reaction of this intensity indicates a considerable amount (30% ±) of this component. The clay-mineral component cannot be identified, except that kaolinite is not present because the reactions caused by the abundant nonclay-mineral components conceal those of the clay minerals. If kaolinite were present in appreciable amounts, it would be evident because of the intensity of its reactions.

Fuller's earth, Georgia (Fig. 12) contains montmorillonite, according to the thermal curve data. The exothermic re-

Fig. 14.—Samples of fire clay from clay pit of refractory plant, northern Ill., scale B (scale on Fig. 3).
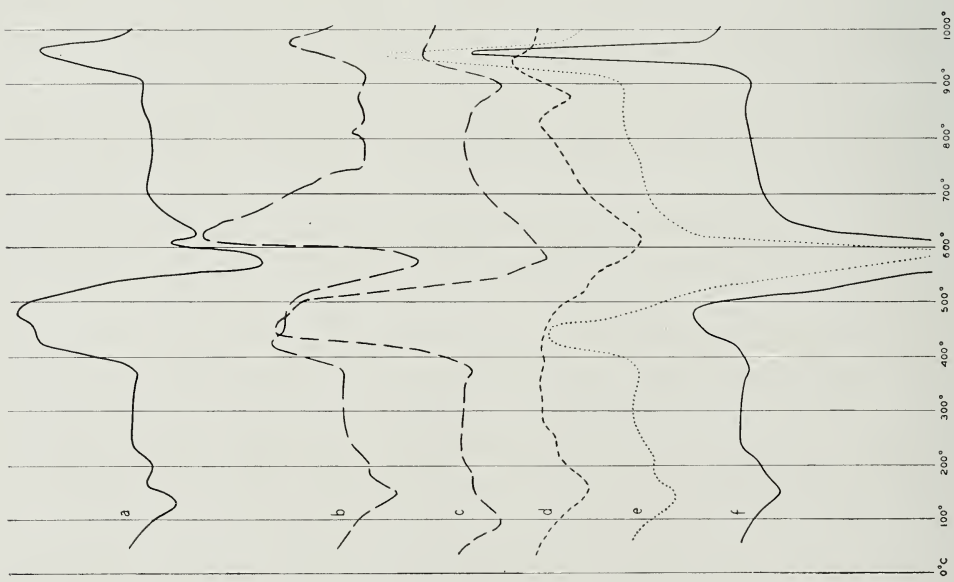
Fig. 13.—Samples of fire clay from clay pit of refractory plant, central Ill., scale B (scale on Fig. 3).

action between 400° and 500°C. indicates pyrite, and the endothermic peak between 500° and 600°C. suggests nontronite or illite, probably the latter.

VI. Correlation of Differential Thermal Characteristics and Ceramic Properties

The thermal curves of the various types of clay illustrate certain general relationships between clay composition, as reflected in the curves, and ceramic properties that may be summarized as follows:

(*a*) An endothermic reaction below about 200°C. usually indicates the presence of montmorillonite or illite. A clay material containing these components is apt to have high plasticity and high shrinkage and will probably be nonrefactory and will burn red. In general, the larger this reaction, the higher are the plasticity and shrinkage.

(*b*) Endothermic reactions between about 300° and 550°C. usually indicate a hydroxide of alumina or ferric iron oxide. If the component is a hydroxide of alumina, the clay will be very refractory and will have low shrinkage.

(*c*) A broad exothermic reaction between about 200° and 600°C. is the result of organic material. Clays yielding such thermal reactions will frequently be very plastic and will require careful burning to insure complete oxidation of the carbon without ruining the ware.

(*d*) A sharp exothermic reaction be-between 400° and 500°C. indicates pyrite or marcasite.

(*e*) A sharp intense endothermic reaction at about 600°C. and a sharp exothermic reaction at about 975°C. indicates the presence of kaolinite. A clay with this component is apt to be refractory and light firing and to have low plasticity and a relatively long vitrification range.

(*f*) A clay with a slight endothermic reaction at about 500° or 700°C., followed by another endothermic reaction at about 900°C., and then a final slight exothermic reaction is composed of illite or montmorillonite. A clay containing either of these clay minerals is not refractory or light firing and is apt to have a short

vitrification range. If the component is montmorillonite, it will also have high plasticity and shrinkage.

(*g*) A small endothermic break at 575°C. shows the presence of considerable free silica (quartz) which will reduce the plasticity and shrinkage of the clay.

(*h*) A sharp intense endothermic reaction at about 850°C. indicates the presence of carbonate and therefore a clay requiring careful preparation and firing technique.

It must be emphasized that experience and caution are necessary in interpreting the composition and properties from the differential thermal curve of a clay. In studying a large number of clays, some curves will be encountered that cannot be evaluated satisfactorily without additional analytical data from optical, X-ray, or chemical analyses.

VII. Application of Differential Thermal Procedure to Prospecting

The curves shown in Figs. 13 to 17 represent differential thermal analyses of sequences of samples collected from the mines of several operating clay products plants. These figures illustrate the variations in curve characteristics that can be expected within a single pit and therefore the variations in ceramic properties that can be detected by this method.

(*A*) *Refractory Brick Plant in Central Illinois (Pennsylvanian, Cheltenham Underclay)*: The mine shows 6 to 12 feet of gray-brown underclay that usually appears homogeneous from top to bottom. At some places in the mine, however, a sandy zone is present in the middle of the bed; at other places, a greenish shaly clay is interstratified in the lower part of the clay.

The curves in Fig. 13 show the differential thermal characteristics of samples collected at intervals from the top to the bottom of the mine and at different lateral positions. Curves *a* and *b* from samples near the top of the mine indicate a kaolinite clay with some illite and a considerable amount of pyrite. Curves *c* and *d* from samples near the bottom of the mine at the same location (as *a* and *b*) indicate a clay composed of illite without kaolinite. Curve *c* also shows the presence of pyrite. Curves *e* and *f* from samples
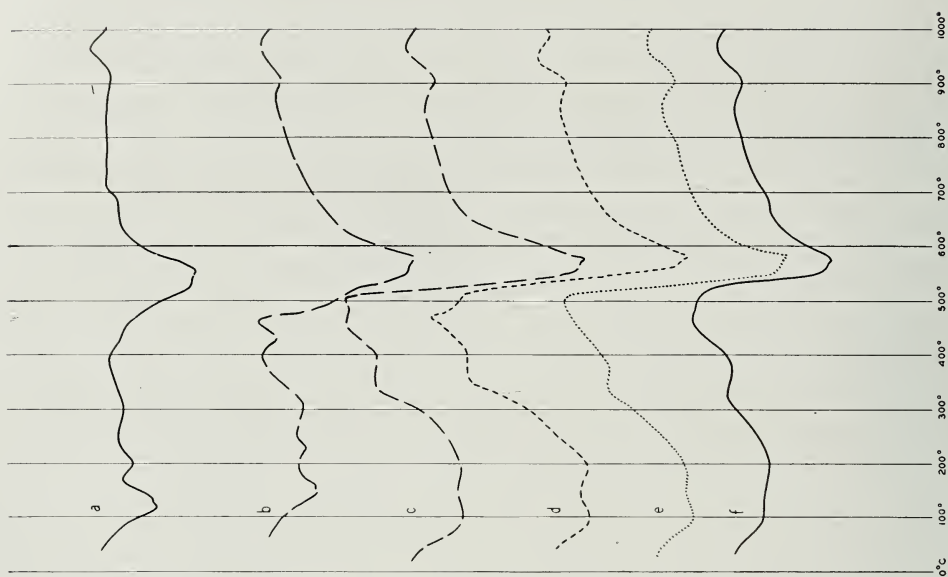
Fig. 16.—Samples of shale from pit of face brick plant, southern Ill., 50 ohms series resistance.

Fig. 15.—Samples of shale from pit of face brick plant, northern Ill., 50 ohms series resistance.

near the top and bottom, respectively, at another location in the mine indicate a clay composed of kaolinite with some illite and pyrite. The amount of kaolinite is larger and the amount of illite and pyrite is smaller at the location of *e* and *f* than that of *a* and *b*.

The plasticity and refractoriness of the clays vary as the relative amounts of illite and kaolinite vary. Samples *e* and *f* with the higher kaolinite content are more refractory than *a* and *b* from the same vertical position but at a different location in the mine. Samples *c* and *d* without kaolinite are nonrefractory.

(B) *Refractory Brick Plant in Northern Illinois (Pennsylvanian, Lower Pottsville Underclay)*: The pit shows 5 feet of gray-brown underclay (samples *a b, c, d*) grading below into one foot of gray-white underclay (sample *e*).

The curves in Fig. 14 show that all the samples from the pit at this plant contain kaolinite, illite, pyrite, and organic material. The intensity of the reactions in *a* and *b* is less than would be expected for clays composed only of these minerals, and it is likely therefore that they also contain a considerable amount of free silica. The curves indicate that the relative abundance of these component minerals varies in clays selected from different places in the pit. The ceramic properties of the clay change with these variations in composition.

(C) *Face Brick Plant in Northern Illinois (Pennsylvanian, Sheffield Shale)*: The pit shows about 16 feet of yellow-green shale (samples *a, b, c*) grading below into about 8 feet of blue-gray shale (samples *d, e*).

The curves in Fig. 15 show that all the samples from this pit are composed essentially of an illite. Samples *a* and *b* contain also a high percentage of quartz (free silica) as is shown by the endothermic break at about 575°C. and by the relatively low intensity of the thermal reactions in comparison with those of the other samples. All the samples show some organic material, but *d* and *e* have more than the others. Samples *c, d,* and *e* contain pyrite, and *e* contains also a considerable amount of carbonate.

The ceramic properties of the material vary with the foregoing variations in mineral composition; for example, the plasticity and the shrinkage decrease as the relative abundance of quartz increases.

(D) *Face Brick Plant in Southern Illinois (Pennsylvanian, Shale Overlying Collinsville Limestone)*: This pit shows 10 feet of brown shale (samples *a* and *b*) overlying 24 feet of blue shale (samples *c, d, e, f*).

All of the samples from this pit, as shown by the curves in Fig. 16, are composed essentially of illite. The slight endothermic hump at about 575°C. in all the curves indicates the presence of a considerable amount of quartz. Each sample also contains organic material, and the curves indicate that this material is least abundant in the top (*a*) and bottom (*f*) samples.

The greatest variation in the composition of the samples from this pit is in the relative abundance of the illite as shown by the variation in the intensity of the illite thermal reactions. The plasticity and shrinkage of the clay vary with this change in composition.
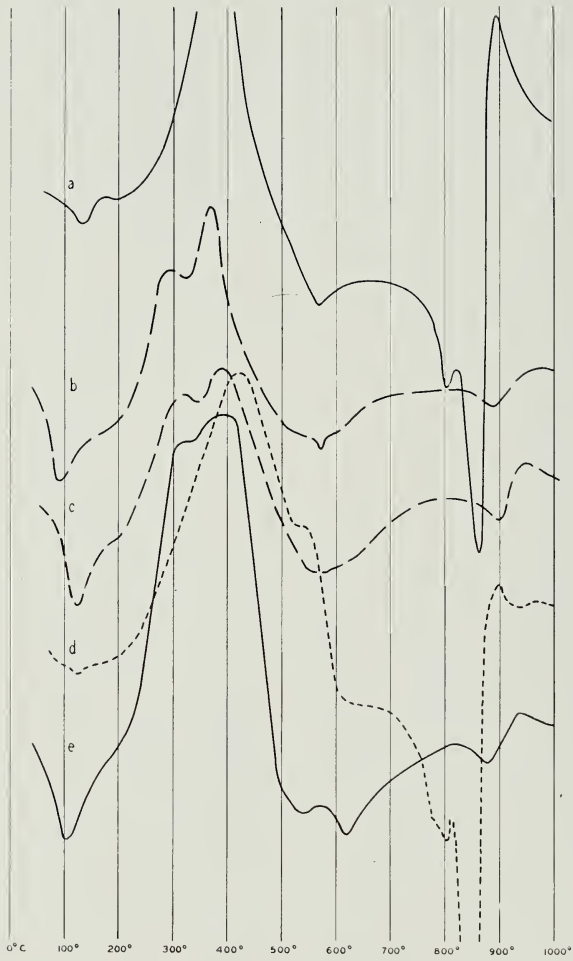
FIG. 17.—Samples from clay pit of common brick plant,
Chicago, Ill., 50 ohms series resistance.

(E) *Common Brick Plant, Chicago, Illinois (Pleistocene Till)*: This pit shows about 18 feet of light gray-blue till (sample *a*) overlying about 15 feet of dark gray till (sample *d*). The upper and lower tills are frequently separated by a thin (1± foot) bed of gray silt.

Samples *a* and *d* (Fig. 17) are raw glacial till with such large amounts of carbonate and organic material that the other components are concealed. Samples *b*, *c*, and *e* are the clay-size grade (−2 micron) of several tills from which the carbonate has been removed. These curves show that the dominant component of the clay-size grade is an illite. The curves show also that there is considerable variation in the composition of the clay grade which can be expected to cause important variations in ceramic properties. A distinct variation thus occurs in the amount of organic material, and curve *e* shows an endothermic reaction between 600° and 700°C. suggesting the presence of some montmorillonite-type clay mineral.

It is evident from the foregoing differential thermal analyses of pit samples that the method is adequate to detect variations in the composition of clays and shales in a single pit that are responsible for significant variations in ceramic properties. The method is therefore a rapid means of evaluating the properties of clays and shales for plant control and prospecting. Before the method could be put to full use in a plant, however, it would be necessary to run a considerable number of curves of a range of samples representing the particular clays to be used and for which determinations of properties were available. These preliminary curves would provide a correlation of curve characteristics with clay properties and would form the basis for the later interpretation of the curves of samples with unknown properties. Only after these data were at hand could trustworthy interpretation of properties be made from the thermal curves.