THE EFFECT OF SAMPLE PREPARATION ON THE
CHARACTERISTICS OF DIFFERENTIAL THERMAL ANALYSIS
CURVES OF STANDARD CLAYS

by

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INTRODUCTION

The various clays differ considerably in their physical and chemical properties, and each reacts differently to agronomic practices. Because of this the agronomist is concerned as to the type or types of clay present in a soil being studied.

Several methods of clay identification are being used. Among these are chemical analysis, X-ray diffraction, electron micrographs, thermal dehydration curves, differential thermal curves, and various optical methods. While no one of these methods is always sufficient for positive identification, a combination of two or more methods will usually determine which particular clay mineral is present. This investigation was initiated in an attempt to find a method that would give sharper definition and greater reproducability of differential thermal analysis curves. Specifically, this paper deals with the effect of particle size, moisture content, and adsorbed cations on the differential thermal curves of pure clay samples.

The differential thermal method of studying clays and related materials originated as an outgrowth of suggestions made by Le Chatelier in 1887; since that time it has been rather extensively investigated. The explanation of the thermal activity of a substance is that as a sample is heated, changes take place that either take on or give off heat. This energy change may be due to any one or several of the following: burning of any combustible material present, loss of water of hydration, loss of combined water, or the rearrangement or breakdown of a crystalline structure. By making use of differential thermocouples with one

junction buried in the active sample and the other buried in an inert sample and heating the entire system at a constant rate, the characteristics of the thermal reactions can be studied. The temperature at which the reactions occur are characteristic of the material being investigated and thus can be an aid to identification.

REVIEW OF LITERATURE

Hendricks and Alexander (6) used chemical analysis, X-ray diffraction, and differential thermal analysis to identify material present in the colloidal fraction of certain soils. Certain clay minerals and other minerals were identified. They found that for differential thermal analysis it was necessary to remove the organic matter from a colloid since it undergoes combustion over a wide temperature range and would thus obscure thermal peaks characteristic of the different minerals. Another point noted was that the endothermic peaks at relatively low temperatures exhibited by montmorillonite and possibly hydrous mica were dependent to some extent on relative humidity.

Hendricks, et al., (7) saturated bentonite clays with various cations, dried them over phosphorus pentoxide in a vacuum to a constant weight, and then exposed them to a range of relative humidities from 5 percent to 90 percent for a week or longer. Differential thermal curves of these samples indicated that at higher humidity more water was adsorbed regardless of the saturation cation. It is interesting to note that less water was adsorbed at all humidity levels by the sodium, potassium, and

cesium saturated Mississippi montmorillonite.

Grim (1) discussed different possible crystalline structures for various clays and attempted to explain the hydration, dehydration, and loss of lattice water at various temperatures on the basis of their structures. The effect of various cations on hydration and on possible replacement of ions in the crystal lattice was also discussed. Using differential thermal analysis, Grim and Rowland (5) concluded that many of the clay and related minerals that have been given various different names are actually mixtures of two or more materials known by other names. Thermal reaction temperatures for various clay minerals were also given. Page (9) used the differential thermal method to study bentonite clays from a number of different locations. His work indicated that bentonites from different sources gave different curves due to a difference in the amount of lattice substitutions. He suggested that thermal analysis curves would aid in learning the extent of these substitutions and would lead to a better understanding of soil colloids.

Berkelhamer (Speil, et al., 10) presented data on the design of a complete differential thermal analysis apparatus. He also listed a table giving the temperatures and relative intensities of the differential thermal curves of a number of compounds commonly found in the soil. Speil, et al., (10) dried samples over anhydrous magnesium perchlorate for 24 hours before applying the differential thermal analysis technique. He also tried five different rates of heating. He found that at the more rapid heating rate of 20° C. per minute, thermal reactions gave peaks

that were sharper with more displacement than when a lower heating rate was used. The peaks, however, were not spread over as great a temperature range, and using heating rates from 5° to 20° per minute, the areas defined by the peaks and a plotted base line were very nearly the same. The actual peak on the curve came at a somewhat higher temperature when the faster heating rate was used. He also reported on the way in which different size fractions of kaolinite gave somewhat different thermal curves. He found that as the size decreased from 20 to about one micron the intensity of the 600° endothermic peak was increased. Below this size the sample was contaminated with increasing amounts of bentonite and gave weak thermal reactions characteristic of this mineral.

Grim (2 and 3) states that caution must be used in identification of clay minerals by the differential thermal method since the curve produced by a mixture is sometimes very easily misinterpreted. Grim and Bradley (4) heated samples of bentonite, illite, kaolinite, and halloysite to various degrees and then allowed them to remain at atmospheric humidity for various lengths of time and ran differential thermal curves on them. Bentonite heated to less than 600° regained adsorbed water quite rapidly, but when heated to 600° or more this readsorption of water was quite slow. Crystal lattice water was not regained to any extent in less than 146 days. The final endo and exothermic peaks were not influenced by heating to 800°. A point of note is that the crystal lattice water taken on by the clay after it had been heated to 600° showed two endothermic peaks, one about 150° below

the normal 700° peak.

EQUIPMENT

The equipment consisted of a program control which included items #1 through #3, and the temperature difference indicating equipment which includes items #4 through #6.

> Item #1   Leeds and Northrup Model S. Speedomax - G
> Strip Chart Indicating and Recording Program
> Controller.
>
> Item #2   Leeds and Northrup Electric Control Unit, PAT
> (series 50) with rate action and automatic re-
> set.
>
> Item #3   Control relay to shut down furnace when
> temperature has risen to end rise.
>
> Item #4   Leeds and Northrup Model S Speedomax-G single
> point indicating recorder.
>
> Item #5   Leeds and Northrup Stabilized DC Microvolt
> indicating amplifier.
>
> Item #6   Superior Electric Co. Type MZ1126 Powerstat
> variable transformer 2KVA, 115 volt, 60 cycle
> input with 0 to 135 volt output.

The furnace was not purchased but was constructed with a design similar to the one used by Dr. R. C. Mielenz, Head, Petrographic Laboratories, Building 53, Denver Federal Center, Denver 2, Colorado. The primary difference between the furnace constructed and the one at the Petrographic Laboratories is in the design and pattern of the heating elements.

The furnace was housed in sheet metal and consists of three sections made from Johns-Manville JM 2600 insulating brick. The center section contains a moulded refractory containing the heating elements. The heating elements used were of the type designed for use in a Sargent type 80, 115 volt crucible furnace. The two halves of the heating element were connected in parallel, giving a total DC resistance of 7 1/2 ohms for the heating circuit.

The sample block was machined from 1 1/2 inch nickel bar stock and was made of three sections. The diagram (Fig. 9) shows the details of its construction.

The sample was positioned in the center of the heating area by placing it on a block of insulating brick of the same type used in the furnace construction. A similar block was placed on top of the sample holder in order to keep the heating area as symmetrical as possible and to allow more even heating.

The thermocouples were brought into the sample block from the bottom through standard porcelain double hole insulators. The junctions of the differential thermocouples were located in the geometric center of the two 5/16 inch holes of the center section of the sample block, and the furnace control and temperature indicating thermocouple had its junction in the center of one of the 7/32 inch holes.

Finely ground anhydrous aluminum oxide was packed around one juncture of the differential thermocouple and around the indicating thermocouple, while the clay sample was packed around the other juncture of the differential couple. Samples were packed around

the thermocouples with a glass tube using moderate pressure.
The use of a tube which slipped over the thermocouple bead pre-
vented undue pressure from being exerted on the thermocouple,
thus preventing damage to it.

The thermocouples were fabricated from 24 gauge platinum
and platinum 10 percent rhodium wire. The actual junction was
made by fusing the two wires together in an oxy-acetylene flame,
taking care to make the junctions of the differential thermo-
couples as much alike as possible. The differential thermocouples
were then matched by cutting away a portion of the more sensitive
couple.

SAMPLES AND SAMPLE PREPARATION

Four standard clay samples were used in this investigation.
Wyoming bentonite was furnished by the American Colloid Co.,
Chicago, Illinois. Illite from Illinois was sent by W. A. White,
University of Illinois, Urbana, Illinois. Kaolinite, furnished
by Ward's Natural Science Establishment, Inc., came from Drybranch,
Georgia. Halloysite was sent by S. B. Hendricks, USDA, Washington,
D. C.

The sample of illite appeared to have possible contamination
of organic matter, and was treated with 30 percent hydrogen per-
oxide and heated on a hot plate to remove contamination. In an
effort to keep as nearly the same sample treatment as possible
on all four samples, the other three clays received the same
treatment. The excess hydrogen peroxide was removed by centri-
fuging and decanting the supernatant liquid.

The next step was to disperse the clay by suspending it in
2 percent sodium carbonate and boiling for 30 minutes. The sample
was allowed to cool, the supernatant liquid decanted, and the
clay fractions separated into the 2-0.2, 0.2-0.08, and less than
0.08 micron fractions by passing it through a Sharples Super-
centrifuge (motor driven type) following the method suggested by
Jackson (8).

After separation the clay samples were saturated with
calcium by suspending each sample in normal calcium chloride with
a ball mixer, then centrifuging, decanting, and resuspending until
a total of four washings had been completed. The clay was then
washed with absolute methanol until it tested free of chlorides
as shown by a silver nitrate test.

A portion of the 0.2-0.08 and the less than 0.08 micron
fractions of bentonite, and the 2-0.2 fraction of kaolinite was
then saturated with magnesium by washing it four times with normal
magnesium acetate, once with normal magnesium chloride, and then
washing free of chlorides with absolute methanol. A similar
procedure was carried out on the same size fractions using
potassium solutions so as to obtain a potassium-saturated clay.
A hydrogen-saturated clay was obtained similarly by washing the
samples with normal hydrochloric acid. Excess chlorides were
again removed with absolute methanol.

All samples were divided into three parts and a portion of
each stored at different relative humidities for subsequent anal-
ysis by the differential thermal method.

A chart from a research laboratory in applied chemistry at

the Massachusetts Institute of Technology was used to determine
the concentration of the sulfuric acid necessary to give specific
relative humidity levels. The different humidity storage chambers
were obtained by the following method. A 100 percent relative
humidity level was obtained by storing the clay samples in a
large desiccator having a free water surface in place of a drying
agent. The 50 percent relative humidity level was obtained by
using a 43 percent solution of sulfuric acid. A relative
humidity of close to zero percent was achieved by using 98
percent sulfuric acid.

DISCUSSION OF RESULTS

Figure 1 shows the differential thermal curves of calcium-
saturated bentonite which had been stored at three different
relative humidity levels. This comparison indicates that the
high temperature reactions were unaffected by the level of ad-
sorbed water. One point of interest was that the doublet endo-
thermic curve at about 100° - 200° was sharply influenced by
storing the samples at the zero percent relative humidity level.
The first and normally most outstanding peak of the doublet was
eliminated while the second was almost unaffected. This would
indicate that there are two types of adsorbed moisture. It is
possible that the water that is lost at the slightly lower temper-
ature is what has been classified as planer water that is held due
to unsaturated valence, while the water lost at the higher tem-
perature is probably adsorbed at the edge of the crystal due to
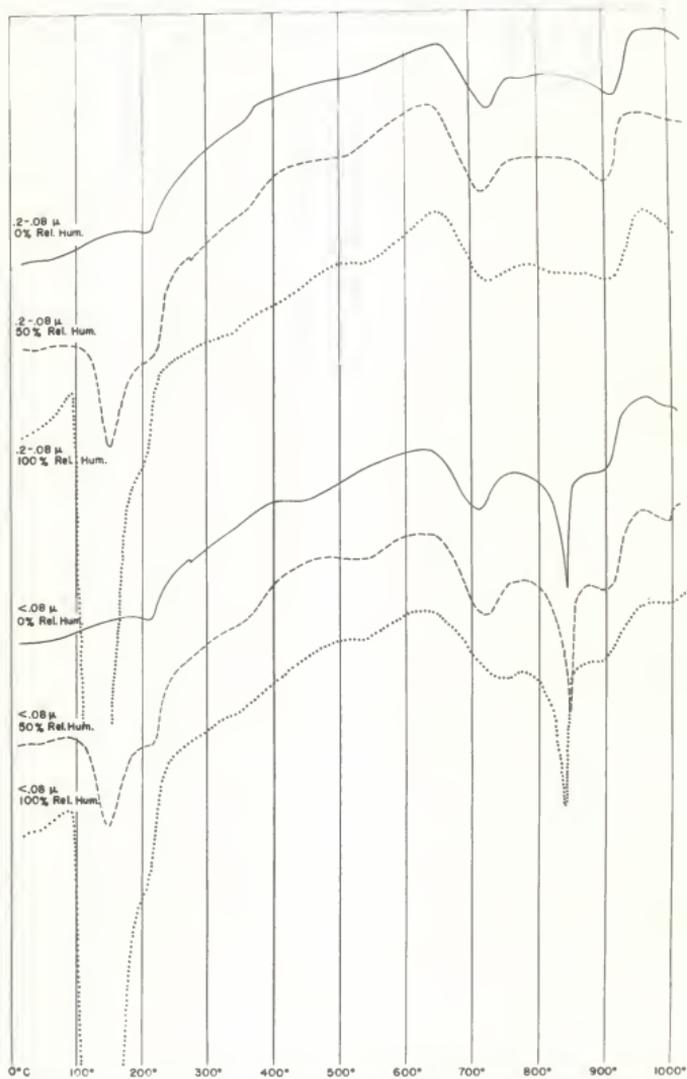broken valence bonds. The smaller size fraction of bentonite

.2 - .08 μ
0% Rel. Hum.

.2 - .08 μ
50% Rel. Hum.

.2 - .08 μ
100% Rel. Hum.

<.08 μ
0% Hum.

<.08 μ
50% Rel. Hum.

<.08 μ
100% Rel. Hum.

0°C   100°   200°   300°   400°   500°   600°   700°   800°   900°   1000°

Fig. I - Calcium Saturated Bentonite showing effect of particle size & hydration - Scale 4

gave a very sharply defined endothermic peak at about 840° which was not present on the curves traced by the larger sized fraction. A small but well defined endothermic peak was apparent on some traces at about 270°. This is probably due to an impurity, possibly gibsite which undergoes a sharp endothermic reaction near this temperature.

Figure 2 shows the effect of particle size and hydration on calcium-saturated illite. These curves show little conformity, and a great deal of difficulty was experienced with this sample as it appeared to vitrify at just over 900°, causing much difficulty in removing the sample from the sample well. The low temperature endothermic curve associated with adsorbed water was markedly affected by storage at the different relative humidity levels, but the higher temperature reactions were not well enough defined to be critically analyzed. One point of note was that on some differential thermal curves a very sharp endothermic peak occurred between 250 and 300 degrees. Why this trace was outstanding only at the lower humidity levels is not clear.

Figure 3 shows the influence of particle size and relative humidity on the differential thermal trace of calcium saturated kaolinite. As is the case with Figs. 1 and 2, relative humidity of storage has no effect on the high temperature peaks. Kaolinite adsorbed water from the saturated atmosphere. Since this water was lost at about 100° it can be assumed that it was held at a very low energy level. No other changes were noted for Kaolinite.

Figure 4 shows a calcium saturated halloysite with respect to size fraction and relative humidity of storage. It would be
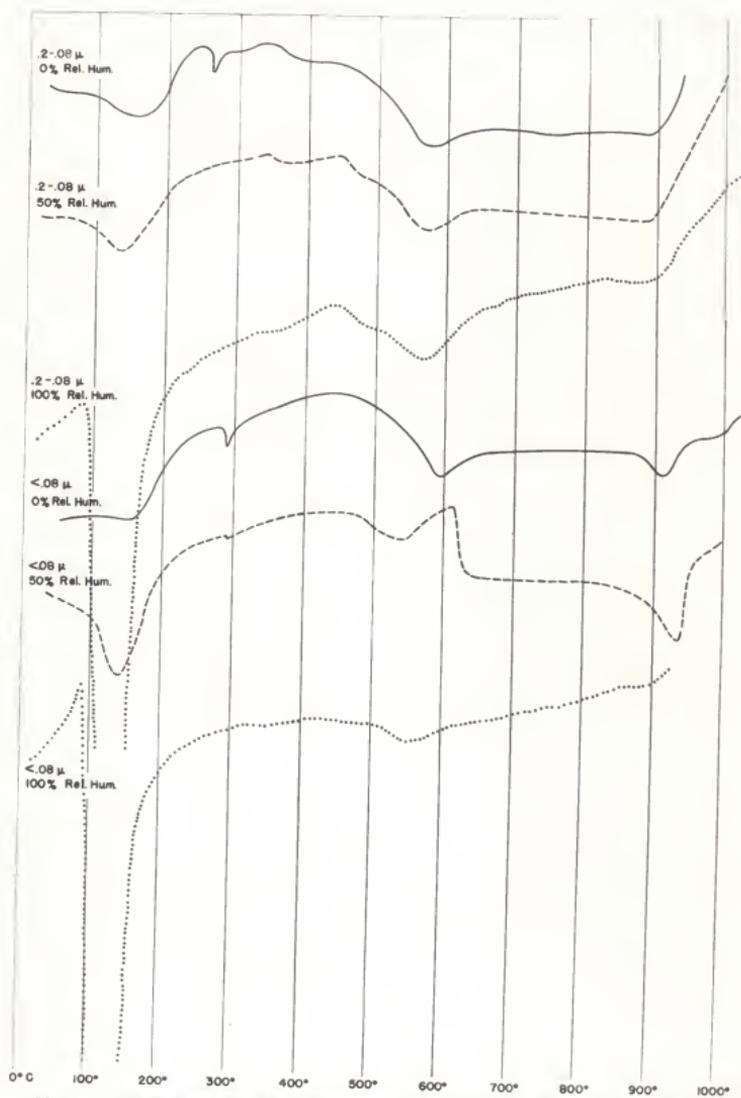
.2 -.08 μ
0% Rel. Hum.

.2 -.08 μ
50% Rel. Hum.

.2 -.08 μ
100% Rel. Hum.

<.08 μ
0% Rel. Hum.

<.08 μ
50% Rel. Hum.

<.08 μ
100% Rel. Hum.

0° C   100°   200°   300°   400°   500°   600°   700°   800°   900°   1000°

Fig. 2 — Calcium Saturated Illite showing effect of particle size & hydration – Scale 4

2 - .2 μ
0% Rel. Hum.

2 - .2 μ
50% Rel. Hum.

2 - .2 μ
100% Rel. Hum.

.2 - .08 μ
0% Rel. Hum.

.2 - .08 μ
50% Rel. Hum.

.2 - .08 μ
100% Rel. Hum.

0°C   100°   200°   300°   400°   500°   600°   700°   800°   900°   1000°
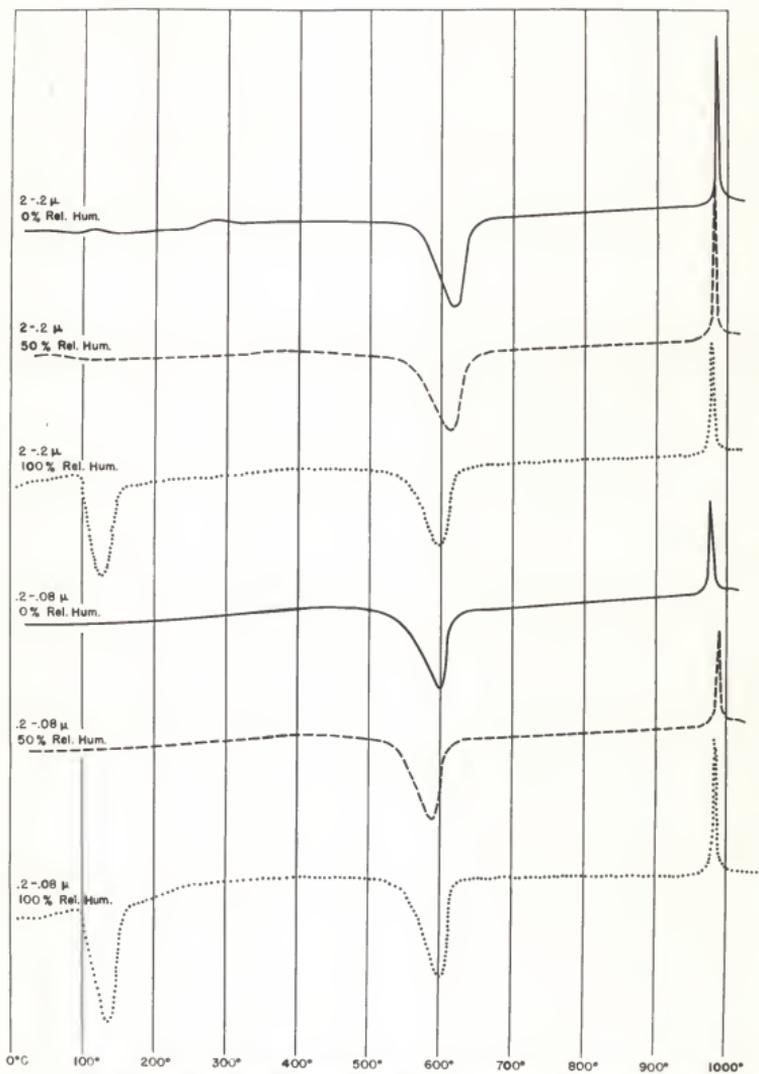
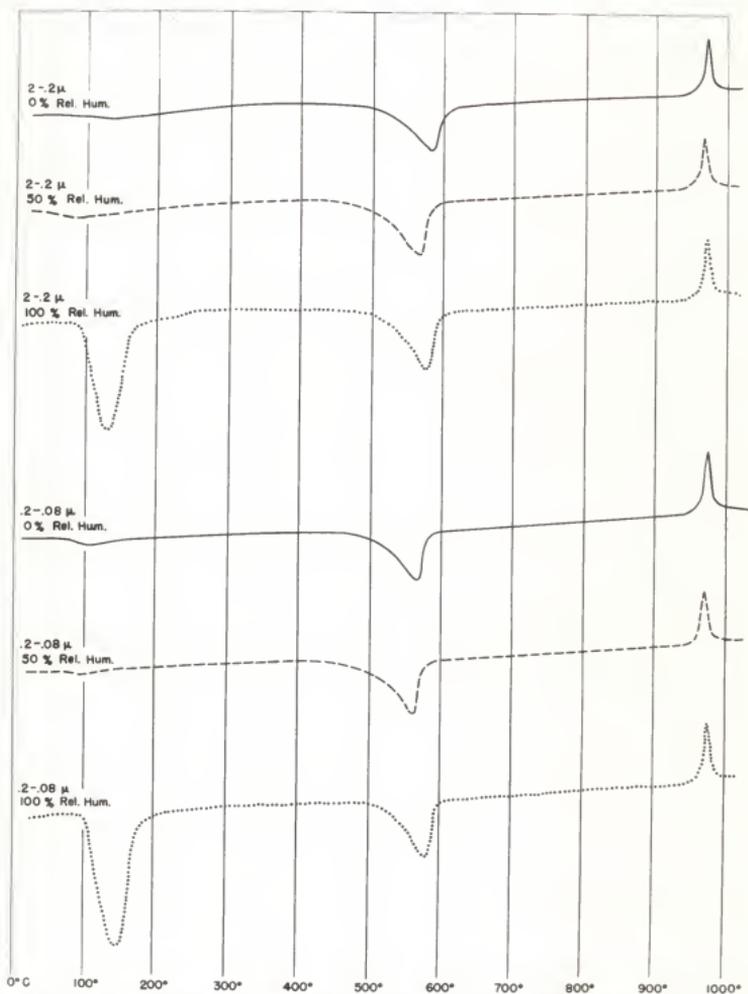Fig. 3 – Calcium Saturated Kaolinite showing effect of particle size & hydration – Scale 20

Fig. 4 – Calcium Saturated Halloysite showing effect of particle size & hydration – Scale 20

very difficult to differentiate between the kaolinite curve obtained from a sample stored at 100 percent relative humidity and a sample of hydrated halloysite if it were not for the fact that halloysite loses its hydroxal water at a slightly lower temperature than kaolinite and that kaolinite at about 970° undergoes a much more intense exothermic reaction than halloysite. Halloysite also shows a slight endothermic reaction at 100° when it has been stored at 50 percent relative humidity as well as a very slight reaction at the same temperature on the samples stored at zero percent relative humidity. It is entirely possible that if these samples had been stored for a longer period of time at the designated humidity level, these small peaks at 100° would not have been present. The endothermic reaction at 100° on the sample stored at 100 percent relative humidity is more pronounced with halloysite than with kaolinite. The differences between the halloysite curves and the kaolinite curves are distinct enough so that there should be little difficulty in distinguishing the two as long as the samples are relatively pure, but in mixtures with other clays or similar compounds the differences will be extremely small and much confusion may be expected.

Figures 5 and 6 show bentonite stored at three different relative humidity levels and saturated with various cations. The cations used for saturation were calcium, magnesium, potassium, and hydrogen. The curve for the hydrogen saturated bentonite at 100 percent relative humidity is missing since during this particular run a tube burned out in the amplifier and no thermal reactions were plotted. Sufficient sample was not present to
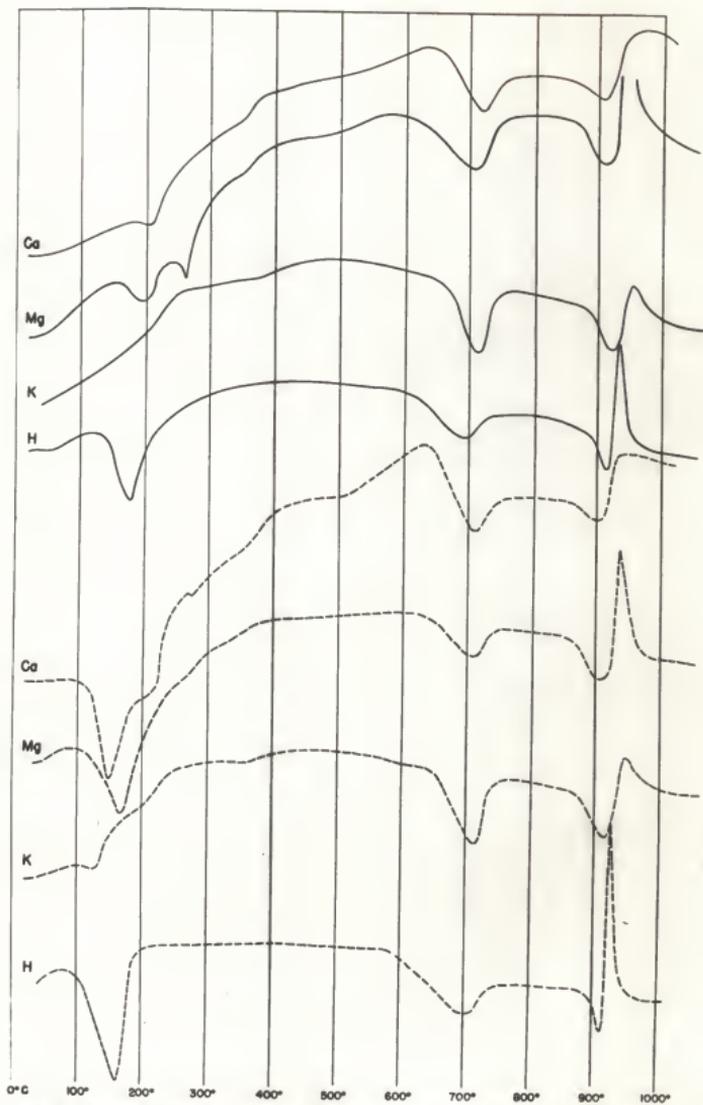
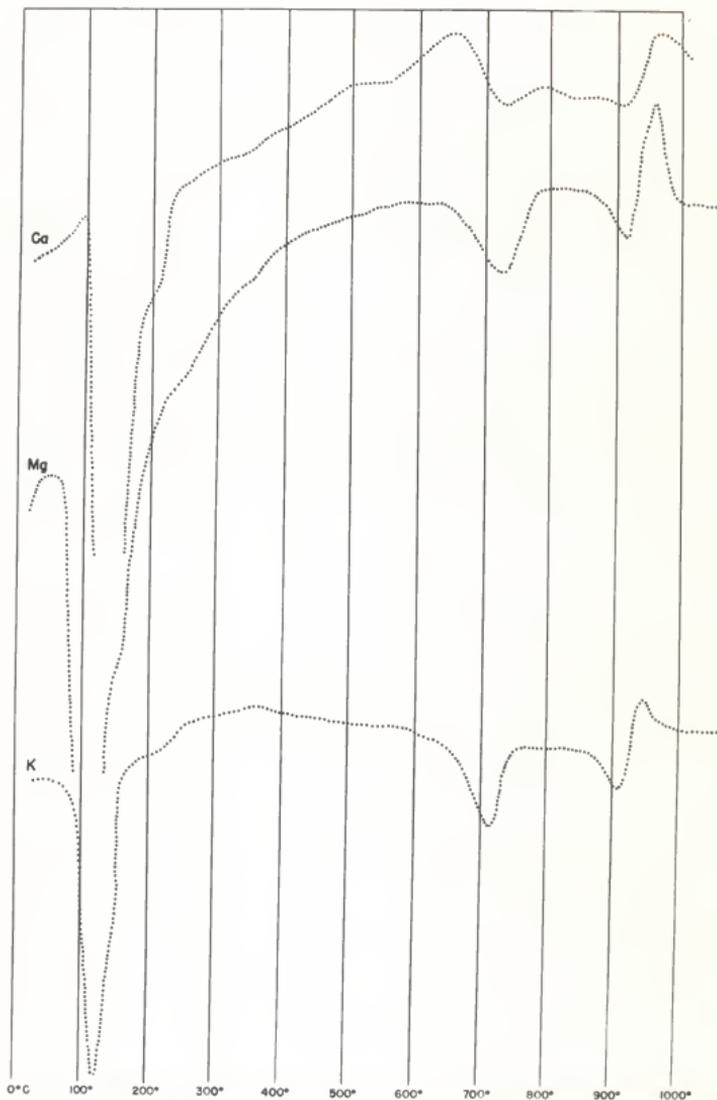Fig. 5 – Bentonite (.2 –.08 μ) saturated with various cations at 0 & 50% rel. hum. – Scale 4

Fig. 6 – Bentonite (.2 –.08μ) saturated with various cations at 100% relative humidity – Scale 4

attempt another trace. Another discrepancy that appears on these
two figures is that a difference in zero drift is apparent. This
is due, at least in part, to a change in differential thermocouples.
These curves show that saturation with different cations will
make quite a change in the differential thermal curve obtained
from bentonite.

As compared with calcium, magnesium saturation appeared to
exaggerate both the initial endothermic peak and the final exo-
thermic peak. No difference was noted in the temperature at
which the various peaks occurred.

When the curves obtained from potassium-saturated bentonite
were compared with those for calcium-saturated bentonite, an out-
standing difference was noted in the amount of water lost at the
initial endothermic peak at 150° to 200°. With potassium-satu-
rated bentonite this peak was absent at the low humidity storage
and it was greatly decreased at both higher humidities as compared
with the calcium-saturated bentonite. It is possible that this
change may be involved in potassium fixation by bentonite type
clays. This point should doubtlessly be investigated further.
There were essentially no differences in the characteristics of
the high temperature peaks.

The hydrogen-saturated bentonite had differences in thermal
reactions that caused it to stand out from the other cation
treatments. The initial low temperature doublet peak that is
characteristic of bentonite was replaced by a single endothermic
reaction at a slightly lower temperature. The characteristic
700° endothermic reaction appeared to be slightly lower as did

the 900° exothermic reaction. This final exothermic reaction
was also outstandingly different in that it was of higher magni-
tude than any of the other traces. The fact that the hydrogen-
saturated clay gave a marked endothermic reaction at 170° may
indicate that the hydrogen colloid will tend to hydrate to a
greater degree. To obtain conclusive proof of this, a more
carefully standardized humidity storage procedure would be
necessary.

Figure 7 shows differential thermal curves for the 2 to 0.2
micron fraction of kaolinite which had been stored at the zero
percent and 50 percent relative humidity levels. Curves were
traced from clays having calcium, magnesium, potassium, and
hydrogen saturation.

At these relative humidity levels, water of hydration was
not apparent on any of the cation treatments. The only difference
noted by the different treatments in Fig. 7 was the fact that the
final endothermic peak exhibited by kaolinite appeared to be at
a slightly higher temperature in the case of the potassium satura-
tion than for any other cation.

Figure 8 shows the traces of the 2 to 0.2 fraction of
kaolinite with the various cation saturations stored at 100 per-
cent relative humidity. All samples picked up water of hydration
which was lost at slightly above 100°. The final exothermic re-
action was again at a somewhat higher temperature with potassium
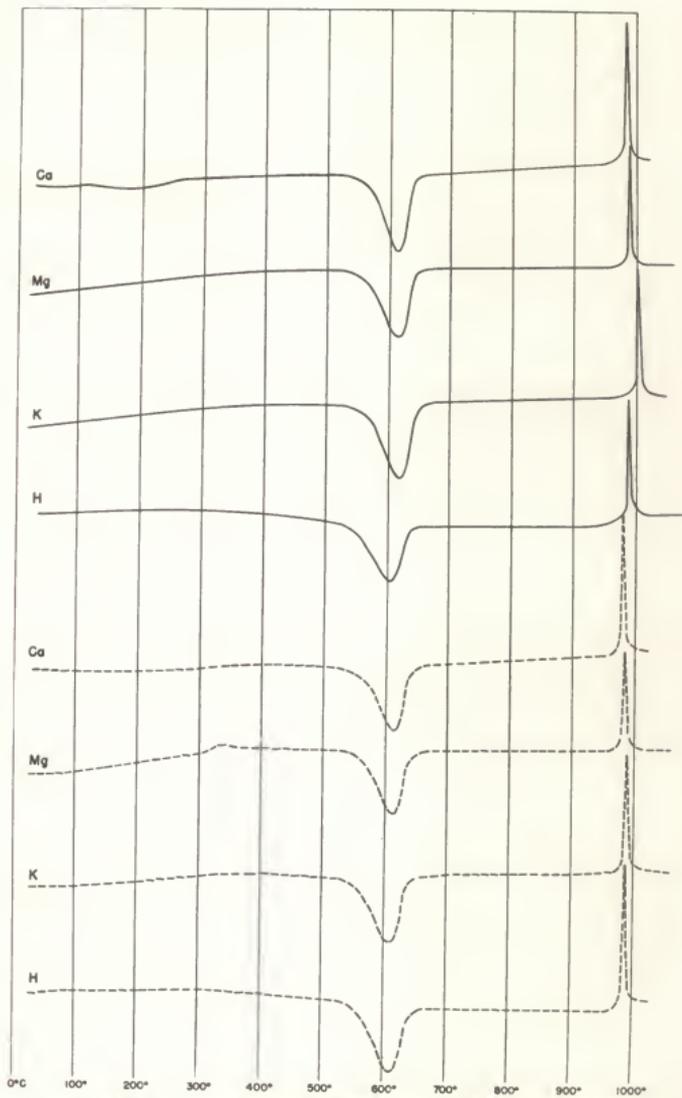saturation than with the other cations used.

Fig. 7 – Kaolinite (2 -.2 µ) saturated with various cations at O & 50% rel. hum.- Scale 20
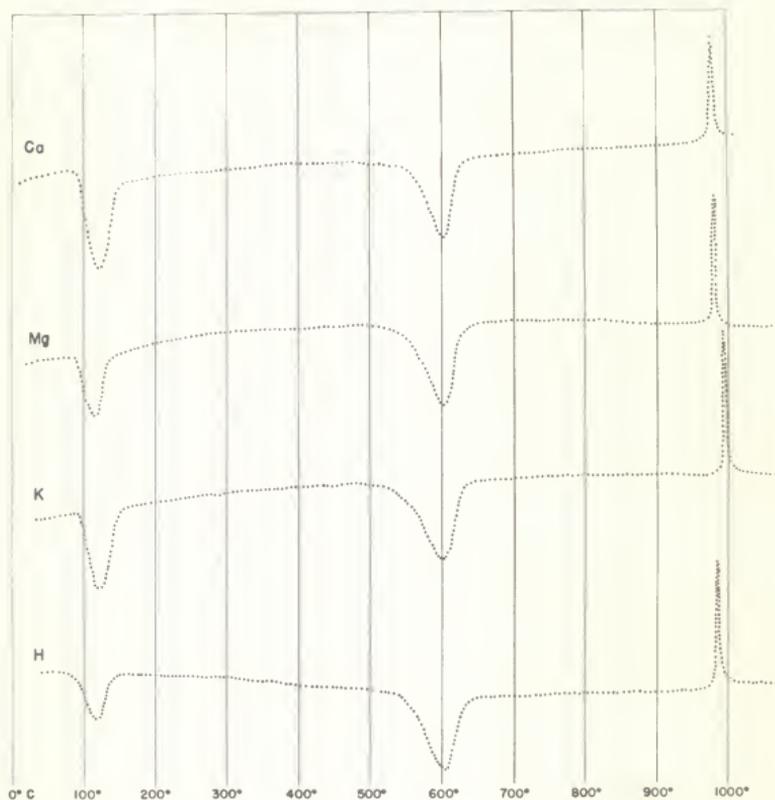
Fig. 8 - Kaolinite (2 -.2μ) saturated with various cations at 100 % Rel. Hum. - Scale 20
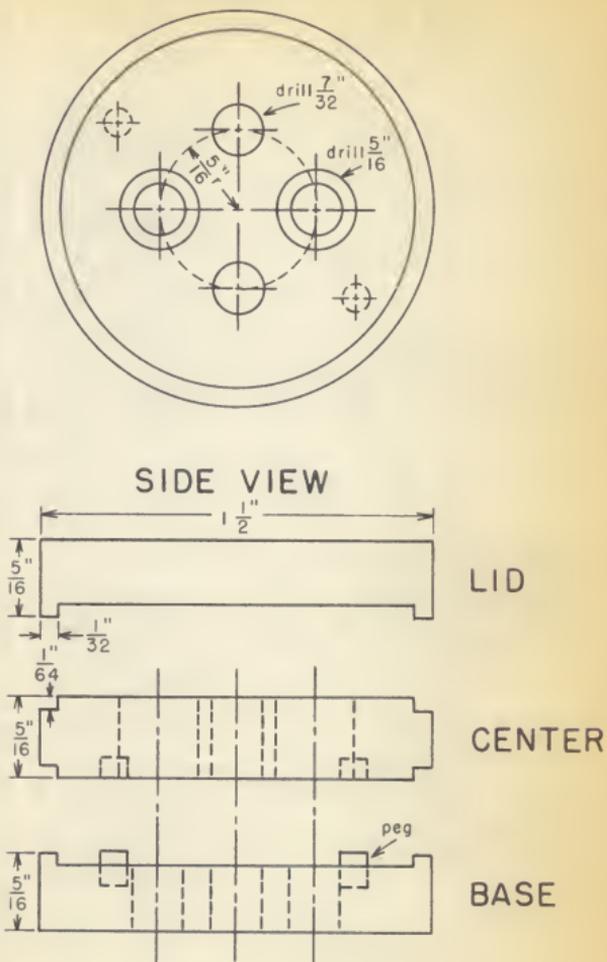
Fig. 9. Diagram of sample holder.

CONCLUSIONS

Sample treatment will modify the characteristics of dif-
ferential thermal analysis curves of clays and related substances.
One of the most outstanding factors is the degree of hydration as
influenced by the relative humidity under which the clay sample
has been stored. These differences, however, were apparent only
at the low temperature thermal reactions which were caused by
water of hydration being driven off. It should be carefully
noted that the hydration of a colloid may take a long time, and
it is doubtful if it is feasible to wait for an equilibrium to
be established. It is therefore suggested that a routine be set
up so that samples would be held at a given relative humidity
condition for a pre-set period of time and that the time schedule
be adhered to until all samples in question are investigated.
This would give relative data that should help to answer some
questions regarding the hydration mechanism of certain colloids.
It is not recommended that a sample be left in contact with a
saturated atmosphere for more than a few days since various molds
or other organic growths may cause possible contamination of the
samples.

The cation with which a clay is saturated will tend to in-
fluence the hydration mechanism to a marked degree. It also may
influence the temperature at which thermal reactions occur. Since
studies of this nature are compared on a relative basis it is
doubtful if the saturation cation will influence results very
much. One exception to this appears to be hydrogen, since it may

cause some replacement within the crystal structure of some clays. This effect could possibly be avoided by the proper choice of reagent and concentration used for hydrogen saturation.

Size of the particles studied is important with reference to clay minerals because it influences the sharpness of the peaks and the temperatures at which these peaks occur. Fractionations would be even more important in the case of soil colloids as this would be an aid to separating one mineral from another.

Differences in individual equipment will cause variation in trace characteristics such as intensity of peaks, and drift away from the base line. One difficulty experienced with the equipment used in this study was the fact that the heating rate was not always exactly linear. This caused some difficulty in plotting the various curves on a single sheet. This difficulty could be easily avoided if the plotting mechanism were of the type to show an X-Y plot so that the chart speed would be a function of furnace temperature.

With all these in mind it appears that before a soil is to be studied as to clay mineral content, a set of standard samples should receive the same pretreatment as the soil will receive, and a set of standard traces obtained. Should instrumental difficulties be encountered, such as replacement of the differential thermocouples, it is entirely possible that a new set of standards should be used.

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I would like to acknowledge the help given to me by Dr. A. E. Hostetter, of the Department of Industrial Engineering and Industrial Arts, in the construction and wiring of the furnace used in this investigation.

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Special acknowledgment is given to my wife for help both in the laboratory work and in preparation of the thesis.

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This investigation was initiated for the purpose of determining the influence of sample preparation on the characteristics of differential thermal analysis curves. The sample treatments investigated were size fractionation sample storage at different relative humidity levels, and saturation of the clay with different cations. Size fractions studied were 2 - 0.2, 0.2 - 0.08, and less than 0.08 microns. Samples were stored at one hundred, fifty, and zero percent relative humidities. Cations used for saturation were calcium, magnesium, potassium, and hydrogen.

Since the equipment used in this investigation was newly purchased, the first step was getting the equipment into operation. This entailed construction of a suitable furnace and sample holder. The furnace was patterned, with minor changes, after the one used at the Petrographic Laboratories in Denver, Colorado. The sample holder had no specific pattern, but followed certain characteristics of several described in the literature.

Fractionation of samples was accomplished by following the procedure described by Jackson, Madison, Wisconsin, in his laboratory manual, Chemical and Physicochemical Methods. The relative humidity levels were maintained by storage of samples over water, or the appropriate concentration of sulfuric acid. Clay saturation was accomplished by repeated washing and centrifuging with a solution containing a relatively high concentration of the proper cation. Excess salts were removed by washing with absolute methanol.

The comparison of the differential thermal curves show sample

preparation can markedly influence the characteristics of the traces. The smaller fraction of montmorillonitic type clay gave somewhat sharper traces. Samples stored at high relative humidity adsorbed more water of hydration and caused the initial endothermic peak to be of a relatively great magnitude. The higher temperature thermal reactions did not seem to be influenced by storage humidity. The storage period allowed at the various humidity levels was probably not sufficient for equilibria to be established. Literature cites examples of clays continuing to hydrate after as long a period as 146 days.

Different cation saturation of the clays appeared to influence both the magnitude and the temperature at which the reactions occurred. Specifically, potassium saturation of bentonite appeared to reduce the amount of water adsorbed, also the final exothermic peak of potassium saturated kaolinite appeared to take place at a slightly higher temperature than with any other cation saturation. Hydrogen saturated bentonite gave curves which were quite different than those obtained when other cations were used. This may have been due to removal of some of the aluminum from the crystal lattice by action of the rather strong (one normal) acid treatment.

From the preceding it would appear that when studying clays by the differential thermal method, careful standardization of sample preparation is necessary so that relative comparisons can be made between the curve of an unknown sample and that of a standard that has been subjected to identical preparation technique.