A new method for thermal dehydration studies of clay minerals.

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Summary. The water vapour released upon heating the specimen is driven through a water absorber. The intensity of the exothermic reaction produced by absorption of the water is recorded against the temperature of the specimen. A series of curves obtained with various clay minerals are presented to illustrate the method. The significance of results in the identification of the clay minerals and the determination of their structure is considered.

THE present equipment originated in a search for a sensitive procedure able to detect the possible release of small amounts of water by clay minerals above 800° C. For example, it was desired to verify whether any water-loss is connected with the endothermic reaction of montmorillonites around 900° C., and whether the slight endothermic feature sometimes preceding the exothermic reaction of kaolinites at about 950° C. is accompanied by any dehydration. The curves obtained by thermogravimetric and differential-thermal methods do not provide completely convincing information on these matters, and it was thought that a more sensitive procedure might be helpful. Also it was desired to study the rate of evolution of water vapour versus temperature.

Apparatus and method. The principle of the new method is as follows: The water vapour evolved from the specimen is carried by a flow of nitrogen, previously dried, through a water absorber; the absorption of water causes an exothermic reaction, which causes a slight increase in the temperature of the carrying gas, which is detected by means of a differential thermocouple and recorded as a function of the temperature of the specimen.

Details of the apparatus are shown in fig. 1. The furnace is made of a tube of Vycor glass, 40 cm. long and 12 mm. inside diameter. Five feet of Nichrome wire, of 0·02 in. diameter, is wound in a double layer around the central part of the tube with a sheet of asbestos for insulation. The ends of the tube remain cool so that rubber stoppers can be used. The

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applied voltage is automatically raised by a 'Variac' transformer driven by an electric motor through a speed reducer; the temperature of 1100° C. was reached with 40 volts and 5 amps. An approximate heating rate of 15° C. per minute was chosen for the curves reported herein. A platinum, platinum-rhodium thermocouple indicates the temperature of the specimen, which is placed in a small flat porcelain crucible.
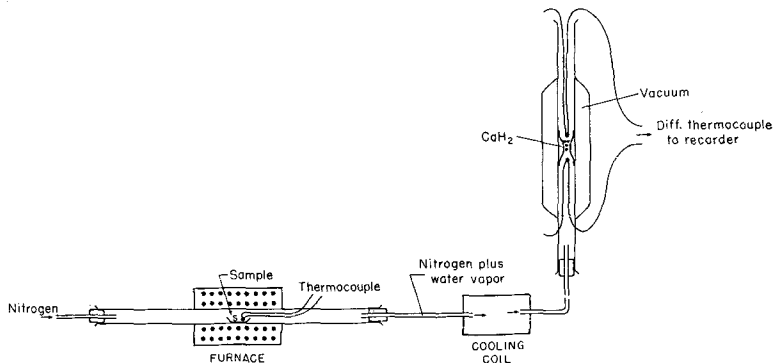

FIG. 1. Sketch of apparatus used in obtaining vapour-absorption curves.

Dried nitrogen gas is directed through the furnace at a constant rate of 25 ml. per minute to sweep out any water vapour. The nitrogen with any water vapour is cooled to room temperature in a small coil and then directed through the absorber.

The absorber is a vertical glass tube with a silvered vacuum jacket for thermal protection. A grid holds some pellets of a dehydrating agent and a differential thermocouple records the changes in temperature of the gas before and after absorption of water. In the first series of experiments, the thermal sensitivity of crystal diodes was used for detecting the temperature variations of the gas flow. Two germanium diodes mounted on a Wheatstone bridge were utilized as differential thermal gauges; however, the extreme sensitivity of the device created many experimental difficulties. For example, the weight of the specimen had to be kept at a fraction of a milligram and very complete thermal insulation was necessary. Finally, differential thermocouples of chromel and alumel wires were adopted.

Several water absorber compounds were tried. Calcium hydride gave the best results, but silica gel was also used successfully. The curves were recorded on a Brown electronic potentiometer. Operating under

the above conditions, the dehydration of 40 mg. of kaolinite produced a deflection of about 15 cm.

Analytical results. The curves in fig. 2, for halloysite with gibbsite, for kaolinite, and for dickite, show peaks for loss of water of a size and shape that would be anticipated from D.T.A. (differential thermal analysis) curves (Grim, 1953). It is not expected that the vapour curves should be precisely the same as the D.T.A. curves since any structural changes accompanying dehydration are not reflected in the vapour curves.

Each of the vapour curves, fig. 2, shows a faint depression at about 950°–1000° C. D.T.A. curves for these minerals frequently show a slight endothermic reaction at this temperature which has been interpreted (Grim, 1953) as being caused by the destruction of the dehydrated kaolinite structures. The present data suggest that, at least during very rapid heating, a small amount of water is present in the so-called meta-kaolin structure and is expelled when this structure is destroyed. In this conclusion we agree with V. Stubičan (this issue, p. 38), who presents infra-red absorption spectrum evidence for the presence of hydroxyl groups in metakaolin.

The fireclay sample, fig. 3, which has a clay mineral composition of about 75 % kaolinite and 25 % illite, produces the vapour-loss curve expected from its mineral composition and D.T.A. curve.

The illite samples, fig. 3, show the expulsion of adsorbed water at low temperatures. The curves show that the hydroxyl water is driven off gradually over a considerable temperature interval, at least at the rapid heating rates of the experiments. There is no suggestion of any water loss at high temperatures corresponding to the third endothermic reaction shown on D.T.A. curves (Grim, 1953) of these minerals.

The nontronite sample shows a vapour-loss curve that corresponds closely to the D.T.A. curve of the mineral (Grim, 1953). The hectorite sample shows the loss of adsorbed water at low temperatures, and the expulsion of hydroxyl water between about 650° and 950° C. The diocta-hedral montmorillonites studied, fig. 4, show the expulsion of the hydroxyl water at a somewhat lower temperature and often more abruptly than this trioctahedral montmorillonite. The talc sample, fig. 3, shows only the loss of hydroxyl water over a wide temperature interval extending from about 700° C. to above 1000° C.

The curves for the three montmorillonite samples, fig. 4, show peaks for the loss of adsorbed water corresponding to those on the D.T.A. curves, fig. 5. The peaks for the expulsion of hydroxyl water also
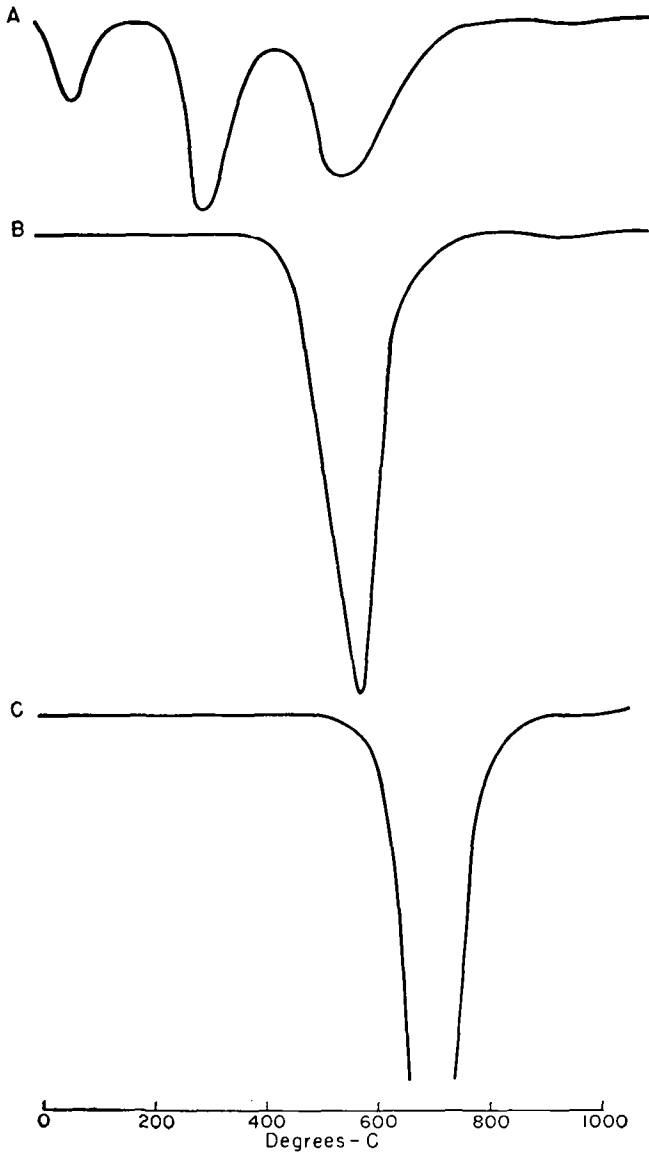
Fig. 2. Vapour-absorption curves: A, Halloysite (with gibbsite), Bedford, Indiana; B, Kaolinite, McIntyre, Georgia; C, Dickite, Baraboo, Wisconsin.
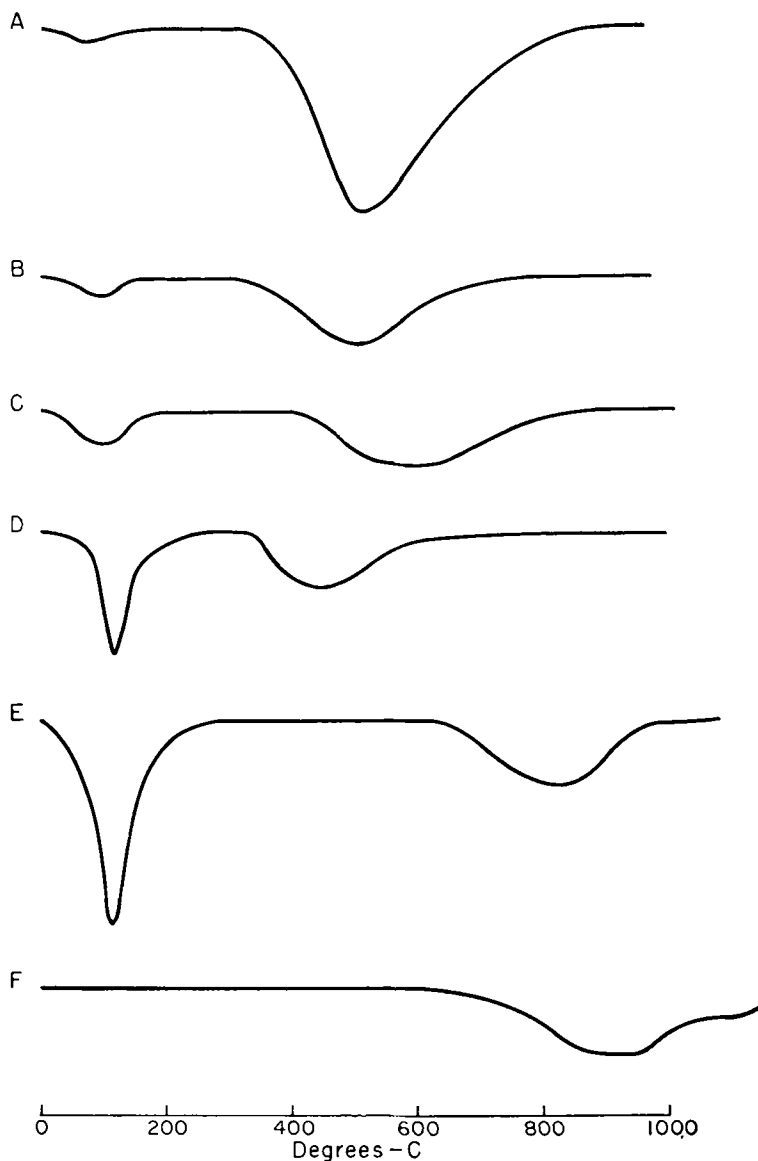
FIG. 3. Vapour-absorption curves: A, 75% kaolinite, 25% illite (fireclay), Grundy County, Illinois; B, Illite, Vermilion County, Illinois; C, Illite, Grundy County, Illinois; D, Nontronite, Manito, Washington; E, Hectorite, Hector, California; F, Talc, New York.
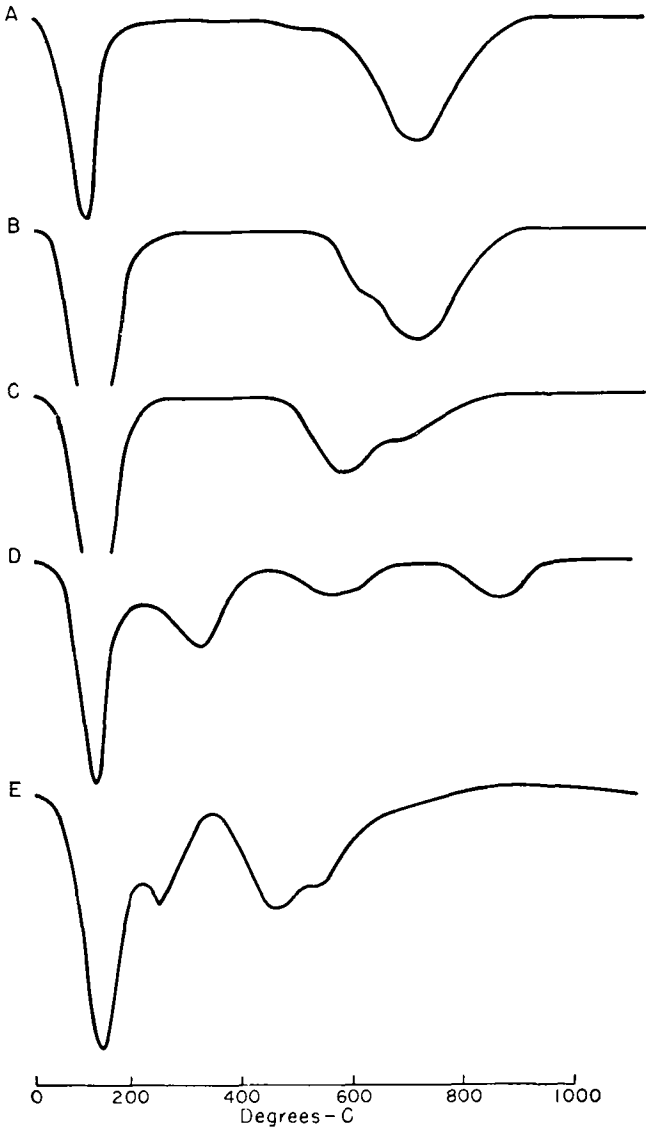
Fig. 4. Vapour-absorption curves: A, Montmorillonite, Colony, Wyoming; B, Montmorillonite, Amory, Mississippi; C, Montmorillonite, Mendoza, Argentina; D, Sepiolite, Vallecas, Spain; E, Palygorskite, Attapulgus, Georgia.
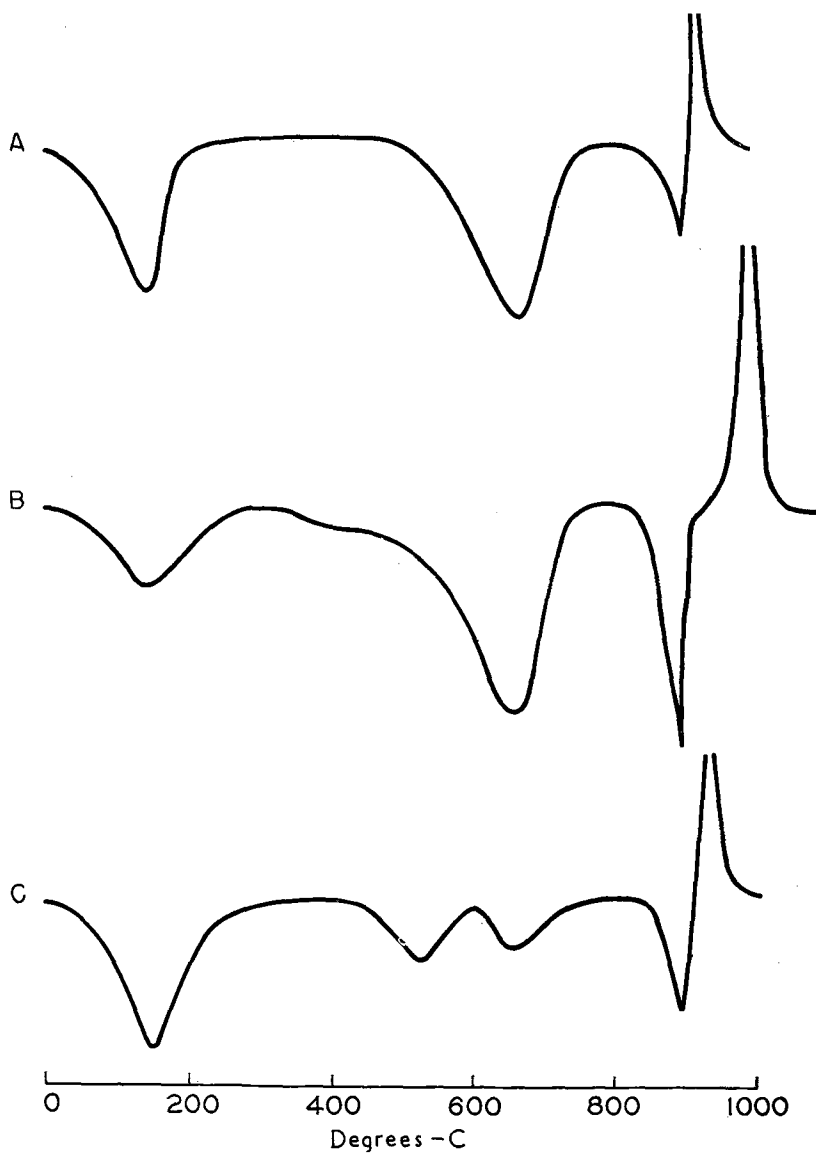
FIG. 5. Differential thermal analysis curves: A, Montmorillonite, Colony, Wyoming; B, Montmorillonite, Amory, Mississippi; C, Montmorillonite, Mendoza, Argentina.

FIG. 6. Differential thermal analysis curves: D, Palygorskite, Attapulgus, Georgia; E, Halloysite (with gibbsite), Bedford, Indiana; F, Sepiolite, Vallecas, Spain.

correlate in the two types of curves. When the hydroxyl dehydration peak is a doublet on the D.T.A. curve, it is also a dual peak on the vapour-loss curve indicating that both parts of the doublet are related to water loss. The vapour-loss curves are at least as sensitive in detecting such doublets as are the D.T.A. curves. The vapour-loss curves do not indicate any expulsion of water corresponding to the high-temperature endothermic peaks of the montmorillonites on the D.T.A. curves, fig. 5.

The vapour-loss curve for the palygorskite (attapulgite) sample, fig. 4, corresponds to the D.T.A. curve, fig. 6, except that the vapour-loss curve resolves the higher-temperature endothermic peak into a doublet.

The low temperature portion of the vapour-loss curve for the sepiolite sample, fig. 4, corresponds to endothermic reactions on the D.T.A. curve for the same sample, fig. 6. The vapour-loss curve shows a definite vapour expulsion at 500°–600° C. which is only suggested on the D.T.A. curve. Also the vapour-loss curve shows that for the sepiolite the endothermic reaction at about 800° C. is accompanied by a loss of water. Martin-Vivaldi and Cano-Ruiz (1956) have recently published a detailed study of the dehydration of the same palygorskite (attapulgite) and sepiolite. Their data correlate exactly with the vapour-absorption curves. In fact the correlation is far superior to that with the D.T.A. curves.

Discussion of results. It is believed that the analytical method presented herein provides a simple means of obtaining additional definitive characteristics of hydrous minerals. Using other absorbents, similar curves could undoubtedly be obtained to record the expulsion of other gaseous materials produced on heating minerals, for example, carbon dioxide from carbonates.

The new method can contribute to structural studies by showing whether or not loss of water accompanies a thermal reaction. In the temperature range for the loss of hydroxyl water, the vapour-loss method appears to be extremely sensitive. In this interval the vapour-loss curves may indicate reactions shown only very slightly on the D.T.A. curve (e.g. montmorillonite from Mississippi), or not at all (e.g. palygorskite).

In the temperature interval of the loss of the adsorbed water the vapour-loss curve appears to be less sensitive than the D.T.A. curve. Thus the double peak of the Mississippi montmorillonite is shown as a single peak in the vapour-loss curve. It should be pointed out that this apparent difference in sensitivity between the vapour-loss and D.T.A. curves may have another explanation, namely, that these thermal reactions shown on D.T.A. curves are a consequence of structural changes to a greater degree than has heretofore been considered. Thus the double

nature of the peak for loss of adsorbed water from calcium montmoril-
lonites as shown on D.T.A. curves may be due to a change in water
structure after a certain amount of moisture is lost rather than to any
periodicity in the water loss. Further work is necessary to resolve this
matter.

It must be remembered that some variations in the vapour-loss curves
would result from different heating rates, different particle size of the
sample, &c.

References.

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