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SIMULTANEOUS X-RAY DIFFRACTION–DTA*

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Abstract– Simultaneous X-ray diffraction-differential thermal analysis equipment for an X-ray diffractometer was evaluated. A brief description of the apparatus and of the method of preparing the sample was given.

Simultaneous XRD–DTA was used to study various clay minerals and inorganic hydrates. It was found in the study of clays such as hectorite, montmorillonite, kaolinite, and attapulgite that information concerning the rate of removal of water and hydroxyl units at various temperatures could be correlated to changes in the X-ray diffraction pattern. Various inorganic hydrates such as barium chloride dihydrate, nickel sulfate hexahydrate, and potassium ferrocyanide trihydrate were examined under dynamic and static conditions of analysis along with vacuum conditions. It was found that good correlation could be obtained between the X-ray diffraction pattern and the loss of water from the hydrates as indicated by the DTA curves.

INTRODUCTION

For the past several years, a number of workers (McAtee, 1967, 1969; Rowland, 1959,) in the field of clay mineralogy have been utilizing a technique of X-ray diffraction referred to as heating-oscillating diffractometry. This method is a technique whereby a specimen is placed in a diffractometer and oscillated back and forth about a specific Bragg angle while the temperature of the sample is increased at a constant rate similar to that in DTA experiments. The method has proved valuable in differentiating between several types of clay minerals that normally give the same X-ray diffraction pattern.

Clay mineralogists for many years also have utilized DTA methods for differentiating various types of clays. In fact, in order to fully characterize most clay minerals, it usually has been necessary to run both X-ray diffraction and DTA on the samples. Heating-oscillating X-ray diffraction aided greatly in the analysis of difficult materials but often this method was not sufficient. It has long been thought that a combination of X-ray diffraction and DTA might further aid in the analysis and characterization of many of these materials. This paper describes an apparatus which combines X-ray diffraction and DTA and illustrates some of the uses of simultaneous XRD–DTA.

EXPERIMENTAL

The apparatus used was a Rigaku unit built for a General Electric XRD diffractometer. The device consists of three major components: (1) high temperature furnace to be attached to the goniometer of a General Electric XRD diffractometer; (2) temperature controller and DTA amplifier; and (3) three pen recorder.

The furnace unit is attached to the diffractometer stage in the same manner as a standard sample holder. The sample holder has the following adjustments: translation, which allows positioning exactly in the center of the X-ray beam; inclination, which permits alignment exactly parallel to the line focus of the X-ray beam; and fine theta, which positions the sample for para-focusing conditions. The differential and control thermocouples enter through the base of the sample positioning device into the specimen holder.

The specimen holder consists of a nickel block with machined cavities for the reference and unknown samples. The block also contains holes that allow the thermocouple to be in intimate contact with the specimen and reference sample. The block is positioned in the holder so that the reference sample faces the back side of the furnace while the specimen faces the front side and is in X-ray para-focusing alignment. With such an arrangement, simultaneous X-ray diffraction–DTA can be accomplished.

The furnace heater consists of a platinum–rhodium winding which uniformly encircles the sample area. Temperature uniformity about the sample block is increased by means of a ceramic cylinder with a nickel foil equalizer inserted between the sample and the furnace. On the outside of the heater winding there is still another ceramic cylinder containing nickel foil which provides additional temperature equalization and

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smoothing in the sample area. Finally, a metal cylinder with either aluminum foil or mylar X-ray windows is positioned so that the specimen can be examined under various gas flows and under vacuum.

The sample and reference material are compacted into the specimen holder by means of glass plates and a set of jigs. The jigs are used to position the sample and reference so that they will be in intimate contact with the thermocouples when the specimen holder is placed in the furnace.

The controller consists of a number of different components used to control the heating rate of the furnace, the amplification of the various thermocouple signals and the oscillation of the X-ray diffractometer. The heating-rate programmer is unique in that it has six individual control regions; thus, one can have several different heating or cooling rates, as desired. A three pen recorder records the temperature, the DTA pattern, and the X-ray diffraction pattern. There is a fourth pen which shows the change in the diffractometer angle 2θ.

RESULTS AND DISCUSSION

Simultaneous X-ray diffraction-DTA has been used to study various clay minerals, inorganic hydrates, organo-clay complexes and ligand-inorganic-clay complexes.

Hectorite clay is a trioctahedral montmorillonite with all the octahedral positions in the clay structure occupied by magnesium atoms, with some Li^+ for Mg^{2+} substitution. The mineral has a cation exchange capacity near 100 meq./100g clay. Upon heating, the adsorbed water associated with the basal surfaces and with the exchangeable cations is readily removed at low temperatures. On the other hand, hectorite does not show a pronounced dehydroxylation peak in the region of 500–700°C. as do other montmorillonites. It was of interest to study the dehydroxylation of the clay by simultaneous X-ray diffraction-DTA. Figure 1 shows the simultaneous X-ray diffraction-DTA pattern (001) for hectorite clay with sodium ions in exchange positions. It can be seen that the DTA endotherm reaction near 100°C is accompanied by very pronounced changes in both the intensity

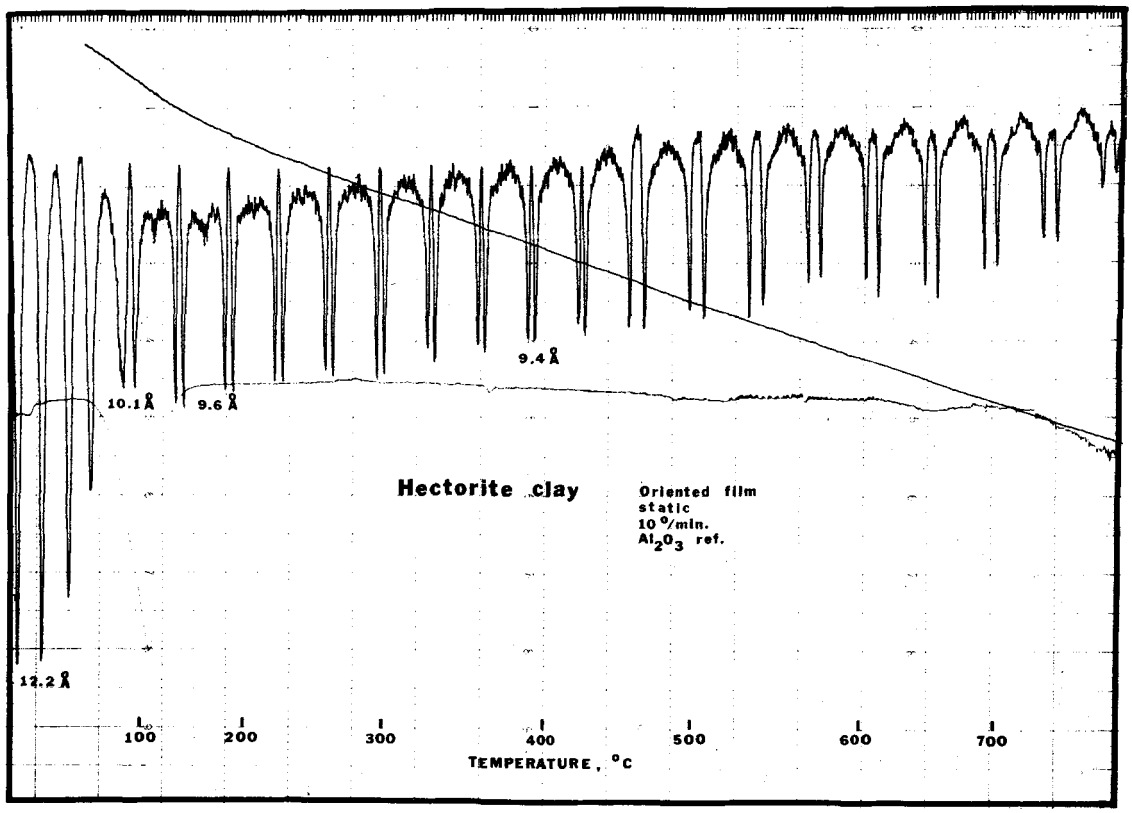


Fig. 1. Simultaneous XRD–DTA of the trioctahedral montmorillonite hectorite.

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and the value of the 001 *d*-spacing. This sharp change is followed by a lesser change in the *d*-spacing and a slight increase in its intensity. The relationship of these changes to the endotherm peak of the DTA curve shows that the first large change in X-ray intensity starts slightly before the initiation of the DTA endotherm. This suggests a reorientation of the water molecules before they are actually desorbed from the clay and a thermal gradient in the DTA sample holder. It will also be noted that the relatively weak *d*-spacing of 10·1 Å occurs before the DTA maximum is reached. By the time the endotherm has returned to the base line the X-ray peak has increased in intensity at a spacing of about 9·6 Å. As the heating of the sample is continued, the intensity of the 001 spacing decreases slightly accompanied by a gradual change to 9·4 Å. At about 600°C the intensity starts rapidly decreasing until close to 800° the (001) spacing has almost disappeared. This change is accompanied by only a small endotherm starting at about 725°C. Apparently, the main dehydroxylation does not start until 725°C is reached, although the slight decrease in the intensity of the 9·4 Å X-ray peak starting at 300° suggests that dehydroxylation may begin at the lower temperature.

Kaolinite is a two layer clay mineral consisting of a silica tetrahedral layer combined with an alimina octahedral layer, and differs from hectorite which is a three layer mineral having a magnesium octahedral layer sandwiched between two silica tetrahedral layers. Kaolinite generally has a very low cation exchange capacity and a small affinity for adsorbed water. Its DTA pattern consists of a major dehydroxylation endothermic peak at 500°C and a recrystallization exothermic peak at 900°C.

Simultaneous X-ray diffraction (001)-DTA patterns for kaolinite are shown in Fig. 2. It can be seen that the X-ray *d*-spacing of 7·1 Å remains constant until dehydroxylation begins at about 400°C. In fact it is apparent that the DTA dehydroxylation begins well before there is any indication of change in the X-ray diffraction pattern. It will also be noted that the intensity of the 001 peak completely disappears at 540°C, the same temperature as the maximum of the DTA endotherm.

Another example of simultaneous XRD (001)-DTA of a clay mineral is shown in Fig. 3 for attapulgite. Attapulgite is fibrous instead of platy as are hectorite and kaolinite. Attapulgite contains exchangeable cations which retain a fairly high adsorbed water content. The DTA curve in Fig. 3 shows two endotherms in the vicinity of 100°C, one peak at a little less and one at a little more than 100°C. It will be noted that the intensity of the (001) increases almost two fold

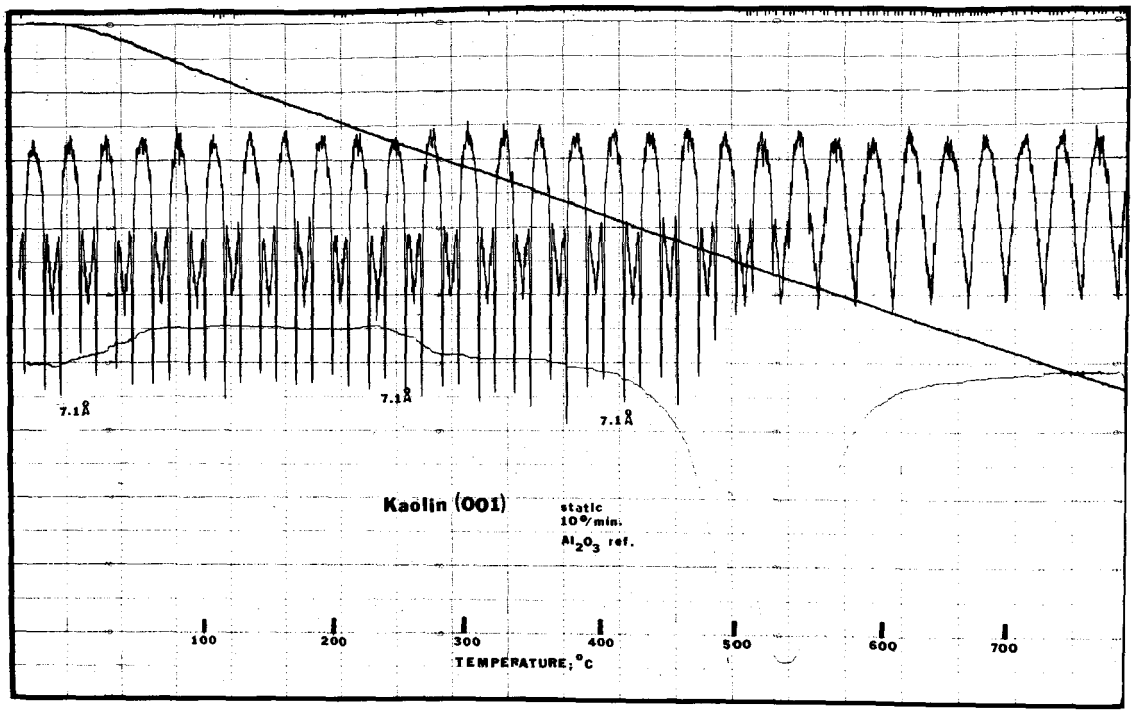


Fig. 2. Simultaneous XRD–DTA of kaolin.

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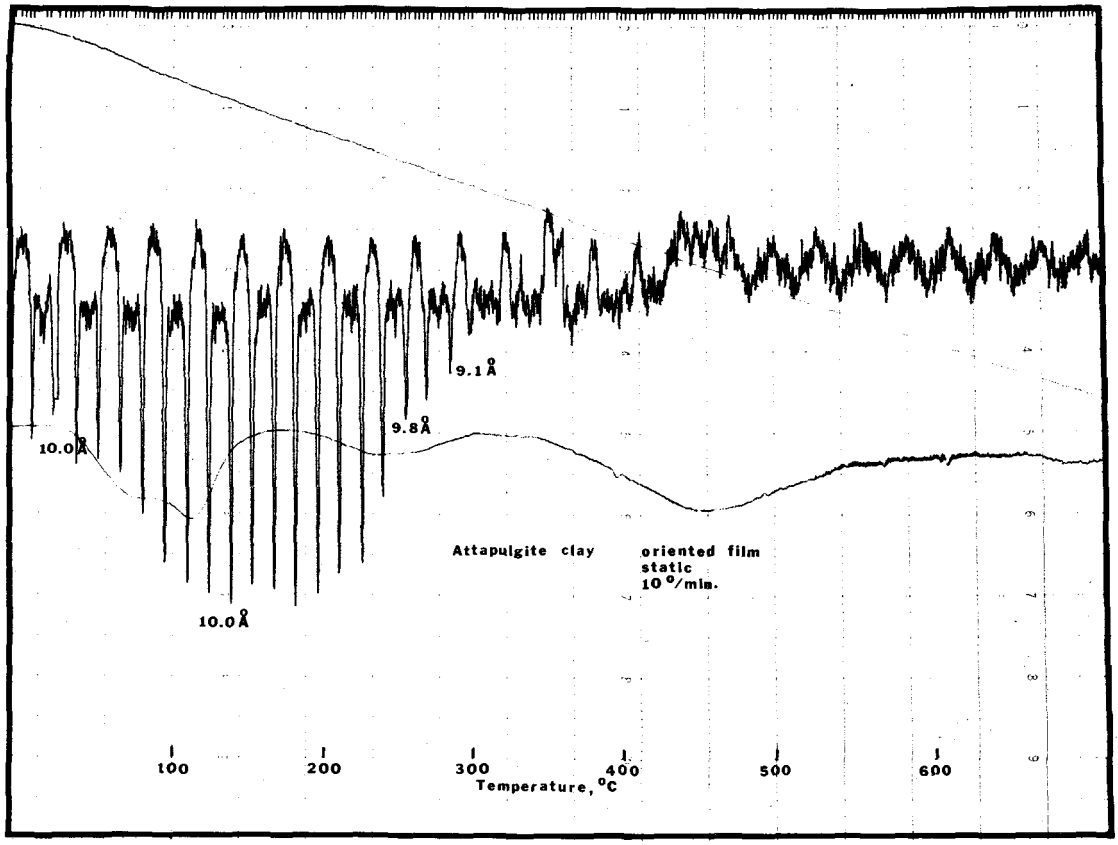


Fig. 3. Simultaneous XRD–DTA of attapulgite.

while these two endothermic reactions are occurring. Furthermore, the *d*-spacing does not change in this region, remaining at 10·0 Å. As this water is lost the irregularities in fiber alignment are apparently reduced thereby causing the increase in intensity of the (001).

The third endothermic peak, starting at a temperature of about 200°C and continuing to a temperature of 300°C, coincides with a rapid change of *d* (001) from 10·0Å to 9·1Å. The peak then disappears from the X-ray diffraction pattern either from loss in intensity or because it shifts outside the range of the oscillation. It is concluded that this endothermic peak is related to a major change in the attapulgite crystal structure. This endotherm has been associated with water in the channels attached to the silicate units (Grim, 1968). Apparently, the arrangement of the individual fibers is disrupted causing the (001) spacing to change to a value outside the region of oscillation of the diffractometer. The last endothermic peak at about 450°C is associated with the dehydroxylation of the clay.

Simultaneous XRD–DTA curves for the low temperature dehydration of barium chloride dihydrate are shown in Fig. 4. These curves show the results obtained when such a material is heated at the relatively slow rate of 2°/min. The various endothermic reactions are clearly shown along with the changes in the *d*-spacing and intensities associated with the various states of hydration of the barium chloride. The first endotherm starts at a temperature of about 40°C. Simultaneously the intensity of the 2·9 Å (131) barium chloride dihydrate X-ray peak starts decreasing with no change in the *d*-spacing. At a temperature of about 50°C this *d*-spacing completely disappears and immediately a peak occurring at 3·06 Å starts increasing in intensity. The 3·06 Å reflection is associated with $BaCl_2.H_2O$.

The large endothermic peak starting at about 65° and reaching a maximum at about 80° is not associated with any change in X-ray *d*-spacing although there is a small change in the intensity of the diffraction peak. At a temperature of about 95°C the intensity of the 3·06 Å peak suddenly

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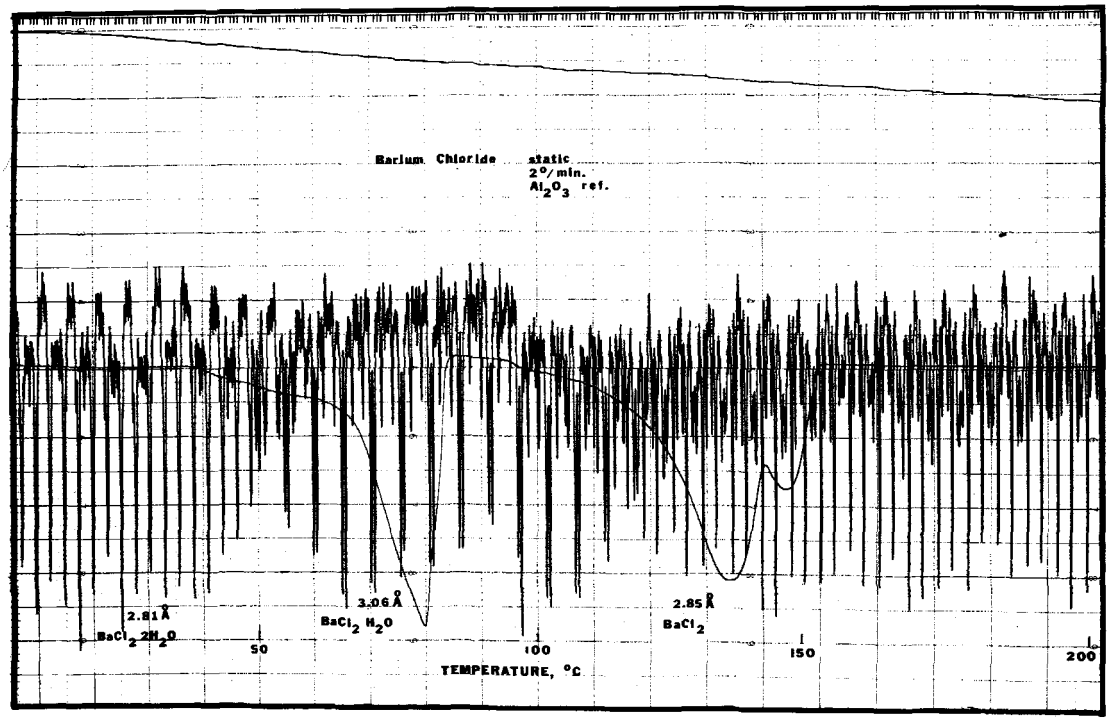


Fig. 4. Simultaneous XRD–DTA of barium chloride dihydrate.

increases and then decreases, a change which occurs simultaneously with the start of the third endothermic reaction. This third endotherm has its maximum at about 135°C and is then followed by another endotherm with a maximum close to 145°C. It will be noted that the 3·06 Å $BaCl_2H_2O$ peak decreases in intensity and disappears at a temperature of 130°C and at this temperature a peak at 2·85 Å (121) associated with barium chloride anhydride occurs. This peak increases in intensity until the maximum of the fourth endotherm reaction occurs. This set of curves illustrates how simultaneous XRD–DTA permits direct correlation of the changes in *d*-spacing and intensities of the X-ray pattern with the various thermal effects. For example, the change in intensity of the 3·06 Å peak that takes place between 60°C and 95°C is apparently associated with rearrangements of the monohydrate crystallite in the sample. The intensity decrease is probably associated with disorder followed by an ordering which starts at 95°C. The change from a monohydrate to an anhydride does not occur until about 115°C, shown by the curves.

Figures 5 and 6 show the dehydration of nickel sulfate hexahydrate under nitrogen flow and vacuum conditions, respectively. In Fig. 5 a very large change in the X-ray diffraction pattern occurs over a very small temperature range associated with the first endothermic peak of $NiSO_46H_2O$ about 60°C. A somewhat larger endothermic peak at 95°C is accompanied by only a slight change in the X-ray pattern. The *d*-spacing of 4·35 Å (112) remains essentially the same throughout this temperature range. The third endothermic peak at about 150°C is accompanied by the disappearance of the X-ray diffraction peak.

Nickel sulfate hexahydrate was also run under a vacuum of 63 mm of mercury and the results are shown in Fig. 6. It can be seen that a rather large broad endothermic reaction occurs with a maximum at 100°C and a shoulder at 115°C. The X-ray pattern shows that the 4.62 Å X-ray peak of the hexahydrate decreases in intensity and finally disappears at a temperature of about 60°C. Under vacuum, the 4.35 Å X-ray peak is not observed; therefore, it is concluded that there are differences in the various states of hydration obtained when $NiSO_46H_2O$ is heated under vacuum and when heated under the dynamic condition of flowing nitrogen.

Figure 7 is the simultaneous XRD–DTA patterns for potassium ferrocyanide trihydrate heated at 5°/min under conditions of flowing

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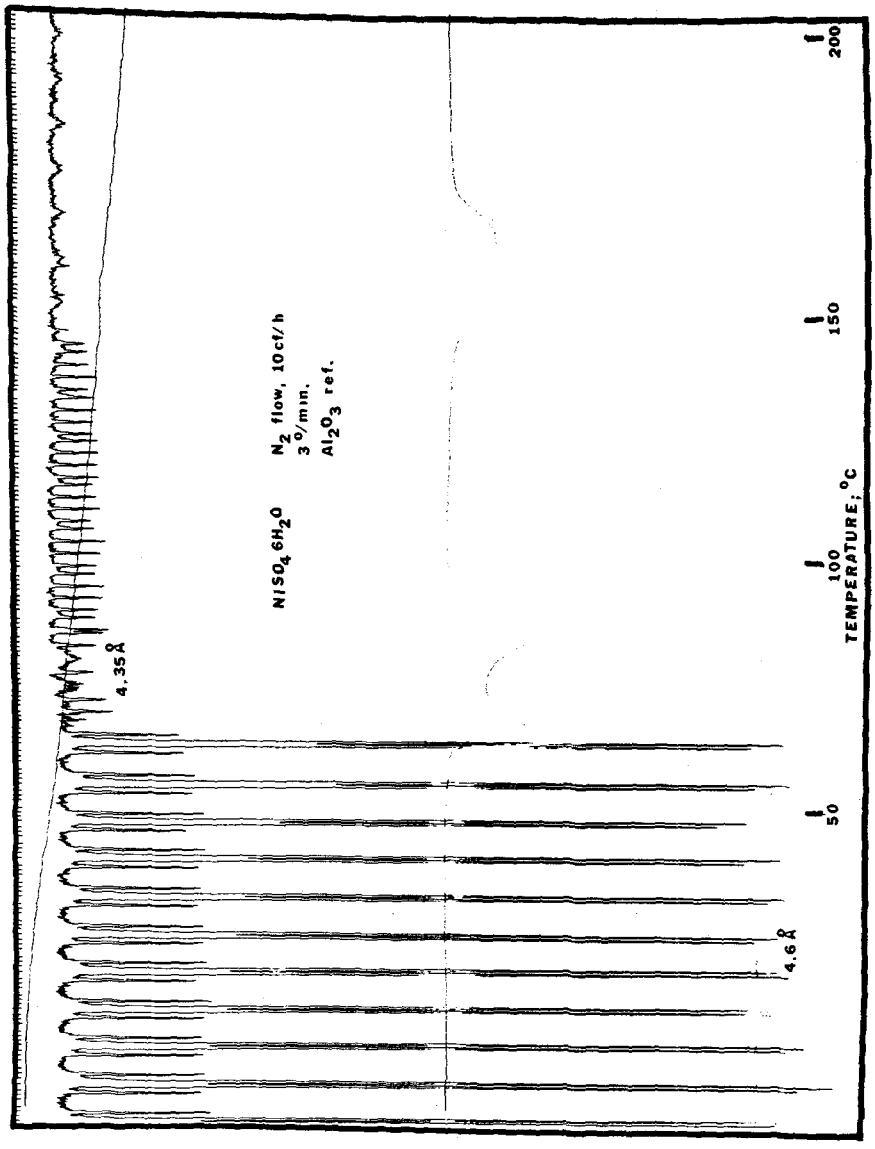


Fig. 5. Simultaneous XRD–DTA of nickel sulfate hexahydrate under nitrogen flow.

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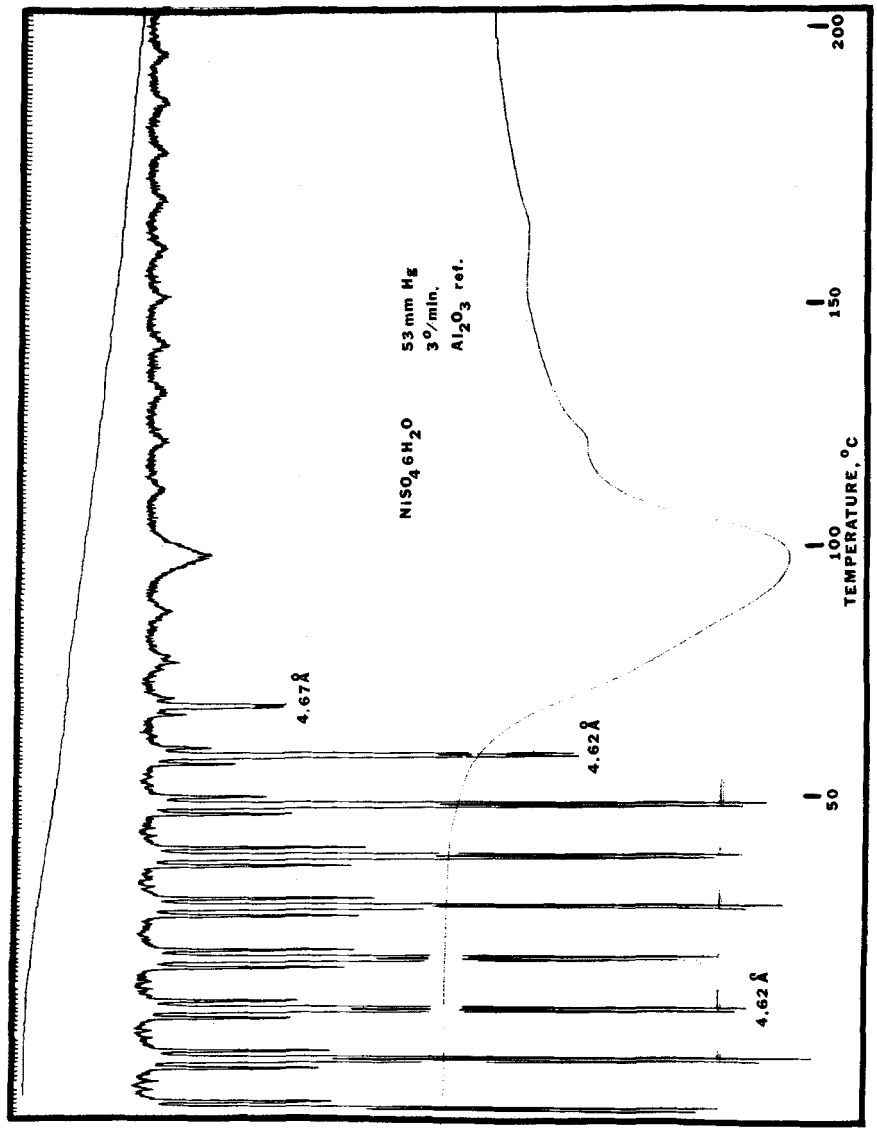


Fig. 6. Simultaneous XRD–DTA of nickel sulfate hexahydrate under vacuum.

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nitrogen and nitrogen saturated with water vapor (100%r.h.). The purpose of this experiment was to determine what effects water vapor in the dynamic gas flow experiment would have on the X-ray diffraction and DTA patterns. In both cases an endotherm occurred at a temperature of about 85°C. The specimen heated in the presence of water vapor gave a much more intense peak. The change in the *d*-spacing from 2·79 Å(0012) to 2·84 Å occurred at about the same rate in both samples, with a complete shift to the 2.84 Å value before the maximum of the dehydration endotherm was reached.

Potassium ferrocyanide trihydrate heated under both air flow and vacuum conditions is illustrated in Fig. 8. In vacuum the dehydration starts at a lower temperature than when the same sample is heated under dynamic conditions of air flow. This result is similar to that discussed above for nickel sulfate dihydrate. The dehydration endotherm under vacuum is somewhat broader than that found under dynamic conditions and the change in the diffraction spacing at 2.79 Å occurs at a lower temperature. The intensities of the diffraction peaks start decreasing at about the same temperature that the first indication of the endotherms occur. Also, the peak has completely changed to the anhydride form at a temperature somewhat before the actual maximum of the endotherm is reached.

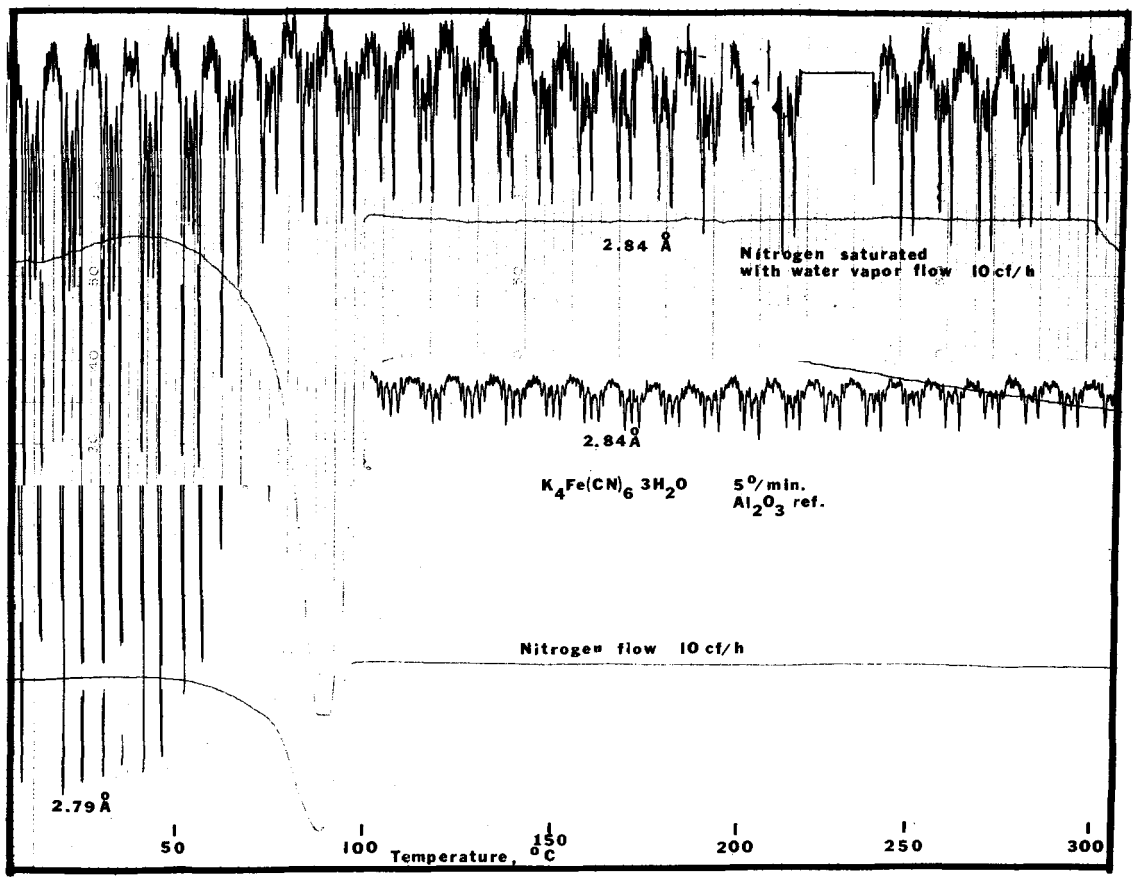


Fig. 7. Simultaneous XRD–DTA of potassium ferrocyanide trihydrate under nitrogen flow.

These are but a few examples of the way simultaneous XRD–DTA can be used. The information obtained by this method allows one to recognize more clearly structural changes associated with corresponding thermal effects. With further improvements in the apparatus to permit easier following of the change in *d*-spacing and less thermal lag in the DTA the combined technique should prove to be most useful.

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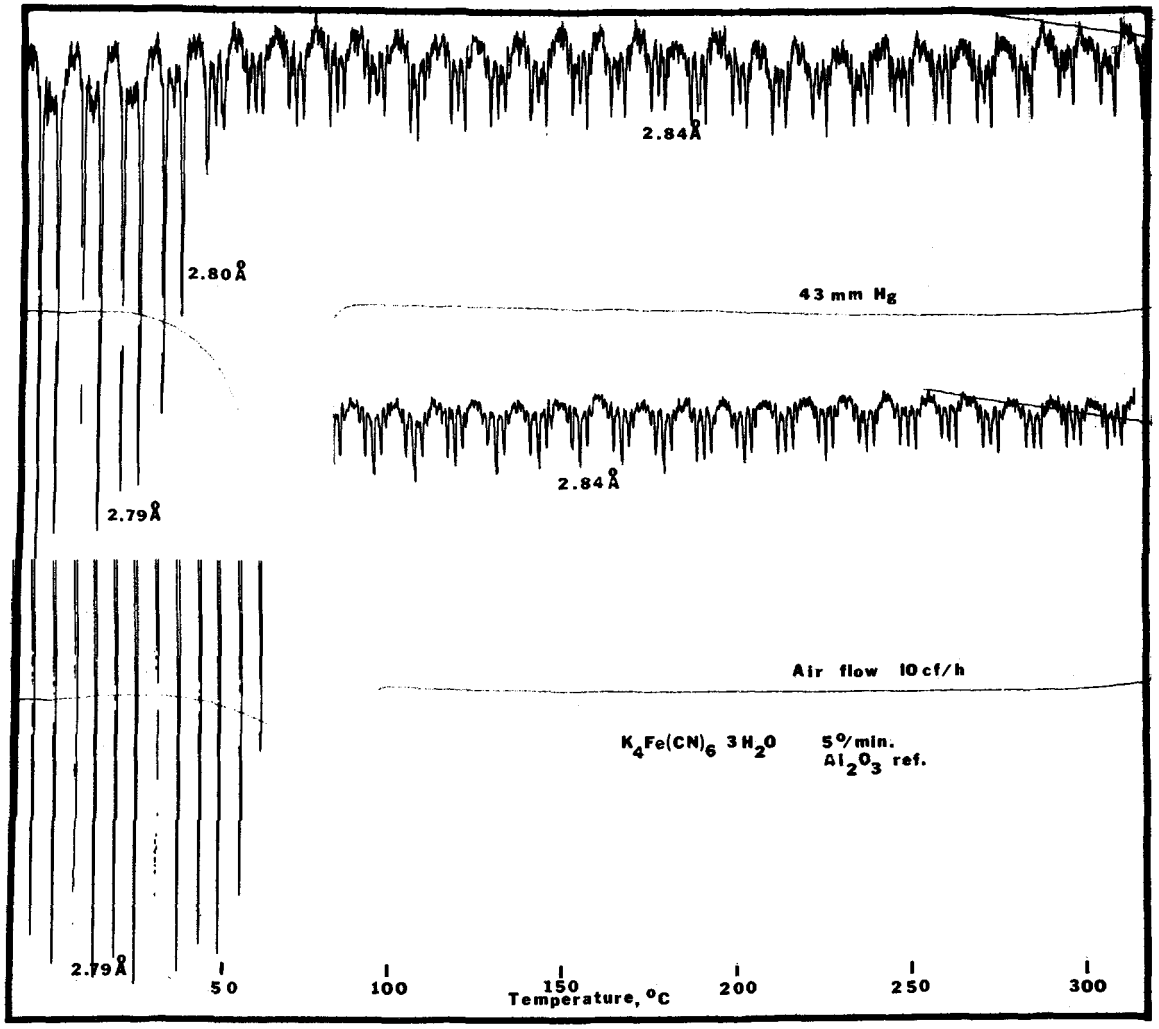


Fig. 8. Simultaneous XRD–DTA of potassium ferrocyanide trihydrate under air flow and under vacuum.

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Résumé—L'équipement destiné à un diffractomètre à rayons X pour effectuer simultanément l'analyse thermique différentielle et la diffraction des rayons X a été évalué. Une brève description est donnée de l'appareil et de la méthode de préparation de l'échantillon.

La diffraction des rayons X et l'analyse thermique différentielle simultanées ont servi à étudier divers minéraux argileux et des hydrates inorganiques. On a trouvé que dans les argiles tels que la hectorite, la montmorillonite, la kaolinite et l'attapulgite, l'information concernant le taux d'extraction de l'eau et des groupes hydroxyles à des températures variées peut être accordée aux changements du

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modèle de diffraction des rayons X. Les différents hydrates inorganiques tels que le dihydrate de chlorure de baryum, le hexahydrate du sulfate de nickel et trihydrate du ferrocyanure de potassium ont été examinés dans des conditions d'analyse statiques et dynamiques en même temps que sous vide. Il y a un bon accord entre le modèle de diffraction des rayons X et la perte d'eau des hydrates ainsi que le montrent les courbes d'analyse thermique différentielle.

Kurzreferat – Die Ausrüstung eines Röntgen Diffraktometers für gleichzeitige Röntgenbeugene und Differential-Thermoanalyse wird einer Beurteilung unterzogen. Es wird eine kurze Beschreibung des Gerätes und der Vorbereitung einer Probe gegeben.

Die gleichzeitige Röntgenbeugung-Differentialthermoanalyse (XRD-DTA) wurde zur Untersuchung verschiedener Tonminerale und anorganischer Hydrate verwendet. Im Laufe der Untersuchung von Tonen wie Hectorit, Montmorillonit, Kaolinit und Attapulgit wurde festgestellt, dass die Geschwindigkeit der Entfernung von Wasser und von Hydroxyleinheiten bei verschiedenen Temperaturen in eine Beziehung zu Veränderungen im Röntgenbeugungsmuster gebracht werden konnte. Es wurden verschiedene anorganische Hydrate wie Bariumchlorid-Dihydrat, Nickelsulfat-Hexahydrat und Kaliumferrocyanat-Trihydrat unter dynamischen und statischen Bedingungen, sowie unter Vakuumbedingungen analysiert. Eine gute Korrelation zwischen dem Röntgenbeugungsmuster und dem Wasserverlust der Hydrate, veranschaulicht durch die DTA Kurven, konnte festgestellt werden.

Резюме—Описана приставка для рентгеновского дифрактометра, позволяющая проводить одновременно рентгенографическое и дифференциально-термическое исследование. Дано краткое описание аппаратуры и метода препарирования образцов.

Одновременные рентгенографический и дифференциально-термический анализ были использованы для изучения различных глинистых минералов и неорганических гидратов. В процессе исследования глин (гекторит, монтмориллонит, каолинит и аттапульгит) обнаружилось, что определенная информация относительно скорости удаления воды и гидроксильных групп может быть получена по изменению рентгеновских дифракционных картин. Различные неорганические гидраты, такие как дигидрат хлорида бария, гексагидрат сульфата никеля и тригидрат ферроцианида калия, были изучены как в динамическом, так и в статическом состоянии в условиях вакуума. Установлено, что может быть получено хорошее соответствие между рентгеновскими дифракционными картинами и потерей воды, фиксируемой по кривым ДТА.

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