

## MINERALOGY

## Basic Dyestuffs in Clay Mineralogy

BASIC dyestuffs are adsorbed on clay minerals by cation exchange reaction. The amount of dye adsorbed<sup>1</sup> and the resulting colour transformations<sup>2</sup> provide a possible basis for identifying clay minerals, but they are not very reliable. We have found that clay mineral-dye complexes exhibit characteristic thermograms and this method may possibly be applicable to the identification of clay mineral. Certain clay minerals which exhibit similar thermograms can be differentiated by the thermograms of their dye complexes.

Four types of clay minerals, namely, kaolinite, illite, nontronite and montmorillonite, were each treated with excess of aqueous solution of malachite green, methylene blue, methyl violet or piperidine. The unadsorbed organic material was removed by filtration and thorough washing. Thermograms were obtained by carrying out the differential thermal analysis of the complexes semi-automatically, using a Leeds and Northrup programme controller. The rate of heating was maintained at 10 deg. C./min.

Thermograms of kaolinite, illite, nontronite and montmorillonite with three basic dyestuffs, namely, malachite green, methylene blue and methyl violet, have been investigated. Differential thermal analyses of piperidine complexes of clay minerals have also been carried out for comparison. All the complexes exhibit low-temperature exothermic peaks at about 100° C. smaller than those of the untreated samples. The organic matter probably occupies the spaces normally held by the water molecules.

Kaolinite-dye complexes exhibit a small unmistakable exothermal dent between 350° and 435° C. due to the oxidation of a small amount of dye adsorbed by base-exchange reaction. The exothermic peak of kaolinite-malachite green complex is much more intense than the other kaolinite complexes, because malachite green is adsorbed to a greater extent than other dyestuffs.

Illite-dye complexes (Fig. 1a) show two intense exothermic peaks between 200° and 500° C. Nontronite and montmorillonite-dye complexes (Fig. 1b) show three exothermic peaks, two of pronounced intensities.

The second exothermic peak in illite-complexes at 460°-470° C. is less intense than that of nontronite-complexes occurring at about 600° C. Illites can be differentiated readily from nontronites by the second exothermic peak.

In montmorillonite-dye complexes, the higher-temperature exothermic peak at 650°-670° C. serves to differentiate montmorillonites from nontronites and illites, in which it occurs at about 600° C. and 460°-470° C. respectively.

From differential thermal analysis and thermogravimetric analysis it is concluded that low-temperature exothermic peaks are caused by oxidation of the dye molecules adsorbed on the edges of the clay minerals, while the high-temperature exothermic peaks are due to oxidation of dye molecules adsorbed in the interlayer.

Thus differential thermal analysis of clay mineral-dye complexes provides a more efficient method of identifying clay minerals than that of the clay mineral-piperidine complexes suggested by Allaway<sup>3</sup>, Byrne<sup>4</sup> and Carthew<sup>5</sup>. Such complexes exhibit pronounced exothermal inflexions. In addition, the

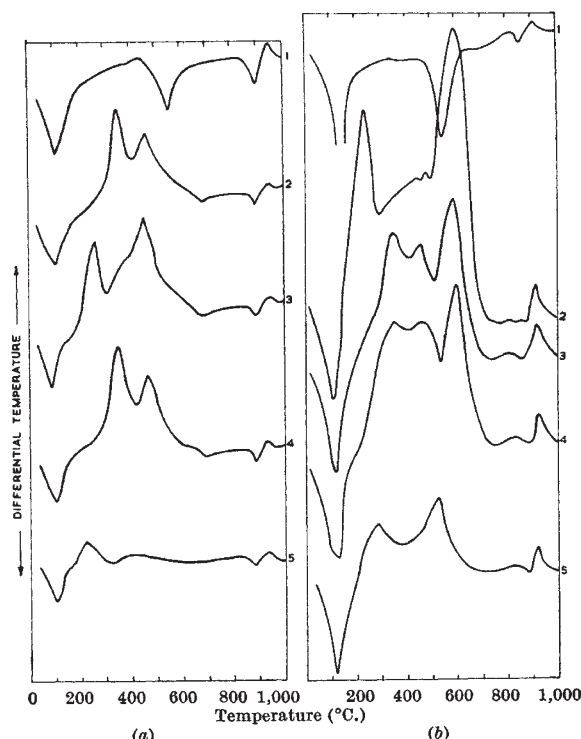


Fig. 1. (a) Thermograms of illite and its complexes: (1) illite; (2) malachite green complex; (3) methylene blue complex; (4) methyl violet complex; (5) piperidine complex. (b) Thermograms of nontronite and its complexes: (1) nontronite; (2) methylene blue complex; (3) malachite green complex; (4) methyl violet complex; (5) piperidine complex

kaolinite-dye complex also shows a distinctive exothermal dent.

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<sup>1</sup> Bossazza, V. L., *Amer. Mineral.*, **29**, 235 (1944). Emodi, B. S., *Brit. Clay Min. Bull.*, **3**, 76 (1949). Robertson, R. H. S., and Ward, R. M., *J. Pharm. Pharmacol.*, **3**, 27 (1951). Worall, D., *Trans. Brit. Ceram. Soc.*, **57**, 210 (1958).

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<sup>4</sup> Byrne, P. J. S., *Proc. Second Nat. Conf. Clay and Clay Minerals, Washington*, 241 (1954).

<sup>5</sup> Carthew, A. R., *Soil Sci.*, **80**, 337 (1955).

## GEOCHEMISTRY

## Hot Spring Areas with Acid-Sulphate-Chloride Waters

WHITE<sup>1</sup>, in a review of the thermal waters of volcanic origin, pointed out the problem of springs with a large flow of acid-sulphate-chloride water, such as Frying Pan Lake (or more correctly, Echo Crater) in the Waimangu area of the Rotorua-Taupo graben. This has a daily discharge of 800 kgm. of sulphuric