THE USE OF PIPERIDINE AS AN AID TO CLAY-MINERAL IDENTIFICATION

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ABSTRACT

It is suggested that piperidine may be useful in the identification of clay minerals during differential thermal analysis, particularly in the differentiation of expanding and non-expanding lattice minerals. Differential thermal analysis of two montmorillonites showing similar X-ray powder photographs indicated large differences in the distribution of cation-exchange sites.

INTRODUCTION

Allaway (1949) introduced the use of piperidine as an aid to clay-mineral identification, making use of its function as a strong base which will fill the interlattice cation-exchange positions of smectite minerals. Differential thermal analysis in an oxidizing atmosphere of acid clays which had been titrated to pH 7.5 with a 0.1N aqueous solution of piperidine gave traces which show large exothermic reactions at 300-350°C and subsequent exothermic reactions which depend on the nature of the mineral under investigation. Thus magnesium-rich montmorillonites gave exothermic peaks at around 700°C, while clays typical of the nontronite group gave peaks in the 450-500°C range. The presence of aluminium in tetrahedral coordination was considered to be associated with exothermic peaks at 600°C. Kandites sorbed insignificant amounts of piperidine and illites yielded reactions on a much smaller scale than smectites. Amines other than piperidine also produced similar effects.

By comparing the rates of carbon dioxide and water production during the differential thermal examination of a piperidine-saturated clay Allaway concluded that the 300-350°C exothermic peaks were due to the oxidation of hydrogen produced by thermal decomposition of the piperidine, as more than 90 per cent. of the total carbon was unoxidized at temperatures below 430°C, remaining as a black deposit of elemental carbon which was only oxidized when the clay lattice was disrupted.

Carthew (1955) has confirmed some of these findings, and concluded that, on differential thermal curves for piperidine-saturated clay minerals, (a) nontronite and montmorillonite give large exothermic peaks at 500°C and 700°C, respectively; and (b) illite can be identified in mixtures with kaolinite or with montmorillonite using

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an exothermic peak at about 550°C, but not in mixtures of all three clay minerals. Carthew also related the corrected areas of the combustion peaks to the cation-exchange capacities of the minerals in question.

**EXPERIMENTAL**

The differential thermal curves shown in Figs. 1, 2 and 3 are for K-saturated clays in nitrogen and piperidine-saturated clays in oxygen. The soil clays were obtained by dispersion with NH₄OH, followed by flocculation with excess potassium chloride and treatment with 100 vol. hydrogen peroxide for five days. The clays were saturated with piperidine by shaking with a 0.5N neutral aqueous solution of piperidine acetate three times before filtering and washing free from piperidine acetate with distilled water. The samples were dried at 40°C and ground to pass a 100-mesh sieve prior to differential thermal examination in oxygen.

The cation-exchange capacities of the clays and soil clays were determined by the micro-method of Mackenzie (1951).

X-ray powder diffraction examination was carried out, after the removal of free iron oxides by the method of Mehra and Jackson (1960), on the Mg-saturated clays in order to standardize the basal spacing of vermiculite (Walker, 1957). Finely ground specimens in Lindemann glass capillaries were saturated with glycerol and mounted in a Debye-Scherrer powder camera of 114.83 mm diameter, as supplied with the Philips X-ray Diffraction Generator Type P.W. 1010, and subjected to nickel-filtered CuKα radiation for two hours, the generator being run at 40 kV and 20 mA.

**RESULTS AND DISCUSSION**

The results for the cation-exchange capacity determinations and

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Cation-exchange capacity (m-eq/100g)</th>
<th>Predominant mineral</th>
<th>Other minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>3</td>
<td>Kaolinite</td>
<td></td>
</tr>
<tr>
<td>Wyoming Bentonite</td>
<td>81</td>
<td>Montmorillonite</td>
<td></td>
</tr>
<tr>
<td>Nontronite</td>
<td>104</td>
<td>Nontronite</td>
<td></td>
</tr>
<tr>
<td>IA</td>
<td>41</td>
<td>Chlorite-vermiculite</td>
<td></td>
</tr>
<tr>
<td>IB</td>
<td>41</td>
<td>Chlorite-vermiculite</td>
<td></td>
</tr>
<tr>
<td>IVB</td>
<td>33</td>
<td>Illite</td>
<td></td>
</tr>
<tr>
<td>VA</td>
<td>58</td>
<td>Illite-vermiculite</td>
<td></td>
</tr>
<tr>
<td>VIC</td>
<td>34</td>
<td>Illite</td>
<td></td>
</tr>
<tr>
<td>VIIIC</td>
<td>39</td>
<td>'Fireclay mineral'</td>
<td></td>
</tr>
</tbody>
</table>
| VIIIC | 68 | Montmorillonite | }

* Unless otherwise stated all clays were <1.2/μ e.s.d.
the main clay mineral component present in the samples as indicated by the X-ray results and differential thermal examination in nitrogen are shown in Table 1. The X-ray data have been presented in detail elsewhere (Oades, 1962), along with other analytical data and descriptions of profiles from which the soils yielding the soil clays were obtained.

![Differential thermal curves for K-saturated clays in nitrogen.](image)

**Fig. 1**—Differential thermal curves for K-saturated clays in nitrogen. All curves in Figs. 1, 2 and 3 were obtained using 500 mg of the <1-2μ e.s.d. material, except for Wyoming bentonite and nontronite where 600 mg and 400 mg, respectively, were used; each division on the ΔT axis represents 3.12°C; temperatures quoted are corrected to temperature of sample.

The differential thermal results for kaolinite, montmorillonite and nontronite samples before and after piperidine saturation (Figs. 1 and 2) are typical, and essentially the same as those of Allaway (1949) and Carthew (1955). However, the curves for the piperidine-
saturated soil clays (Figs. 2 and 3) all show a 360-400°C exothermic peak not present on any of the traces of Allaway or Carthew. In view of the fact that this is present on curves for illites and fireclays containing no expanding-lattice minerals, it is considered that it is due to the oxidation of the carbon residue left after the cracking of the piperidine associated with external exchange positions. Exothermic peaks occurring at temperatures above 400°C are given by expanding lattice minerals, since lattice disruption must occur before carbon associated with internal exchange sites can be oxidized. The shoulder or small endothermic effect on the side of the first large exothermic peak is probably due to the dehydroxylation of goethite (cf. differential thermal curves in nitrogen).

![Differential thermal curves for piperidine-saturated clays in oxygen.](image)

The curves for K-saturated samples IA, IB, IVB, VA and VIC in nitrogen (Fig. 1) are all similar. However, differential thermal analysis of piperidine-saturated soil clays IA and IB in oxygen (Fig. 2) shows the presence of an expanding lattice mineral. The exothermic reaction due to the oxidation of the carbon associated with internal exchange sites is split by the dehydroxylation endotherm of the clay minerals. An X-ray powder spacing of 14.2Å indicates that this expanding lattice mineral is vermiculite. A similar result is given by sample VA, where the curve for the piperidine-saturated clay (Fig. 3) suggests a higher proportion of internal to external exchange sites,
an observation supported by the high cation-exchange capacity of 58 m-eq/100g for this sample. The small sharp exothermic reaction at 459°C is probably due to calcium oxalate formed during the oxidation of organic matter by hydrogen peroxide. The X-ray data for sample VA do not show a basal spacing above 10.1Å—probably a consequence of K-saturation which is known to prevent the expansion of some vermiculites. The curves for samples IVB and VIC (Fig. 3) do not show any exothermic reactions above 400°C as was expected from the X-ray data and cation-exchange capacity values which indicate an illitic mineral with some kaolinitic.

The large peak areas and relatively high peak temperatures of the clay dehydroxylation peaks for samples VII C and IXB in nitrogen (Fig. 1) indicate a ‘fireclay mineral’; this is confirmed by the X-ray data which match those for the ‘fireclay mineral’ described by Brindley (1951). The curves for the piperidine-saturated samples (Fig. 3) indicate the absence of an expanding lattice mineral.

Fig. 3—Differential thermal curves for piperidine-saturated clays in oxygen.
Sample VIIIC is of particular interest. The high cation-exchange capacity indicates an expanding lattice mineral which X-ray results show to be montmorillonite. The spacings obtained are identical to those obtained from the Wyoming bentonite with the exception of several weak lines suggestive of kaolinite, but differential thermal analysis in nitrogen (Fig. 1) shows an abnormal montmorillonite in that two dehydroxylation endotherms are exhibited, at 532°C and 655°C. In addition, differential thermal examination of the piperidine-clay (Fig. 3) shows marked differences from the bentonite in that the sample apparently possesses an abnormally high proportion of external exchange positions as indicated by the sharp 400°C exothermic peak. The alternative explanation for this peak that the lattice is partially broken down at the relatively low temperature of about 350°C seems unlikely.

These observations suggest that in addition to the identification of montmorillonite and nontronite, piperidine will assist in the identification of vermiculite, particularly in the presence of chlorite which has a similar basal spacing. It may also be used to differentiate between normal and abnormal montmorillonites.

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REFERENCES