DIFFERENTIAL THERMAL STUDIES OF DYE-CLAY COMPLEXES

Etudes thermo-différentielles de complexes d'argile de couleur

Differential-Thermal-Studien über Farben-Ton-Komplexe

Studi termo-differenziali su complessi di argilla di colore

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ABSTRACT

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Thermograms of five types of clay minerals, viz., kaolinite, halloysite, illite, nontronite and montmorillonite complexed with organic cations like malachite green, methylene blue, methyl violet and piperidine have been investigated. The dye-clay mineral complexes exhibit much more intense exothermic peaks than those of piperidine clay mineral complexes. Kaolinite and halloysite-dye complexes also exhibit exothermic dents of moderate intensities. Thermograms of dye-clay mineral complexes may advantageously be applied for clay mineral identification. Of the four organic cations studied, methylene blue cations show exothermic inflections of maximum intensity. D.T.A. in conjunction with thermogravimetric analysis indicates that organic cations adsorbed on the edges of the clay minerals decompose at low temperatures (150°–400° C) and those adsorbed in the interlayer are oxidized at higher temperatures (400°–800°C).

SOMMAIRE

Des thermogrammes pour cinq types de minéraux argileux, kaolinite, halloysite, illite, nontronite et montmorillonite, en combinaisons avec des cathions organiques tels que vert malachite, bleu méthylène, violet de méthyle et pipéridine, ont été examniés. Les complexes des minéraux argileux avec des matieres colorantes montrent des points culminants exothermiques plus intenses que les complexes de pipéridine minéraux argileux. Les complexes de couleur-kaolinite et halloysite montrent en outre des abaissements exothermiques d'intensités moderées. On peut utilement employer à l'identification des minéraux argileux des thermogrammes des complexes des minéraux argileux avec des couleurs. Sur les quatre cathions organiques compris par les études, les cathions du bleu méthylène montrent des flexions exothermiques d'intensité maximum. D.T.A. en relation avec des analyses thermographiques annonce que des catholins organiques adsorbés à l'extrémité des minéraux argileux sont detruits à des températures peu élevées (150–400°C), et que ceux adsorbés dans les couches intérieures sont oxydés à des températures plus élevées (400–800° C).

KURZFASSUNG

Thermogramme für fünf Typen Tonmineralien: Kaolinit, Halloysit, Illit, Nontronit und Montmorillonit in Verbindung mit organischen Kationen wie Malachitgrün, Methylenblau, Methylviolett und Piperidin sind untersucht worden. Die Farben-Ton-Mineral-Komplexe ergaben viel mehr intense exothermische Höhepunkte als die Piperidin-Ton-Mineral-Komplexe. Die Kaolinite und Halloysite-Farben-Komplexe zeigen ferner exothermische Senkungen von moderaten Intensitäten. Thermogramme für Farben-Ton-Mineral-Komplexe können mit Vorteil für die Ton-Mineral Identifikation angewendet werden. Von den untersuchten vier organischen Kationen zeigen die Methylenblau-Kationen exothermische Ausslägе von max. Intensität. D.T.A. in Verbindung mit thermogravimetrischen Analysen lässt erkennen, dass am äusseren Rande der Ton-Mineralien adsorbierte organische Kationen bei niedrigen Temperaturen (150–400°C) zerstört werden, und diejenigen, die in den inneren Schichten adsorbiert werden, werden bei höheren Temperaturen (400–800°C) oxydiert.

RIASSUNTO

Termogrammi relativi a cinque tipi di minerali di argilla, caolinite, halloysite, illite, nontronite e montmorillonite, in composizioni con cationi organische quali verde malachite, blu metilens, viola metile e piperidina, sono stati esaminati. I complessi di minerali argillosi di colori mostrano delle sommità esotermiche molto più intense dei complessi di minerali argillosi di piperidina. I complessi di colori di caolinite e halloysite mostrano inoltre abbassamenti esotermiche di intensità moderate. I termogrammi relativi ai complessi di minerali argillosi di colori possono essere impiegati con vantaggio per identificare i minerali argillosi. Delle quattro cationi organiche comprese tra gli studi, le cationi di blu metilene mostrano flessioni esotermiche di intensità massima. D.T.A. in relazione con le analisi te gravimetriche indicano che cationi organiche assorbite all'ostremità dei minerali argillosi si sciolgono a tempera basse (150–400°C) e che quelle che vengono assorbite negli strati interiori si ossidano a temperature più elevate (800° C).

Introduction

The technique of differential thermal analysis (D.T.A.) has been extensively applied in identifying clay minerals[1]. Each clay mineral is identified by its characteristic endothermic or exothermic reactions. For certain clay mineral components of clays a thermal curve cannot be directly applied for elucidating the compositions. For example it is difficult to distinguish illite from halloysite, nontronite and poorly crystallized kaolinite as all these minerals exhibit endothermic peaks below 200° C caused by expulsion of adsorbed water and endothermic peaks at 500°–600° C due to dehydration of the chemically bound water. The exothermic peak at 900°–1000° C is exhibited by most clay minerals and hence is not recommended for identification purposes.

Allaway[2] and Carthew[3] carried out the D.T.A. of clays treated with piperidine. The combustion of piperidine resulted in a series of exothermic peaks in the thermograms from which an apparent relationship was obtained between the exothermic peak temperatures and the composition of the clays. From the thermograms of piperidine-montmorillonite complexes Byrne[4] concluded that all montmorillonites are intimate mixtures of several kinds of unit sheets interleaved with one another.

Much of the earlier work deals mainly with montmorillonite-amine complexes[4-13]. The exothermic inflections of piperidine-illite complexes are small and ill defined. Kaolinite-piperidine complexes fail to show any combustion effects in the thermograms.

In order to obtain well defined peaks of larger intensities for ready identification, the D.T.A. of several clay mineral complexes of kaolinite, halloysite, illite, nontronite and montmorillonite with large basic dye ions like malachite green, methylene blue and methyl violet has been carried out. A note describing the results has been published el- where[14].

Experimental Procedure

Clay Minerals: Particles of size less than 1 of the following samples were investigate

No.	Clay Mineral	Catio Exchan Capaci (m.e./10
1.	Kaolinite, Kerala, India.	7.12
2.	Halloysite, Wagon Wheel Gap, Colorado, U.S.A.	11.37
3.	Illite, Fithian, Illinois.	27.00
4.	Nontronite, Rajasthan, India.	77.21
5.	Montmorillonite (B.D.H. Bentonite).	80.61

Organic Cations:

1. Malachite green, E. Merck-Darmstad
2. Methylene blue, E. Merck-Darmstad
3. Methyl violet B, Riedel-de Haën A.G
4. Piperidine, Purified, E. Merck-Darmstad

Preparation of the Complexes:

Prior to treatment each clay mineral wa saturated with H^+ cation. 0.2% aqueous so- lution of malachite green, methylene blue methyl violet, or piperidine was added to a definite quantity of each of the clay minerals The solutions were kept in contact with the clay minerals for 24 hours with occasional stirring. The unadsorbed dye was completely removed by filtration and thorough washing and was estimated by a Microptic Colori- meter.

Differential Thermal Analysis:

D.T.A. was carried out semi-automatically by raising the temperature of the furnace at a constant rate of 10° C/min. by a Leeds and Northrup programme controller. The differ- ential temperatures were recorded by a semsitive galvanometer. Chromel-alumel thermocouples were used both for furnace and differential temperatures. The specimen holder was of Grimshaw and Roberts pattern[15]. 0.5 g of each material ground to 100 mesh size and kept over a saturated solution of calcium nitrate for 48 hrs. was subjected to D.T.A. studies.

Discussion

Figs. 1 to 5 represent respectively, the thermograms of kaolinite, halloysite, illite, nontronite and montmorillonite with three basic dyes, viz., malachite green, methylene blue, and methyl violet. D.T.A. of piperidine complexes of clay minerals have also been studied for comparison.

All the clay minerals exhibit a low temperature endothermic peak at about 100° C caused by the expulsion of adsorbed moisture. The low temperature endothermic peak is practically absent in halloysite. In some halloysites the adsorbed water is eliminated at low temperatures, often even at the room temperature. The low temperature endothermic effect is suppressed to some extent in the dye-treated samples. The organic cation displaces some of the water molecules and decreases the water content held mechanically. It is also quite probable that the endothermic effect is partly masked by the oxidation of the organic matter below 200° C. D.T.A. of malachite green, methylene blue and methyl violet shows that the oxidation of the dye molecule starts below 200° C (Fig. 6).

In illite, nontronite and montmorillonite-complexes the low temperature endothermic peak is followed by a series of exothermic peaks of varying intensities in the range 235°–670° C (Table 1). The exothermic crystallization inflections above 900° C for nontronite and montmorillonite-dye complexes are sharper than those of the untreated samples. This indicates that the dyes diminish the particle size of nontronite and montmorillonite

Table 1

Temperature and Magnitude of Thermal Peaks of Dye-Clay Mineral Complexes*

No.	Clay Mineral	Cation	Exothermic Peak Temperatures (° C)		
			<400° C	400°–600° C	>600° C
1.	Kaolinite	Malachite green	–	435 (VS)	640 (VS)
2.	Kaolinite	Methylene blue	275 (VS)	420 (VS)	665 (VS)
3.	Kaolinite	Methyl violet	350 (VS)	–	630 (VS)
4.	Kaolinite	Piperidine	–	–	–
5.	Halloysite	Malachite green	–	410 (S)	615 (VS)
6.	Halloysite	Methylene blue	290 (VS)	400 (VS)	–
7.	Halloysite	Methyl violet	–	400 (VS)	620 (VS)
8.	Halloysite	Piperidine	300 (VS)	–	–
9.	Illite	Malachite green	340 (I)	460 (M)	–
10.	Illite	Methylene blue	260 (I)	460 (I)	–
11.	Illite	Methyl violet	360 (I)	460 (M)	–
12.	Illite	Piperidine	235 (S)	400 (VS)	–
13.	Nontronite	Malachite green	360 (I)	465 (S); 585 (I)	–
14.	Nontronite	Methylene blue	235 (I)	500 (VS); 595 (VI)	–
15.	Nontronite	Methyl violet	365 (I)	470 (S); 600 (I)	–
16.	Nontronite	Piperidine	280 (S)	525 (I)	–
17.	Montmorillonite	Malachite green	380 (VI)	–	610 (VS); 670 (I)
18.	Montmorillonite	Methylene blue	250 (I); 350 (S)	450 (VS); 595 (VS)	655 (VI)
19.	Montmorillonite	Methyl violet	–	400 (I); 575 (S)	670 (I)
20.	Montmorillonite	Piperidine	300 (M)	600 (S)	680 (I)

*) VI = Very Intense; I = Intense; M = Moderate; S = Small; VS = Very Small.

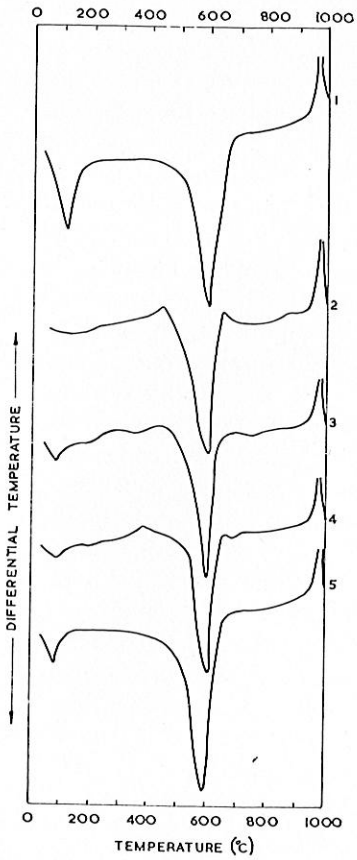

FIG. 1. Thermograms of kaolinite and its complexes. 1. Kaolinite; 2. Malachite green Complex; 3. Methylene blue complex; 4. Methyl violet complex; 5. Piperidine complex

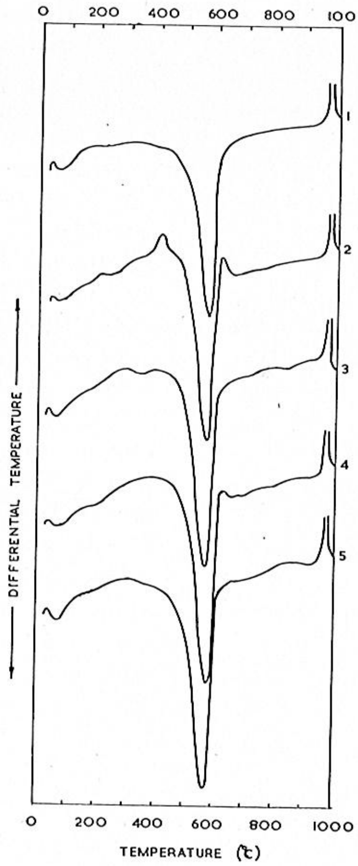

FIG. 2. Thermograms of halloysite and its complexes. 1. Halloysite; 2. Malachite green complex; 3. Methylene blue complex; 4. Methyl violet complex; 5. Piperidine complex

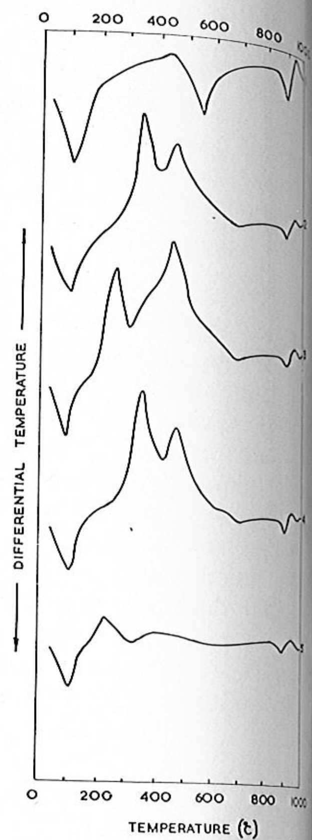

FIG. 3. Thermograms of illite and its complexes. 1. Illite; 2. Malachite green complex; 3. Methylene blue complex; 4. Methyl violet complex; 5. Piperidine complex

clay minerals. The particle size of kaolinite, halloysite or illite is little affected.

Kaolinite-dye complexes exhibit a small exothermal dent in the range 250°–435° C caused by the oxidation of the small amount of adsorbed dyes. The kaolinite-piperidine complex curve does not indicate an exothermal effect. Table 2 shows that the amount of malachite green, methylene blue and methyl violet adsorbed on kaolinite is 0.0375, 0.0225 and 0.0267 g/g respectively whereas the amount of piperidine adsorbed is only 0.0061 g/g. The dehydroxylation peak between 500° and 600° C seems to be affected to a small extent by treatment of kaolinite with malachite green and methyl violet. Of the three dyes, malachite green complex shows the most pronounced exothermic effect due to maximum adsorption[16].

Halloysite-dye complexes behave similarly to those of kaolinite, the halloysite-malachite green complex showing the sharpest exothermic effect.

Illite, nontronite and montmorillonite have large cation exchange capacities and hence their complexes exhibit intense exothermic peaks in the range 235°–670° C. The temperatures and intensities of the exothermic peaks are given in Table 1. For an assessment of the relative magnitudes of the exothermic

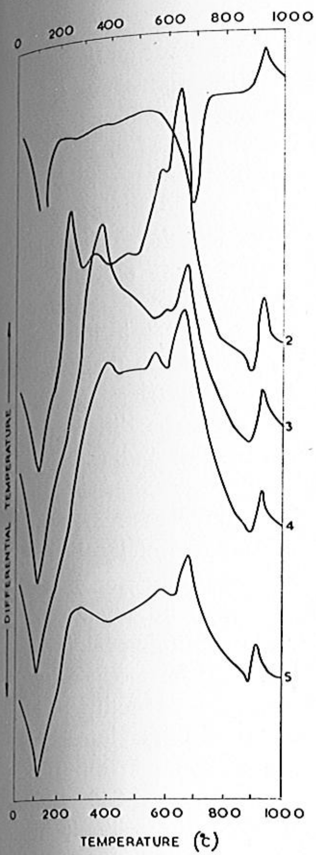

FIG. 4. Thermograms of nontronite and its complexes. 1. Montmorillonite; 2. Methylene blue complex; 3. Malachite green complex; 4. Methyl violet complex; 5. Piperidine complex

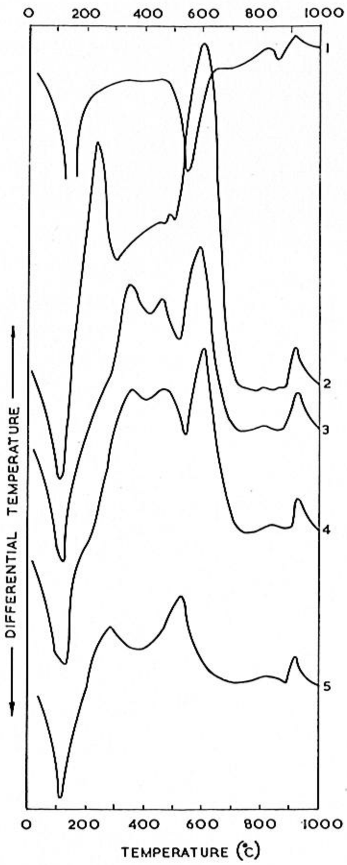

FIG. 5. Thermograms of montmorillonite and its complexes. 1. Montmorillonite; 2. Methylene blue complex; 3. Malachite green complex; 4. Methyl violet complex; 5. Piperidine complex

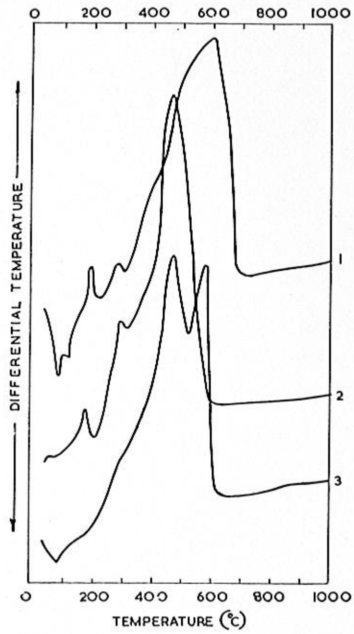

FIG. 6. Thermograms of basic dyestuffs. 1. Methylene blue; 2. Malachite green; 3. Methyl violet

Table 2
Adsorptive Capacities of Clay Minerals

No.	Clay Mineral	Adsorbate	Adsorption (g/g)	No.	Clay Mineral	Adsorbate	Adsorption (g/g)
1.	Kaolinite	Malachite green	0.0375	11.	Kaolinite	Methyl violet	0.0267
2.	Halloysite	Malachite green	0.0353	12.	Halloysite	Methyl violet	0.0353
3.	Illite	Malachite green	0.0544	13.	Illite	Methyl violet	0.0767
4.	Nontronite	Malachite green	0.0870	14.	Nontronite	Methyl violet	0.1900
5.	Montmorillonite	Malachite green	0.0977	15.	Montmorillonite	Methyl violet	0.2450
6.	Kaolinite	Methylene blue	0.0225	16.	Kaolinite	Piperidine	0.0061
7.	Halloysite	Methylene blue	0.0247	17.	Halloysite	Piperidine	0.0096
8.	Illite	Methylene blue	0.0832	18.	Illite	Piperidine	0.0230
9.	Nontronite	Methylene blue	0.1867	19.	Nontronite	Piperidine	0.0656
10.	Montmorillonite	Methylene blue	0.2050	20.	Montmorillonite	Piperidine	0.0690

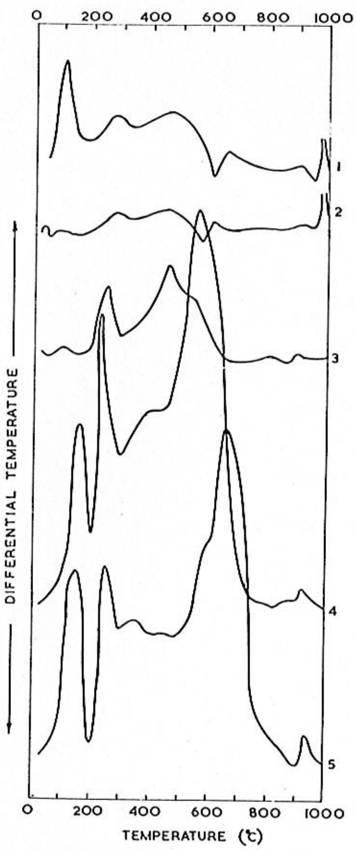

FIG. 7. Corrected thermograms of clay mineral-complexes with Methylene blue. 1. Kaolinite complex; 2. Halloysite complex; 3. Illite complex; 4. Nontronite complex; 5. Montmorillonite complex

peaks, the peaks are arbitrarily designated as, very intense, intense, moderate, small and very small. They denote the relative intensities of various complexes for a constant weight of the clay mineral.

All the illite-dye complexes show two large exothermic peaks. Malachite green and methyl violet complexes exhibit the first exothermic peak at about 340°–360° C and the methylene blue and piperidine complexes, at about 235°–260° C. All the complexes show the second exothermic inflection at 460° C. The dye-complexes show much more pronounced peaks than piperidine complexes. Of the samples studied the methylene blue complex exhibits the most intense peaks.

In addition to the two intense peaks, nontronite indicates a small exothermal effect. The first exothermic peak is of smaller magnitude and occurs in the range 235°–365° C and the second intense exothermic peak, in the range 585°–600° C. Methylene blue complex exhibits a much more intense peak than the other complexes.

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

Montmorillonite complexes also exhibit three exothermic peaks, two of large magnitude. The first occurs in the range 250°–400° C and the second at about 655°–670° C. The second exothermic peak is much more intense than the first for methylene blue and methyl violet complexes. Methylene blue complex exhibits peaks of larger intensity. In montmorillonite-dye complexes the higher temperature exothermic peak at 655°–670° C serves to differentiate montmorillonite from nontronite and illite in which it occurs at about 600° C and 460° C respectively.

From the thermograms it is observed that the dye complexes exhibit the higher temperature exothermic effects at about the dehydration temperature range of the clay minerals. A part of the heat evolved during oxidation of the dye is absorbed by the endothermic effect due to dehydration. Hence the true intensity of the exothermic effect will be represented by the sum of the exothermic area exhibited by the complex and the endothermic area exhibited by the clay mineral. True intensity or corrected curves of methylene blue complexes shown in Fig. 7 should serve as better standards for clay mineral identification.

The mechanism of the decomposition of the dye-clay complexes was followed by thermogravimetric and differential thermal analyses[17]. The studies indicate that the organic matter adsorbed on the edges being easily accessible to oxygen decomposes exothermally in the range 150°–400° C and that adsorbed on the interlayer surface being inaccessible to oxygen is oxidized only after the evolution of (OH) water.

Acknowledgement

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