

THE DETERMINATION OF KAOLINITES BASED ON COLOUR REACTIONS

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As is known from the literature different organic substances stain the different components of clays and conclusions can be drawn from this as to the different mineral groups to which they belong. Particularly in the case of montmorillonites a vivid and in most cases quick discolourisation can be observed. The disadvantage of these examinations is that they only indicate the presence of montmorillonite thus rendering it possible to distinguish it from kaolinite and illite, respectively. However, it cannot be established if kaolinite, illite or a mixture of these minerals is involved.

Vedenejeva and *Ratejev* (7) believe that for the distinguishing of the single clay mineral groups spectrophotometry is the only reliable means.

Vedenejeva (6) distinguishes kaolinite, montmorillonite and illite from one another on the basis of the shift of the adsorption band. As staining material she uses benzidine, chrizoidine and methylene blue the latter also in the presence of KCl.

Vikulova (8) mainly on the basis of *Vedenejeva's* examinations uses methylene blues for staining. In such cases methylene blue stains the kaolinite clays pale light violet, this colour does not change even on the addition of KCl, a mixture of hydromica on the other hand turns according to the increase of the quantity of the hydromicas on the addition of KCl into violet blue, blue, or skyblue. However, the determination of this colour renders the method very unreliable.

Mielenz and *King* (3) use for the determination of kaolinite and for its separation from montmorillonite and illite resp. malachit green dissolved in nitrobenzine and safranine »y«. The adsorption of these dyes brings about a pleochroismus. The extent of crystallization influences the intensity. With malachit green the characteristic colours are blue and yellowish red perpendicularly to the cleavage surface and with safranine »y« yellowish green and purple parallel to the cleavage surface. Benzidine did not give a characteristic colour reaction.

The single dickite crystals did not absorb either malachit green nor safranine »y«. Benzidine does not either produce a change in the colour in the presence of dickite.

Nacrite if it is in large crystals does not adsorb the above dyes, however, small samples presumably show a colour reaction. In this case also benzidine cannot be used for the production of colour reactions.

Halloysite in its original state adsorbs characteristically malachit green and safranin »y« showing blue-green and reddish blue-purple colours. Between benzidine and untreated halloysites colour reactions do not occur.

In their preliminary report *Mielenz, King and Schieltz* (3) attempt to determine the individual minerals of the kaolin group with an essentially identical method.

The difficulty of this determination is that the dye solution may only be used in a concentration which is just enough for the required colouration to appear, but that it may not be in excess which would lead to anomalous results. For example, if in the case of malachit green the colouration is weak the yellow and green colours cannot always be distinguished from the original colour thus rendering the determination unreliable.

These difficulties were already mentioned previously. To produce a good colouration experiments with different organic compounds were carried out, first with paramethyl-aminophenol and para-dioxybenzol and recently with benzidine which proved to be very suitable for the determination of montmorillonites.

In a previous paper it has already been referred to that these kaolinite determinations are not quite reliable and that further investigations are required.

Our recent investigations were based on the following geochemical factors which are also referred to by *Szádeczky* (5) in his book.

Among the clay minerals the cation exchange capacity of the kaolin mineral group is only slight it depends on the free OH anions on the surface of the lattice. On the other hand, the phosphor binding aptitude and the PO₄ and other anion exchange capacity of the OH groups is by virtue of their anion character great. The base exchange and adsorption capacity of the montmorillonites is far greater. In this case the binding is mainly carried out by the ions of the lattice structure. Owing to the deficiency of the valencies caused by the substitution in the crystal lattice of ions of higher value by ones of lower value a cation exchange may be brought about.

The hydromicas and illites mainly bind ammonium and the large alkali ions.

Taking the above into consideration, if a molecule can be bound by means of a phosphate ion on the surface of a kaolinite producing under certain circumstances a colour reaction then among the clay mineral groups the presence of kaolinite can be certainly determined, respectively it can be separated from montmorillonite. In this case the group of hydromicas is the only one which does not show under such conditions a colouration.

The experiments were carried out as follows:

To a dilute solution of phosphoric acid (5 per cent) so much benzidine was added that the solution corresponded to one of 0,1 per cent. In every case a suspension of powdered kaolinite, montmorillonite and illite was prepared from this solution. Immediately at the beginning a few drops of

H₂O₂ (3 per cent) was added. After a few minutes the kaolinite showed a colour reaction, whereas the montmorillonite only changed its colour after some time, however, it always differed distinctly from the colour of kaolinite. Illite never showed any colour reaction.

The following results were obtained for kaolinite from Zettlitz, bentonite from Istenmezeje and illite from Füzéradvány.

	kaolinite	montmorillonite	illite
wet	lilac red (10 pa)	colourless	colourless
dry	lilac ochre	greenish yellow (1 pc)	colourless

After some time the lilac red colour of kaolinite deepened. Simultaneously the montmorillonite suspension showed lilac patches if the montmorillonite contained kaolinite. Otherwise the colour turned into greenish yellow.

If not pure kaolinite is involved, but it may be contaminated with montmorillonite — a very frequent occurrence in the Hungarian kaolinites — then concerning montmorillonite it is advisable to carry out examinations with an aqueous benzidine solution and for kaolinite the phosphoric acid benzidine reaction should be employed with the same material. If the sample contains kaolinite at the one test a lilac colour appears and if it contains montmorillonite at the other one instead of the characteristic dark blue colour a lighter blue is obtained.

Another organic substance suitable for the determination of kaolinite is p-methylamino-phenol it is well known as methol in photography. This is used in the same way as benzidine, it is dissolved in dilute phosphoric acid and to the suspension prepared in this manner a few drops of H₂O₂ are added. After a short time a change in colour may be observed. Kaolinite from Zettlitz, bentonite from Istenmezeje and illite from Füzéradvány produce the following colour reaction:

	kaolinite	montmorillonite	illite
wet	ochre	light green	unchanged
dry	darker ochre	green	unchanged

After standing for some time similiary as at the benzidine test in this case also the colours deepen, whereas illite does not show for a certain time any change.

At these examinations the pH value must not be particularly taken into consideration as a phosphoric acid solution, even, in such concentrations, ensures a pH of 1—2.



Taking the above into account some of the more important Hungarian and foreign kaolin samples were examined with a phosphoric acidic solution of benzidine and methol (p-methyl-aminophenol). The following results were obtained:

Deposites	In the presence of benzidine	In the presence of methol
Telkibánya Baglyas völgy.	lilac	ochre brown
Mád Istenhegyi táró	the lilac colour developed slowly	no change
Mád Bomboly	no change	no change
Sárospatak Királyhegy	lilac	light ochre
Sárospatak Cinegehegy	lilac	brown
Sárospatak Megyerhegy	lilac	brown
Gyöngyössolymos Asztagkő	slower development of lilac	lighter ochre brown
Velencei hegység Nadap	slower development of lilac	lighter ochre brown
Zettlitz Czecho-Slovakia	lilac	brown
Szászkaánya Roumania	the lilac colour developed slower	brown

Generally the reaction with phosphoric acidic benzidine showed a more characteristic colourisation than that with methol, although in certain cases the colour reaction appeared more slowly. The disadvantage of the phosphoric acidic-methol method is that the methol oxidises fairly rapidly and that independently of the clay mineral and the substance contained in the suspension the whole sample turned dark brown after 5—6 hours. In this case the change of colour appearing after half an hour had elapsed was not always characteristic.

It is, however, essential that if this method is used montmorillonite only shows a colourisation after some time has elapsed and illite does not show any change of colour, i. e. after a certain time no change can be observed in the suspension.

The procedure was also examined to establish if Fe^{++} , Fe^{+++} and Mn interfere and concerning the kaolin occurrences whether the frequent pyrite impregnation influences the colourisation.

Ferrous iron which can be detected with α - α' dipyridil interferes, namely H_2O_2 oxidises ferrous iron into ferric iron. Hence the employment of H_2O_2 proved to be disadvantageous. Luckily ferro could mostly not be detected.

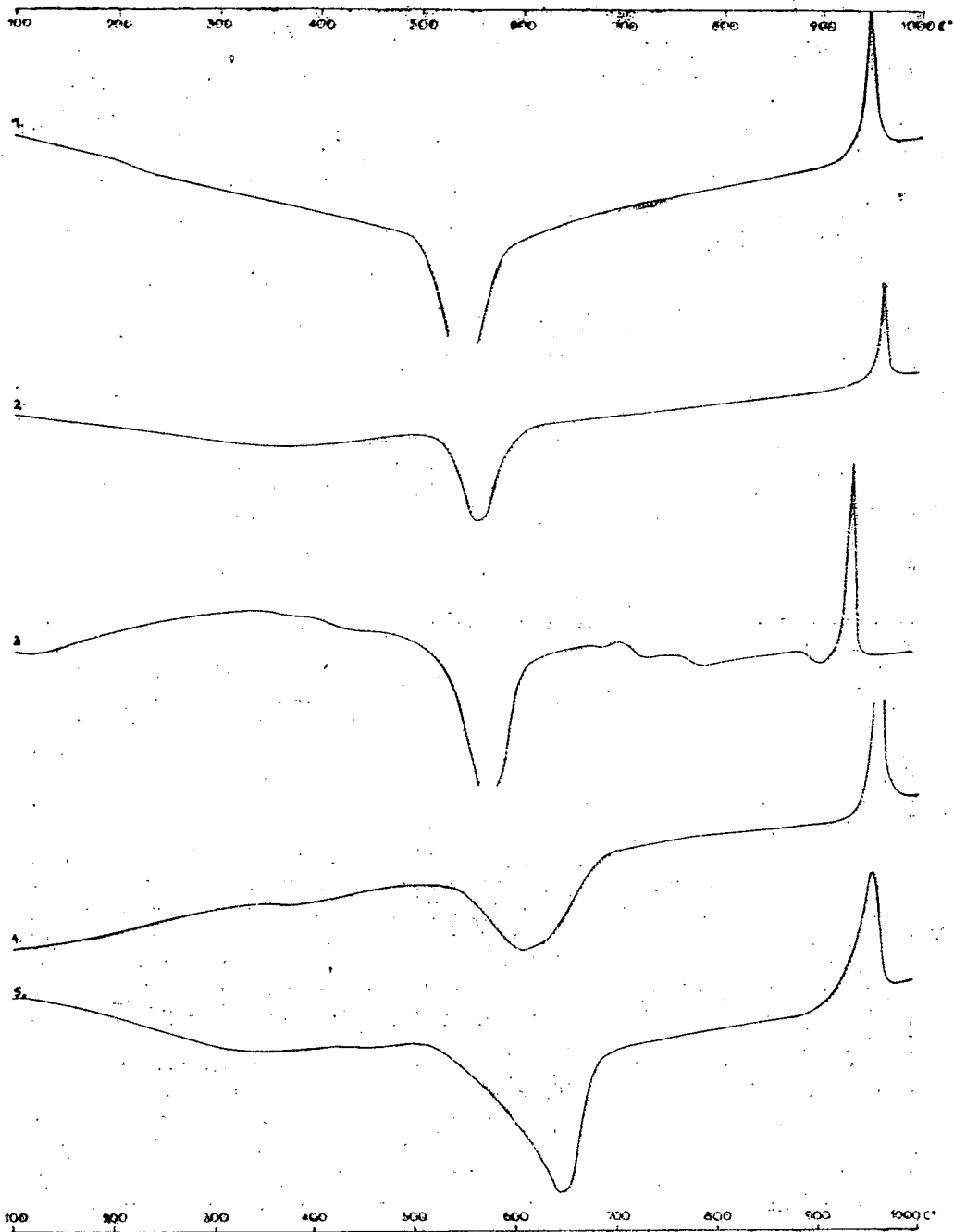


Fig. 1.

DTA curves of some kaolines of different localities:

1. Zettlitz (Czechoslovakia)
2. Sárospatak (Hungary)
3. Sasca montăna (Romania)
4. Gyöngyössolymos (Hungary)
5. Mád, Bomboly (Hungary)

Ferric iron which can be detected with KSCN was also not contained in most of the samples. However, the attempt was made to add FeCl_3 to the suspension and the lilac colour appeared immediately, hence Fe^{+++} ions also interfere in this case as with the montmorillonite group if the determination is carried out with benzidine.

In the case of contamination with limonite the determination is difficult as the ochre yellow colour covers the whole suspension and it is difficult to detect any colourisation.

Like in the case of montmorillonite the interfering Fe^{+++} ion could not be reduced completely with sodium sulphite, at most, the lilac colour faded. Thus this question remained unsolved.

Pyrite always interfered. This could also be proved by adding a substance from Bomboly (Mád) to powdered pyrite in any other way this substance did not show any change of colour, however, on applying the phosphoric acid-benzidine procedure the lilac colouration appeared. What causes the interference can as yet not be explained.

MnO_2 , which may be present in the form of pyrolusite or psilomelane also interferes with the development of the true colour. As, however, as compared to the white kaolin these minerals always have a striking colour substances must be chosen for the test which do not contain minerals.

The silification which is particularly frequent in the case of the kaolins from Tokaj-Hegyálja did not influence the development of the colour.

The examination of the sample from Bomboly (Mád) proved interesting. Although its exterior has a show white colour like any other kaolin and its form is also identical it did not show any colourisation always remaining unchanged. With benzidine most of the kaolinites showed a pale blue colour, whereas this one did not show any change. Its DTA diagram diverged from the characteristic kaolinite curve, i. e. the endothermal peak between 500—600°C was missing and only appeared between 600—700°C. The exotherm peak like in the case of kaolinite appeared at 960°C. Hence the mineral is not kaolinite or at least not pure kaolinite, but probably dickite or a substance mixed with the latter. Consequently it can be stated that not every member of the kaolin group behaves in the same manner in the course of a reaction with phosphoric acid-benzidine. *Mielenz* and *King* also remark that dickite — at least some of its crystals — do not adsorb dyes. Unfortunately, nacrite and halloysite in a pure state are not available, hence their behaviour could not be compared with that of kaolinite.

According to the investigations of *Grofcsik* the clay mineral of the Velence mountain-range is monotermitite, which has also been described in the USSR. The difference is that the exothermal peak of kaolinite at 950°C is missing the rest of the curve is identical with that of kaolinite. Probably the structure of the mineral is a mixed one.

This substance like that of kaolinite underwent a reaction with phosphoric acid-benzidine. As, however, it is strongly impregnated with pyrite the examinations must be carried out with great care.

For the determination of kaolin by means of the phosphoric acid-benzidine method further investigations are, of course, still required. The mechanism of the reaction represents an important part of the detailed

examinations, the more so, as apparently the different structures influence it kaolinite-dickite-monotermite).

It seems important to examine whether the colourisation is only a surface adsorption phenomenon (which is probable) or whether these molecules or the solvent can also penetrate into the interlaminar layers. Furthermore, the investigation of minerals which had been examined with DTA, X-rays and chemical analysis and had unequivocally been proved to be belonging to a pure kaolin group seems desirable.

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