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Note

Dedicated to Prof. Dr. H. J. Seifert on the occasion of his 60th birthday

QUANTITATIVE ESTIMATION OF KAOLIN IN SOIL CLAYS BY DIFFERENTIAL THERMAL ANALYSIS

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Introduction

In spite of the many techniques which are described in the literature it is still impossible to determine quantitatively the exact percentage of minerals in the clay fraction of soils, but only an estimation is obtained, even by using several parallel methods. Accurate values for the results cannot be given [1].

Whenever we need to estimate quantitatively the mineralogical composition of a soil clay we make the following determinations: the montmorillonite (smectite) is estimated by the Cation Exchange Capacity (CEC) of the clay, but we have to subtract the CEC of the kaolinite and that of illite from the total CEC of the clay and have to assume that the CEC of the montmorillonite is 100 milliequivalent per 100 mg [1]. The illite is estimated by determination of total potassium [2] (works well in Israeli soils where we do not have feldspars in our clays); quartz is estimated by X-ray, calcite is determined by the calcimetmeter or by titration with HCl (most Israeli clays contain calcite in the clay fractions). The free oxides of Si [3], Al [4] and Fe [5] are determined chemically by dissolution methods or by atomic adsorption. The problem remains estimation of the percent of kaolinite.

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Jackson [6] proposed a chemical selective dissolution technique for mineral including kaolinite estimation. We tried it and found that this technique is very exhaustive and in our experience when we summed up the percentage of minerals and oxides it added up to only 60–70%. We found that the best method for quantitative estimation of kaolinite is by differential thermal analysis (DTA). However for this purpose a large amount of samples is needed. This will be shown in this short paper.

Experimental

Our DTA is a home-made instrument, built according to Barshad's [7] and Wilburn's [8] apparatus with new parts bought from Gallenkamp Company (England). The thermocouples are made of platinum and platinum + 10% rhodium. The holders for the sample and for the reference material (calcined Al_2O_3) are relatively large and can contain up to 400–500 mg Al_2O_3 or clay (unlike the modern commercial DTA instruments which have very small sample holders and are designed to contain only a few mg samples). The rate of heating is 10 degree per minute so that in 2 h it reaches 1000°. The standards we used were the montmorillonite (Wyoming bentonite), kaolinite (Georgia kaolinite), attapulgite (Georgia), hydrated hallosite (Bedford, Indiana), illite (Montana). All these standards were purchased from Wards Company. Standards of calcite and dolomite were from Israel. In order to have a similar heat transfer in the sample holder and in the inert material, all the clays and standards were mixed with the calcined alumina. Unless otherwise stated, 400 mg of the clay samples were mixed with 100 mg of calcined alumina.

An internal temperature indicator is used in all the runs. As found by Barshad [7] there are different chemicals which give a peak at a fixed temperature. By adding a few milligrams of AgCl close to the thermocouple in the inert material, the AgCl decomposes to Ag and Cl and gives an endothermic peak at 450°. (When adding the AgCl one has to be careful that it will be close to the thermocouple but should not touch it, so that it will not ruin the thermocouple). Because it is added into the inert material, a small exothermic peak will appear in all the curves.

Results and discussion

Figure 1 shows representative DTA curves of some standard minerals which are found in the clay fraction of Israeli soils, recorded by our DTA. Montmorillonite (smectite) is the most common clay mineral in Israeli soils. The endothermic peak of dehydration appears in our instrument at 160°. The percentage of montmorillonite and other minerals cannot be estimated from the low endothermic peak because the size of this peak depends on the relative humidity of the ambient, hence it is necessary to equilibrate the clay in a desiccator with 50% relative humidity for several days before the DTA run. The low temperature endothermic peak is not specific for montmorillonite. Other minerals which are highly hydrated, such as hydrated hallosite and attapulgite also give endothermic dehydration peaks in this temperature range. Consequently, in our laboratory, montmorillonite is estimated from the CEC of the clay fraction [1].

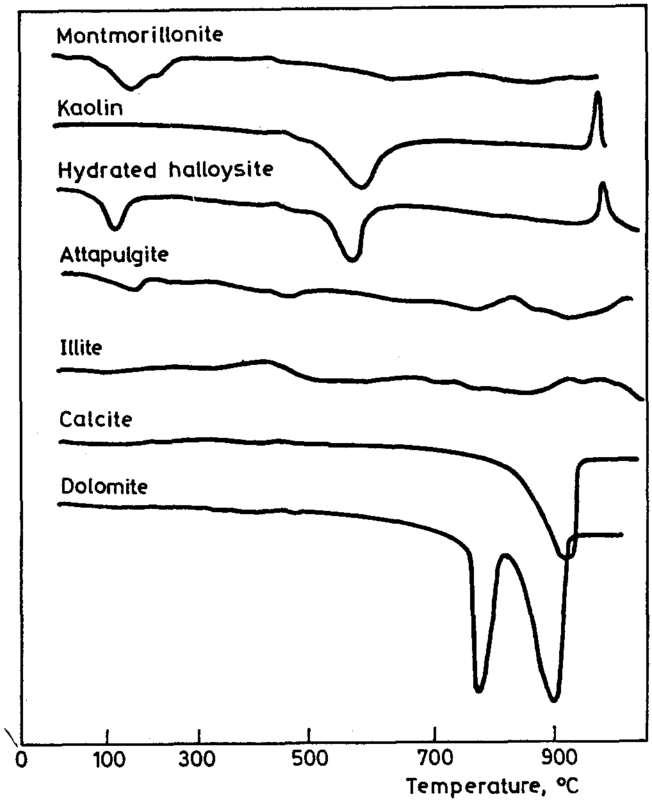

Fig. 1 DTA curves of standard minerals found in the clay fraction of soils 400 mg of the standard were mixed with 100 mg of calcined Al_2O_3

From the shape of the endothermic peak around 550° it is possible to differentiate between kaolinite and hydrated haloysite. The reaction of kaolinite takes a longer time due to the fact that a big amount of clay is reacting in our DTA, a symmetric peak is obtained while the reaction of hydrated halloysite is faster and gives an asymmetric peak. We can differentiate between the calcite and dolomite from their high temperature peaks. The presence of a relatively high percentage of attapulgite or sepiolite is shown by their specific small endothermic peak between 300 and 400°.

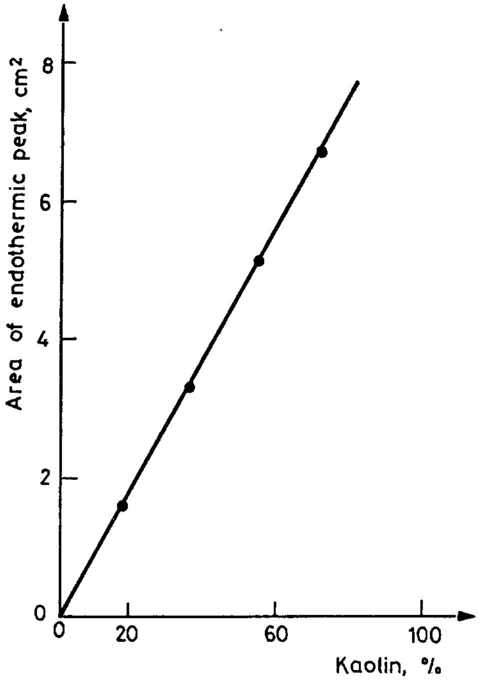

Fig. 2 Calibration curve of kaolinite obtained by mixing Georgia kaolinite with calcined Al_2O_3

The percentage of kaolinite is estimated by the DTA. Our DTA gives very good estimations because we use relatively big sample holders which enable us to use samples which are only slightly ground. The small sample holders of the modern commercial DTA instruments require much grinding in order to get a homogeneous sample. On the other hand, our instrument is designed for samples of few hundred mg, thus, it is not necessary to grind the clays extensively in order to have a representative sample. Miller and Oulton [9], Yariv [10] and Mingelgrin *et al.* [11] showed that when clay minerals are ground for long periods they decompose and loose hydroxyl groups and their surface properties are changed.

The estimation of percentage of kaolinite is done by using a calibration curve which is obtained form DTA curve of mixtures containing different weights of standard kaolinite mixed with Al_2O_3. When the area of the endothermic peak of 550° is plotted against weight of kaolinite a straight line is obtained (Fig. 2). Although we get a straight line, we consider the result to be only an estimation. Miller and Oulton [9] showed that the size of the dehydroxilation peak is dependent on the grain size of the clays and on grinding. For this reason, the standard kaolinite and the soil clay are passed through the same sieve (50 mesh).

Conclusions

One of the problems when the mineralogical composition of the clay fraction of soils is quantitatively estimated by different methods, is to get a total percentage of the minerals and oxides as close as possible to 100%. We found that by using our DTA to estimate kaolinite, and by using our DTA to estimate kaolinite, and by using the aforementioned methods, for the other minerals and oxides, we get a total percentage close to 100% [1].

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