Thermochimica Acta, 83 (1985) 107–112
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Differential thermal analysis as an indicative method for the determination of soil mineral demage.

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Abstract:A DTA method is outlined which enables the characterization of clay mineral structures and their partial destruction. This is done by determination of the peak areas and the temperatures of the dehydroxylation effect of illites as well.The method is compared with x-ray diffractometry.The experimental interaction between illitic clays and different acids showed that the clay mineral structures were strongly affected by these acids and that the presented method is very suitable to characterize these processes.

Introduction:Clay minerals in soils and fine grained sediments are responsible for the fixation of water and dissolved ions. These alumosilikates are characterized by sheet structures(simplified:layers of SiO_4^{4-}tetrahedra and AlO_6^{3-}octahedra)with water and some additional cations in the interlayer spaces.Both,the interlayer water and cations ,as other cations,adsorbed by the large surface of these fine grained particles as well,can be removed easily to contribute to the fertility of the soils and the growth of plants.

The structures of clay minerals are very sensitive to a lot of processes,which may weaken or partly destroy them.Among these the attack of polluted or aggressive(acid) solutions may have a large influence to the stability of clay mineral structures.

In this paper the interaction between clay minerals and acid solutions is studied.The aim of this study is to elucidate a simple and indicative method for the disorder of clay mineral structures and by this for the degree of pollution of the abundant soils, and its correlation to the degree of observed forest damages.

Method: The defect character of clay mineral structures may be determined by means of x-ray or thermal analytical methods.In x-ray diffractograms this interdependence between structural defects and intensity and size of interferences will be mainly observed by the (001) interferences(compare with fig.2).DTA offers another possibility to characterize the degree of structural disorder.Generally clay minerals include OH,sometimes additional water,too.The dehydration resp.dehydroxylation(=evaporation of OH) behaviour of clay minerals is strongly influenced by the defect character:with increasing degree of disorder the dehydroxylation starts earlier,and the intensity of this reaction dereases.Thus the correlation between the degree of structural disorder and the dehydroxylation-behaviour may offer a suitable method for the determination of the abundance of contaminated solutions in soils.-In order to get reproducible and comparable results,it is necessary to investigate under strongly standardized conditions of differential thermal analysis.(Table 1,compare with Smykatz,1974).

Table 1:conditions of differential thermal analysis

heating rate	10°/min
amount of sample	100 mg
thermocouples	Pt/Pt,Rh
inert mater.	Al_2O_3
furnace atm.	air
crucibles	ceramic

The dehydroxylation of clay minerals appears-dependent on the chemical composition,the structural state and the defect character-in the temperature range between 45o and 8oo C(Table 2)

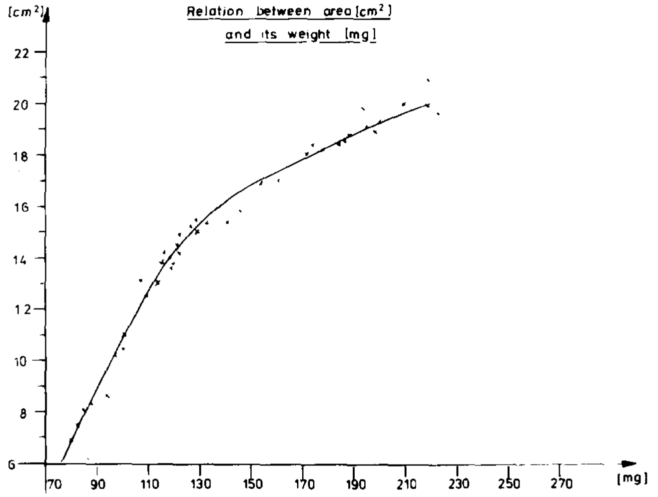
Table 2:Dehydroxylation temperatures of main clay mineral types

mineral group	formula	interlayer water (swelling)	dehydrox.temp.
Kaolinte	$Al_2((oH)_4Si_2o_5$	-	530-580
Illite	$K_{0.7}Al_2((OH)_2Al_{o.3}Si_{3.7}O_{10}$	-	520-600
Fe-Chlorite	Fe-Mg-Silicates	-	55o-620
Mg-Al-Chlorite	Mg-Al-"	-	600-680
Vermiculite	Mg-Al-Silicates	$4H_2O$	480-550
Fe-Smectite	Fe-Al-Silicates	nH_2o-	450-520
Al-Smectite	Al-Mg-Silicates	nH_2O	700-800
ixed layer	Fe-Mg_Al "	varable	500-780

Illites are the predominant clay minerals in soils and sediments. Therefore the present study concerns with this main clay type. Illites are not swelling and show relative stable structures.Of course,they may include some primary differences in the structural state,but in case of abundant series of illites which include atype being relativly undisturbed by external influences,the application of the outlined method should be possible.

In standardized DT analyses the determination of the dehydroxylation effect may be done by measuring the temperatures(peak and onset temperatures) and the areas.It was found that the peak area determination 's weight measurement is more exact than the planimetric method,but there is a good correlation between both kinds of area determination (Figure 1).

Figure 1:Correlation of an area(cm^2)and its weight(mg)



The best way to characterize the peak area is to transfer the peak to a heavy transperent paper,to cut out the contures and to weight.

The used samples were always prepared in the same manner.The different defect characters of the illites were obtained experimentally by the contact with three acids(e.g.HCl.HNO_3, H_2SO_4), under different pH conditions.After being contacted for ten days the clays were dried(50-80 C) and investigated.

Results:The following figures 2-5 summarize the obtained results of the experiments.The x-ray diffractograms show a clear decreasing of the size of all interferences(e.g.for the oo1-interference see Figure 2) and a broadening of the peaks too.Figure 3 represents the thermal behaviour of the treated illites.Generally, peak and onset temperatures and peak area as well decrease with decreasing pH(=increasing acidity).The detailed effects of partial destruction of the illites by acids can be seen in Figures 4 and 5. It emerges from these experiments that

a)there is a significant correlation between pH and degree of structural disorder,

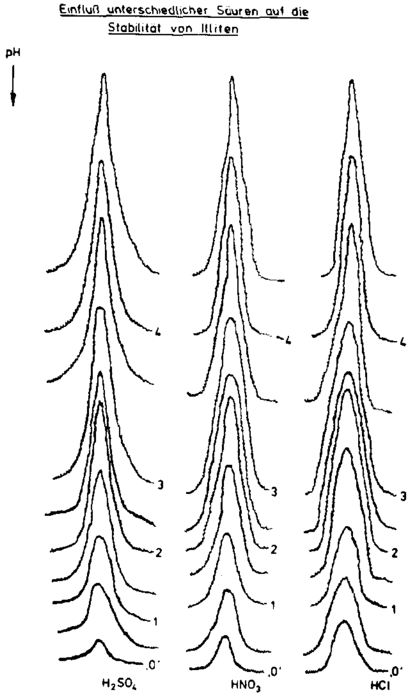


Figure 2:Descreasing of the 001-interference of illitic material in different acids and changing pH.

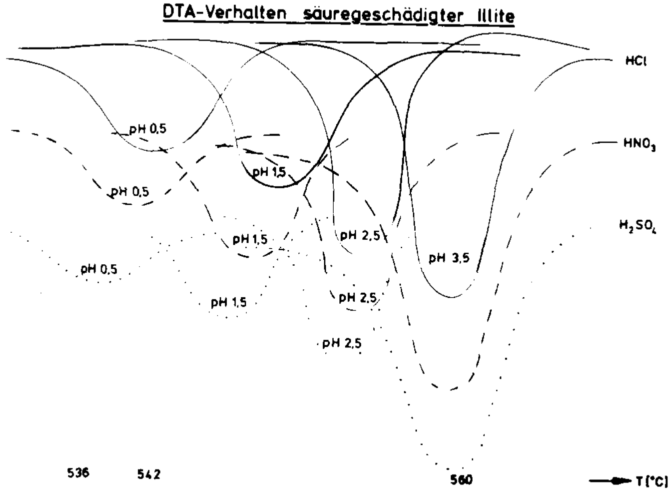


Figure3:Thermal behaviour of acid treated illites.

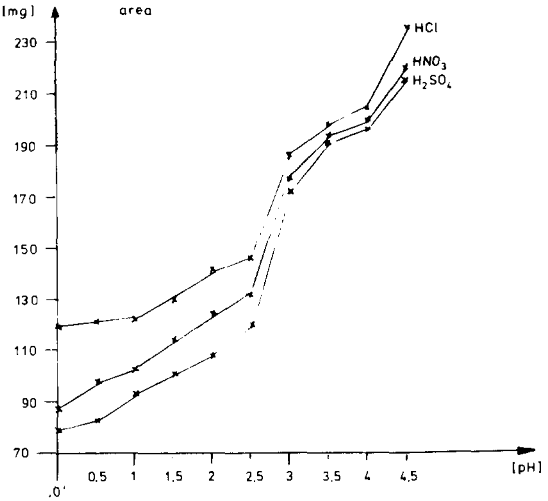


Figure 4:Area(weight in mg)of a DTA-picture in correlation to various acids with decreasing pH.

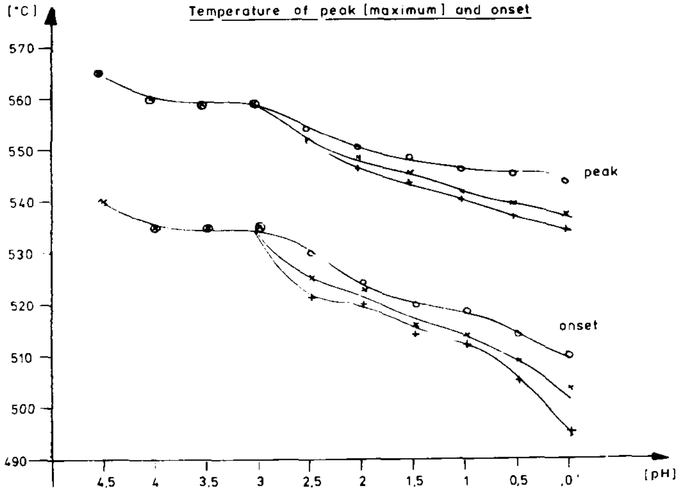


Figure5: DTA temperature of peak\maximum and onset, with o= behaviour in HCl,superior line

x= behaviour in HNO_3,

+=behaviour in H_2SO_4,inferior line.

b)the effect of acid aggression is different for the used acids, in that way: $HCl < HNO_3 < H_2SO_4$;

c)the pH of 2.5 shows to be a critical value below which the structural stability is weakened evidently.

At this pH of 2.5 the amount of cations found in the contacted solutions increased considerably, so pointing out, that the crystal structure became as largely destroyed that it was possible to release a lot of the incorporated ions.

Investigations of soil waters from regions in the Kraichgau and the Black Forest show pH-values between 2.5 and 4, in extreme cases even lower (Blümel, Krüger, Smykatz in preparation).

Acknowledgment: we are grateful to the companies Fuchs and Didier for the delivering of clay material, and to Miss B.Retzel for the photos.

Lit.: Smykatz-Kloss.W.: Differential Thermal Analysis. Application and results in Mineralogy.-K.Springer-Verlag, Heidelberg(1974)