INFLUENCE OF ORGANIC
MATTER ON DIFFERENTIAL
THERMAL ANALYSIS
OF CLAYS

By
LENNART SILFVERBERG

STOCKHOLM 1955
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Contents

Preface ............................................................................................................. 5
§ 1. Introduction ............................................................................................... 7
§ 2. Description of Equipment. Some Standard Curves .............................. 8
§ 3. Influence of Pre-Heating before DTA .................................................. 13
§ 4. Chemical Pre-Treatments ................................................................. 27
§ 5. Discussion of Results ........................................................................... 34
  § 5 a. Range and Importance of Organic DTA Effects ......................... 34
  § 5 b. Effect of Thermal Pre-Treatment ................................................. 34
  § 5 c. Effect of Chemical Pre-Treatment ............................................ 35
  § 5 d. Conclusions ................................................................................. 35
  § 5 e. Further Possibilities of Method ................................................ 36
Bibliography .................................................................................................... 36
Preface

The differential thermal analysis apparatus described in this report was designed, and the laboratory work was performed, under the direction of Mr L. Silfverberg, Head of the Physical Section of the undersigned Institute, with the assistance of the staff of the Section. The report was prepared by Mr Silfverberg.

Stockholm, August, 1955

ROYAL SWEDISH GEOTECHNICAL INSTITUTE
1. Introduction

Natural clay soils are very complex mixtures of both mineral and non-mineral constituents. The exo- and endothermic DTA effects produced by these constituents often occur inside the same temperature intervals, and are thus superimposed one upon another. In certain cases it is possible to make a graphic analysis of the curve so as to separate the superimposed effects. But in many cases this procedure is impossible, one effect being so dominant that a weaker effect can be entirely suppressed.

The great exothermic effects caused by the organic matter practically always present in Post-Glacial clays, and to a lower degree also in Glacial clays, often conceal the real mineral peaks of the DTA curve.

For this reason, different investigators have tried to get rid of the organic influence by a special preparation technique in which the sample is treated with hydrogen peroxide, see, for example, Hauth and Davidson (1). This method is laborious and time-wasting.

Another method to avoid oxidation effects is to run the analysis in an inert atmosphere, for example in nitrogen. This has been performed with samples of a non-argillaceous material by Rowland and Jonas (2), who have investigated two mutually related effects in the DTA curve of siderite. One of these effects was an endothermic peak due to the dissociation of carbon dioxide. The other was an immediately following exothermic oxidation of the ferrous oxide. A nitrogen atmosphere in the furnace completely eliminated the oxidation peak. The same was found by Saunders and Giedroyc (3). In this connection it is worth mentioning that as early as 1915 two investigators, Hollings and Cobb (4), made use of the DTA technique for studying the carbonisation process in coal distillation. As furnace atmosphere they used nitrogen, freed from oxygen and moisture. An interesting result of their investigation is that great exothermic distillation effects occurred. The fact that exothermic peaks might be found even if oxidation is suppressed must be borne in mind when running organic samples in controlled atmosphere.

Running a sample in vacuum is another method to eliminate oxidation and to accelerate processes forming volatile substances. The only notice of this technique found in the literature is the description of a special DTA furnace for vacuum and inert atmosphere published by Whitehead and Breger (5). Their intention was to study coals and organic shales.

Notices of DTA investigations of organic matter are rather seldom found in the literature. In addition to the references (1), (4) and (5), may be noticed

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2 The numbers in parentheses refer to the bibliography at the end of this report.
the work on thermal characteristics of humic acids by Sedletzky and Shmakova (6), the thermograms for slightly and highly decomposed peat published by Widell (7), the curves for clarain and vitrain published by Grim and Roland (8), some curves of Soveri (9) and of de Bruijn and van der Marel (10).

In the course of investigating with the DTA method two long clay cores taken with a soil sampler with metal foils (11) in two different places in Sweden, it soon became evident that the organic matter present in all samples had a very dominating influence upon the thermograms. In order to choose an appropriate method to eliminate this influence, it was considered worthwhile to study the effects of some preparative methods and the effects of some thermal and chemical pre-treatments of the samples before the analysis. It was hoped that this study, at least to some extent, would contribute to showing how the different occurrence forms of the organic material can be reflected in the DTA curves. The effects of vacuum and an inert atmosphere will not be treated in this publication.

As the DTA apparatuses used in different laboratories are not standardized, a short description of the equipment is given in § 2, and the curves obtained with the standard materials distributed by the DTA Committee of the CIPEA¹ are shown for reference.

§ 2. Description of Equipment. Some Standard Curves

A total view of the DTA equipment is shown in Fig. 1. Two furnaces are now available. The upper furnace is intended for running DTA curves in vacuum or controlled atmosphere. In the experiments described below only the lower furnace was used. It is of the ordinary Norton type (12), consisting of a horizontal ceramic tube, wound with Kanthal A 1 wire, 0.8 mm in diameter, insulated with fossil meal. The internal dimensions of the tube are 260 mm × 55 mm. The external dimensions of the furnace are 260 mm × 330 mm. The resistance of the winding is 25 ohms. The maximum power input is 500 watts and the maximum temperature is 1000°C.

The specimen holder is shown in Fig. 2. It consists of a nickel block with a lid made of the same material. The whole forms a prism 25.6 mm × 25.6 mm × 21.5 mm. The two drilled holes are 9.0 mm in depth and 6.5 mm in diameter.

The sample is ground to a fine powder in an agate mortar, and is generally dried at 105°C before being firmly packed in the specimen holder. As reference substance γ-Al₂O₃, prepared by ignition of Al(OH)₃, is used. The sample and the reference substance weigh about 0.3 g each.

The differential thermocouple is made of 0.35 mm platinum and platinum + rhodium (10 per cent) wires. The joints are welded by means of an acetylene-

¹ Comité International pour l'Étude des Argiles.
Fig. 1. Total view of the DTA apparatus.

Fig. 2. The specimen holder.
oxygen microburner. They are placed in the centres of the sample and the reference substance.

The furnace temperature is measured by means of a chromel-alumel element, 0.5 mm in diameter, inserted in a hole in the sample holder.

The furnace temperature is regulated in a very simple manner, as can be seen on the left in Fig. 3. An old clock-work was altered, and was provided with a pendulum, whose length can be adjusted so as to vary the speed of the clock-work. A thread connected to the clock-work operates a variable transformer feeding the furnace. The voltage and the current of the furnace can be read on the instrument panel. The furnace temperature can also be registered by a pen-recorder. The millivoltmeter showing the furnace temperature is calibrated for a certain definite external resistance. To compensate for an alteration in resistance, e.g. caused by an exchange of the chromel-alumel element, a variable series resistance is built in on the instrument panel.

As no programme controller is available, the temperature rise in the furnace is not exactly linear. A gradient of 10°C per min. has been aimed at when adjusting the original current and the rate of voltage increase. Adjustments of the pendulum length during a run have been tried but cannot be recommended. A sudden change in the rate of voltage increase can cause a false deflection of the differential temperature curve. Thus such changes are to be avoided. It is of importance to have a good reproducibility of the temperature curve. The deviations from the ideal gradient are so small that a replotting of the curve to an exactly linear scale is rather easy.
The differential thermocouple is connected to a mirror galvanometer with high voltage sensitivity. The sensitivity can be varied within wide limits by means of parallel and series resistances. The deflection is photographically recorded in a drum camera on a transparent copying paper (Gevaert Diaflex Rapid) having a very low shrinkage when drying.

As only one galvanometer is used, the temperature rise cannot be recorded on the same paper as the differential thermogram. In order to get a temperature scale on the thermogram, a small lamp is placed in front of the camera. The lamp can be lighted by a push button switch on the panel either at millivolts corresponding to even numbers of degrees or, more conveniently, at even millivolt readings.

The instrument panel also contains switches, control lamps, fuses, and so on. If the temperature in the furnace should by accident run too high, a mercury relay operated by a gold fuse in the furnace tube will break the heating current.

The small wooden boxes on the wall just to the right of the furnaces (Fig. 1) contain Dewar vessels. One of them is filled with melting ice for the cold junction of the furnace temperature element. In the second vessel all joints between the thermocouples and the wires connected to the instruments are placed in air at room temperature.

A simplified schematic diagram of the apparatus is shown in Fig. 4.
It is a well-known fact that DTA curves published by different authors are rather difficult to interpret without a thorough knowledge of the apparatus used in each individual case. The DTA Sub-Committee of the CIPEA has collected curves relating to a few standard materials distributed to a great number of laboratories, and has found noticeable variations (13). As long as no international standard for the performance of DTA has been generally adopted, it would be of great value if all publications concerning these subjects also contained a reprint of curves of materials which are well-known to the presumptive readers. For this reason, Fig. 5 reproduces the DTA curves obtained with the apparatus just described on the following minerals: Wyoming bentonite (Na-saturated), Mississippi bentonite (Ca-saturated), kaolinite, bauxite, and bayerite.
§ 3. Influence of Pre-Heating before DTA

The organic matter contained in natural clay samples has a very marked influence on the shape of the DTA curves. The exothermic organic effects range in certain cases from 200°C to about 850°C. Sometimes the total effect is a single, more or less irregular peak, sometimes two peaks are found, as can be seen from Figs. 6 and 7, with peak temperatures of about 400°C and about 700°C, respectively. Some authors, for example Soveri (9), p. 30 to 34, report humus effects round 400°C. He also found a fine structure in some of the peaks, which showed a tendency to split into two separate peaks at 330° and 380° to 470°C. A high temperature effect was found by Soveri only in a Finnish sediment, and was attributed to the presence of free graphite. He found a good correlation between the carbon content of Quaternary clays and the area under the humus peak. Therefore he drew the conclusion that the DTA could give a rather good quantitative estimate of the humus content, at least for clays with a humus content not exceeding 2 per cent.

In view of this background, it seemed to be of interest to study the very broad organic effects found by the Author in Swedish Quaternary clays. As it was supposed that the various exothermic effects were due to combustion of different forms of organic matter, the following procedure was devised for a thermal pre-treatment of the clay samples.

The clay was dried at 105°C and fine-ground. Parts of the sample were heated to constant weight at temperatures up to 500°C in steps of 50°C. The DTA investigations were then undertaken on twelve samples thermally pre-treated in this manner. The samples were almost all of Post-Glacial origin, and were taken at different depths in two places in Sweden. The places and depths at which the twelve samples were taken, the organic carbon content, determined by means of dry combustion, and some geotechnical data, determined in connection with another investigation, are given in Table 1. Figs. 6 to 17 show the effect of heating. The first three clays (Figs. 6 to 8) were selected as examples of clays exhibiting two distinct exothermic peaks. The higher of them is positioned at temperatures higher than those regularly found in organic clays. One possible explanation of the double peak might be that an endothermic peak is superimposed on a huge exothermic peak. But a removal of the organic material by repeated treatment with hydrogen peroxide showed that no great endothermic effect was present in the interval in question.

Thus the two peaks are really separate effects connected with different forms of organic material. The result of the heat-treatments was astonishing. Even after the first heating, to 150°C, a noticeable change in the curve took place. As can be seen from Fig. 6, the high temperature peak was diminished and the peak maximum was shifted to a lower temperature, while the low temperature peak was unaffected. At 200°C the high temperature peak was greatly decreased and the low temperature peak was also influenced. At 250°C the high temperature effect was almost completely obliterated, while about half of the low
temperature effect was still present. At 300°C both effects were removed and a sample ignited to 500°C had an almost identical curve.

Figs. 7 to 8 show the same characteristics. It is remarkable how the high temperature effect can be influenced by the heating to constant weight at such a low temperature as 150°C. In both these curves, a pre-heating to 400°C was necessary in order to eliminate the organic effects completely.

In Fig. 7 an exothermic peak at 800 to 900°C is met with. The effect of the thermal pre-treatment on this peak is different from the effect on the previously mentioned “high temperature peak”. The magnitude of the peak is only slightly influenced but the peak maximum is shifted towards higher temperatures as the pre-treatment temperature increases.
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<th>Unit weight t/m²</th>
<th>Organic carbon content, per cent of sample weight at 105°C</th>
<th>Natural water content, per cent of sample weight at 105°C</th>
<th>Liquid limit per cent</th>
<th>Plastic limit per cent</th>
<th>Shear strength in kg/cm² by cone test</th>
<th>Laboratory vane test</th>
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<td>0.29</td>
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Fig. 7. Thermal pre-treatment of sample 4273.
Fig. 8. Thermal pre-treatment of sample 1773.
Fig. 9. Thermal pre-treatment of sample 2995.
Fig. 10. Thermal pre-treatment of sample 497.
Fig. 11. Thermal pre-treatment of sample 812.
Fig. 12. Thermal pre-treatment of sample 4152.
Fig. 13. Thermal pre-treatment of sample 2945.
Fig. 14. Thermal pre-treatment of sample 2232.
Fig. 15. Thermal pre-treatment of sample 2812.
Fig. 16. Thermal pre-treatment of sample 792.
Fig. 17. Thermal pre-treatment of sample 3463.
A small endothermic effect just above 700°C can be noticed in the three upper curves of Fig. 7 but it is not present in the other cases. Instead of this, a small endothermic peak, probably due to carbonate can be seen in the neighbourhood of 800°C but only in the lowest curves. The extreme effect in the 400°C curve must be due to some special cause, e.g. a piece of a carbonaceous shell.

The following five curves, Figs. 9 to 13, are of a different type. They were selected for thermal pre-treatment because of the existence of a high-temperature peak at 800 to 850°C, which is rather distinct in Figs. 9 to 12, while it is more diffuse and occurs at a lower temperature in Fig. 13. In contradistinction to the high temperature peak in Figs. 6 to 8, it is not diminished as a consequence of the pre-heating. It is worth mentioning that the sample with the smallest humus content, No. 4152, Fig. 12, is of Glacial origin, while the other four samples represent Post-Glacial clays.

The last group consists of four Post-Glacial clays, Figs. 14 to 17. In these samples a high temperature exothermic peak is completely absent. The gradually decreasing combustion peak is an effect of the pre-heating. The double peak in some of these curves is only apparent, and is caused by the superimposed endothermic lattice-break-down effect. It is striking that the thermal pre-treatment to constant weight can leave a small residue of apparently rather homogenous composition unoxidized (see, for example, the 350°C curve in Fig. 14). Heating to constant weight at 350°C leaves a portion of organic matter undestroyed, and it can be burnt between 490°C to 530°C in the DTA running.

Further discussion of the curves will be found in § 5.

§ 4. Chemical Pre-Treatments

As the DTA curve is very sensitive to the presence of organic matter, it is well adapted for studying the effect of chemical agents upon the organic content of the soil.

As has been mentioned above, hydrogen peroxide is often used in order to remove the organic substance from the soil samples. However, the removal is not quite complete, and is dependent on the manner in which it is performed. A systematic study of the technique of hydrogen peroxide treatments lies beyond the scope of this publication. The treatment was performed in the following manner, mainly according to Robinson (14): 2 to 5 g of the air-dried sample was heated in a high beaker on a hot plate together with two subsequent portions of 100 ml 15 per cent hydrogen peroxide. Then the mixture was boiled to dryness, and the residue was ground in a mortar and oven-dried at 105°C. Hydrogen peroxide can oxidize the real humus substance, but leaves the more difficultly oxidizable parts of the organic substance mostly unaffected.

In the experiments described below, use is also made of a second chemical agent with a specific effect, namely acetyl bromide (CH₃COBr). The treatment
is carried out according to Springer (15) as follows: To 1 to 5 g of soil in a 100 ml flask are added 40 ml acetyl bromide. The mixture is heated for three days at 45°C in an air thermostat. The treatment is performed in a flask with a ground neck and a long glass tube for reflux cooling. The contents of the flask must be shaken up several times daily. The soil is transferred to a glass filter crucible and washed first with about 30 ml acetyl bromide and then with ethyl ether, which has previously been shaken with hydrochloric acid in order to destroy acetates which may possibly be present. The final washing is done with pure ether, and the sample is dried at 105°C. The effect of acetyl bromide is nearly contrary to that of hydrogen peroxide. Karrer and Bodding-Wiger (16) found that fresh plant rests, including various groups of substances, such as lignins, cellulose, proteins, fats, and waxes, were dissolved by acetyl bromide, while the humified parts of the organogenic substances ("vertorfte Moor- substanz") were mostly left undissolved.

Thus a treatment with hydrogen peroxide and acetyl bromide of the twelve samples chosen for thermal pre-treatment was supposed to give valuable information concerning the chemical state of the organic substances in these soils.

Figs. 18 to 22 reproduce the results of these two chemical treatments together with the DTA curves of the unheated samples dried at 105°C. Fig. 18 shows the first group of samples with two separate exothermic peaks, and Figs. 19 to 22 show the five samples with a high temperature peak which is unaffected by the heat pre-treatment described in § 3. Figs. 21 to 22 show the four samples in which the high temperature peak is almost absent.

The curves will be interpreted in § 5. Only the typical trends of the curves will be mentioned here. The effect of acetyl bromide is to remove those components of the clay which cause exothermic effects beyond 600 to 700°C. Those parts of the organic matter which cause exothermic effects between 200 and 600°C are removed only to a small extent, and in some cases they are almost unaffected.

The effect of the hydrogen peroxide treatment is quite different. The high-temperature components are sometimes unaffected, see Fig. 20. In other cases they are influenced but to a lower degree than by acetyl bromide. On the other hand, the low-temperature material seems to be almost completely removed by the hydrogen peroxide, the treatment being performed as described above. Yet it is important not to be misled by an almost straight "zero line". Organic matter may be present in such an amount that an endothermic peak is just cancelled.

Two special effects of hydrogen peroxide may be mentioned here. 1) In the neighbourhood of 300°C (sometimes lower, sometimes higher) a small sharp exothermic peak is met with (Figs. 19 to 20). It has been found that this peak is caused exclusively by the hydrogen peroxide, and not by the clay or the organic matter. 2) The treatment with hydrogen peroxide and the subsequent evaporation to dryness are sufficient to diminish the endothermic carbonate
Fig. 18. Chemical pre-treatments of samples 3747, 4273, and 1773.
Fig. 19. Chemical pre-treatments of samples 2995, 497, and 812.
Fig. 20. Chemical pre-treatments of samples 4152 and 2945.
effect at about 750°C (see sample 812 in Fig. 19). This effect has been studied separately, and it was found that in some cases the carbonate can be completely removed by the hydrogen peroxide. A possible cause of this is that an acid stabilization agent in the commercial hydrogen peroxide is so concentrated during the evaporation that the carbonate is destroyed.
Fig. 22. Chemical pre-treatments of samples 792 and 3463.
§ 5. Discussion of Results

§ 5 a. Range and Importance of Organic DTA Effects

The experiments have shown that organic exothermic effects can range from 200° to about 850°C.

The heat of reaction developed during the combustion of the organic material is so great that the organic peak or peaks tend to be very broad. Another consequence of the magnitude of the heat of reaction is that the organic effects can conceal other effects, e.g. those caused by mineral decomposition, even if the latter effects arise from components present in much higher percentage than the organic material. Thus it is quite necessary to eliminate the organic effects if it is intended to study the mineral effects. In some cases the range of the exothermic organic effects is dependent on the experimental conditions, as will be seen from the following.

§ 5 b. Effect of Thermal Pre-Treatment

The DTA method is dynamic. The specimen is submitted to a steadily rising temperature, and is never in thermal and chemical equilibrium with the surroundings. Therefore the reaction velocity has a very marked influence on the exo- or endothermic peak connected with the reaction in question. The thermodynamics of the various types of reactions under DTA conditions are not quite cleared up, but it is a well-known fact that high velocity reactions are recorded as very sharp, high, and narrow peaks, while slow reactions show less distinct and broader peaks in the thermograms.

One possible interpretation of the unexpected effect of the thermal pre-treatment of the samples 3747, 4273, and 1773 (Figs. 6 to 8) is that a part of the organic material is so slowly or difficultly oxidizable that in the ordinary DTA running the oxidation process is not initiated and completed until the furnace temperature has reached the higher values indicated by the position of the second exothermic peak. Naturally this low reaction velocity is partly caused by the deficiency of oxygen in the reaction atmosphere. During the thermal pre-treatment, on the other hand, the reaction conditions are quite different, the time and access of oxygen being enough for a complete oxidation of some substances which have a low reaction velocity which, under the conditions in DTA with a rapidly rising temperature, are completely oxidized at a temperature exceeding the pre-treatment temperature by several hundred degrees.

It is not necessary to suppose that the part of the organic matter causing the high temperature effect is originally present in the sample. It may be a distillation product of bituminous character. This is also in accordance with the results of Sedletsky and Shmakova (6), who explained a high temperature effect at 700 to 900°C as an oxidation of bituminous substances.
If one or both of these explanations of the results were correct, the DTA curve should be different if the analysis were run without a cover over the specimen holder. A few control runnings without the lid have been undertaken, and have shown that the high temperature effect is then absent. When experimental conditions are altered in this manner, the access of oxygen and/or the possibility of departure of volatile distillation products increase to such a degree that the reaction conditions in the DTA furnace and in the thermal pre-treatment oven are almost equivalent.

§ 5 c. Effect of Chemical Pre-Treatment

The investigations have clearly established that the highly dominating exothermic effects are not only a consequence of the amount of organic matter or the reaction conditions but that the chemical nature of the organic substances has a marked influence on the appearance of the curve. A survey of the complex chemistry of the organic matter lies beyond the scope of this publication. Thus only a rough differentiation between two main groups is made by means of the chemical agents used in the pre-treatments described in § 4. In particular, the acetyl bromide treatment may be employed for estimating the chemical state of the organic substances.

As can be seen from Figs. 18 to 22, the general effect of acetyl bromide is the removal of the organic substances, otherwise causing the high temperature exothermic effect. The hydrogen peroxide curve, on the other hand, is more or less generally flattened out, but a thorough comparison between the peroxide and the acetyl bromide curves will show that the last parts of the curves (above 650°C) are more straight in the acetyl bromide case. This indicates that hydrogen peroxide is less effective in removing the high temperature material. In particular, the samples 4152 and 2945 (Fig. 20) must contain a component that is quite inert in relation to hydrogen peroxide, but is soluble in acetyl bromide. The main effect of the hydrogen peroxide is the more or less complete removal of the low-temperature organic material.

§ 5 d. Conclusions

The organic matter in soils can roughly be divided into two parts: the completely humified material and the non-humified part. The second part may be present in all possible transitional forms. In peat, for example, the humification degree often is characterized by means of a 10-degree scale. According to the results mentioned above, it is reasonable to suppose that the high-temperature exothermic effect is caused by plant substances which are undecomposed and in process of decomposition or by products into which these substances are transformed by dry distillation due to insufficient oxygen admission. Among these plant rests, there are sometimes substances which are so difficult to oxidize that they are still present in the sample after thermal
pre-treatment up to 500°C as well as after treatment with hydrogen peroxide. It is also possible that the last-mentioned substances are not present in the sample from the beginning but are non-volatile decomposition products formed by thermal dissociation or dry distillation.

§ 5 c. Further Possibilities of Method

Whether DTA is suitable for quantitative analysis of organic matter or not, is still an open question. Different authors have expressed divergent opinions about this problem. A planimetric determination of the peak area has been used as a measure of the energy released during the reaction. The apparatus must first be calibrated by means of substances with known values of the heat of reaction, and this quantity must then be determined for those types of organic substances which are present in soils. Experiments in this direction have been started.

As the experiments have shown that different forms of organic material give characteristic peaks in the DTA curve, it is possible to continue these investigations for studying the effect of treatment with acids, alkalies, and so on, upon the organic material. Thus DTA can aid in the pure chemical humus research.

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