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NEW POSSIBILITIES IN THE PHASE ANALYSIS OF ROCKS WITH A DERIVATOGRAPH-C

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The advantages of one of the latest generation of thermoanalytical instruments of the Hungarian Optical Works (the Derivatograph-C) are summarized. The paper contains some practical examples of the phase analysis of geological samples.

The Derivatograph-C is one of the latest, microcomputer-operated generation of thermoanalytical instruments. It can be used for the simultaneous recording of thermogravimetric (TG), derivative thermogravimetric (DTG), thermogastitrimetric (TGT), differential thermoanalytical (DTA) and thermodilatometric (TD) curves. The second derivatives of the primary curves (DDTG, DDTA, etc.) can also be produced with the microprocessor. Besides dynamic thermal analytical measurements, examinations can be carried out with isothermal or quasi-isothermal heating programs. With the quasi-isothermal heating program, the rate of transformation can be regulated not only via the DTG signal, as with the Q-Derivatograph, but also in the case of the DTA or DTG curves. Investigations can be carried out in different gas atmospheres (e.g. in oxygen or in nitrogen).

The measuring and the heating control are performed by a microprocessor. During the measurement the signals are continuously loaded into the memory and are drawn on the display at the same time. The measurement results can be archivated on a disk, from which they can be recalled at any time [1].

This paper illustrates the advantages of the new apparatus for the phase analysis of rocks.

1. Data handling by computer. Rich software is available for determination of the weight change or the exact temperature at certain points of the curves and for presenting curves as a function of time or temperature. The curves can be magnified, and submitted to various mathematical operations. It is also possible to cut out certain sections of the curves and to make com-

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parisons between different curves. Further possibilities are base line correction, calculation of peak area and determination of peak symmetry.

2. Sample quantity. The sample quantity is a critical question in thermal analysis. For identification, the use of a small sample quantity is favourable, as the temperature and material gradients are then negligible, the reactions take place in relatively narrow temperature intervals and the overlapping of neighbouring reactions is rare. Nevertheless, a larger sample quantity is often taken for the quantitative and qualitative phase analysis of geological samples. This permits increase of the limit of detection for certain phases, and the statistical deviation in the composition of the sample can be decreased (representative sample). A larger quantity of sample is often advantageous for the calculation of kinetic parameters. In thermoanalytical measurements, the quantity of sample varies in a relatively wide interval (1 g - 1 μg). In phase analysis, suitable sample masses range between 10 and 500 mg.

The Derivatograph-C has a semi-microelectronic and automatic balance.

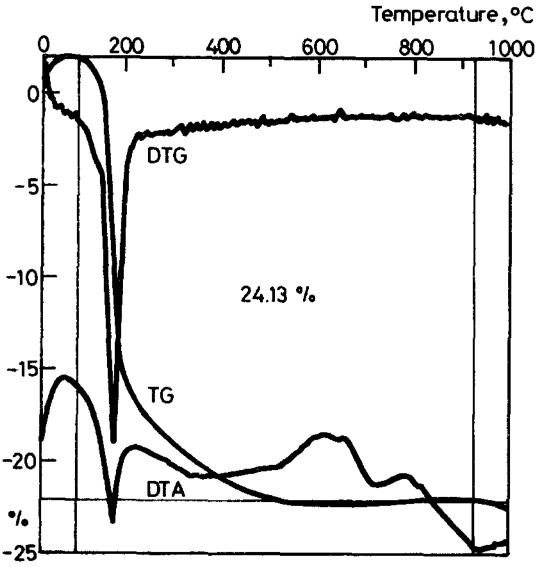

Fig. 1 Derivatogram of vivianite. Locality: Egyházaskeszö (Hungary). Sample weight: 13.8 mg. Heating rate: 10 deg/min

Measuring domains between zero and 5, 10, 50 or 100 mg, respectively can be chosen.

Figure 1 demonstrates the small quantity of sample and the measuring accuracy of the Derivatograph-C. The surface of some bore samples from a bentonite deposit exhibits dark-blue spots. The thermoanalytical investigation of a 13.8 mg sample indicates that the mineral is vivianite, ($Fe_3(PO_4)_2 \cdot 8H_2O$. On heating, vivianite undergoes two reactions, the endothermic liberation of water at 179°, and the exothermic oxidation of iron with a maximum at 631°. The first step results in a stoichiometric mass loss of 28.7%, and the second in a mass increase of 4.8 %. The measured mass change in our case is 24.13 %. The small difference (0.2 %) at this small sample mass is not due to a measuring error. This phenomenon is attributed to two causes: the oxidation is not perfect, or there is some substitution in the vivianite lattice. With such a small quantity of sample, the oxygen in the air probably sufficed for quantitative oxidation; at the same time, the results of microprobe analysis show some Mg-substitution in the structure. The calculated composition is $Fe_{2.92}Mg_{0.08}(PO_4)_2 \cdot 8H_2O$.

3. Limit of detection. Figure 2/a shows the diagram of a bore sample with a high content of carbonate (iron-dolomite). Because of the large mass

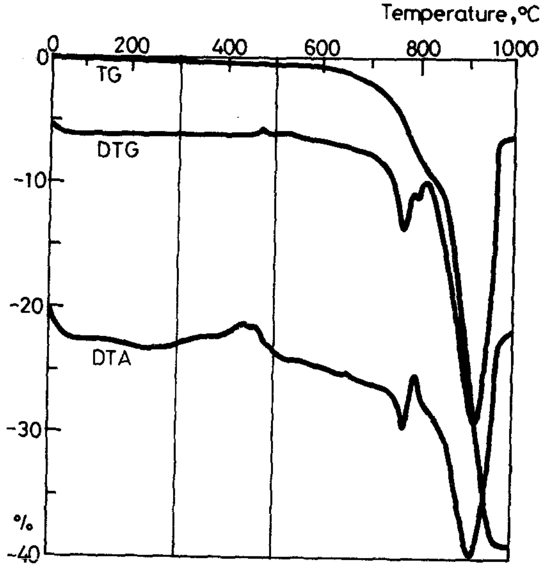

Fig. 2/a Derivatogram a carbonatic rock. Locality: Erdősmecske (Hungary). Sample weight: 257.7 mg. Heating rate: 10 deg/min change of the carbonate, a lower measuring sensitivity must be employed (100 mg).

Magnification of the interval between 300 and 500°, which in the original diagrams is a straight line, clearly reveals the reaction of 0.08 % organic substance, and the decomposition and subsequent oxidation of the small quantity of pyrite. The TG curve shows well the mass increase due to the oxidation (Fig. 2/b).

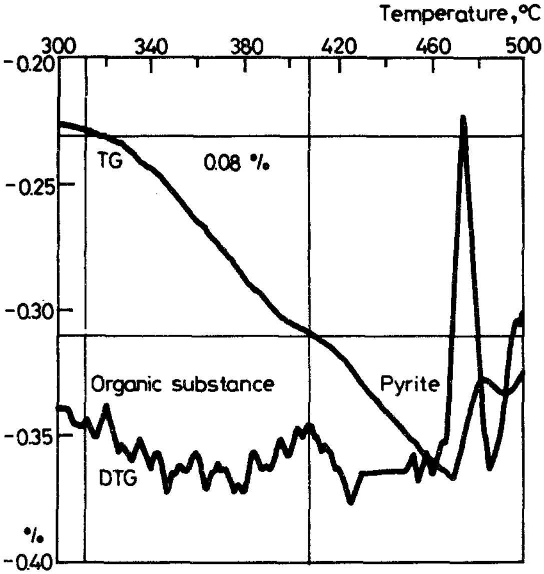

Fig. 2/b Thermogravimetric curves of the same sample between 300 and 500°C

4. The second derivatives of the curves give new possibilities for detailed investigations.

In smectites, the interlayer space may contain free water molecules, with water adsorbed to the active sites directly or in the second or third layer. Due to the large spaces and hence comparatively weak binding, this water can escape at relatively low temperature. Part of the water is coordinated around the interlayer cations. This has a larger binding energy, its value depending on the size of the cation. For larger cations (generally Ca or Mg), the loss of this water appears as an inflexion on the side of the large water peak (Fig. 3). It is better characterized in the second derivative of the TG curve (DDTG).

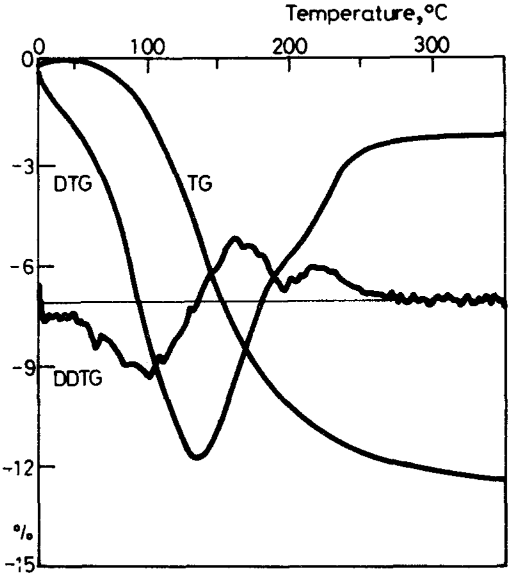

Fig. 3 Thermogravimetric curves of the liberation of water from the interlayer space from a bentonite. Locality: Egyházaskeszö (Hungary). Sample weight: 119.7 mg. Heating rate: 10 deg/min

The method is also useful for the separation of overlapping reactions. The decompositions of böhmite and kaolinite often overlap between 400 and 650° (Fig. 4/a).

Magnification of this temperature interval reveals an inflexion on the right side of the decomposition effect (Fig. 4/b). The second derivative of the TG curve separates the overlapping reactions and the mass losses of böhmite and kaolinite can be determined.

5. Investigation under quasi-isothermic and quasi-isobaric conditions. This method makes the thermal curves independent of the influence of the experimental conditions [2]. One advantage is that overlapping reactions can be separated. With this method, the previous bauxite shows similar mass losses for the reactions of böhmite and kaolinite (Fig. 4/c).

6. Calculation of virtual kinetic parameters. A frequent question in the thermal analysis literature is the physical backround of the mathematics of

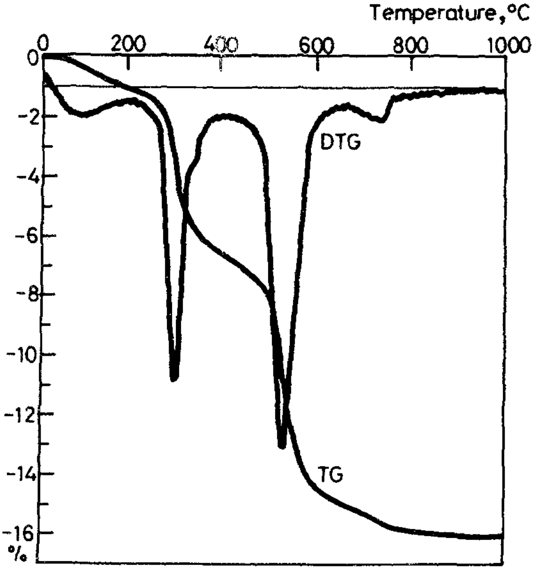

Fig. 4/a Derivatogram of a standard bauxit sample. Sample weight: 265.7 mg. Heating rate: 10 deg/min

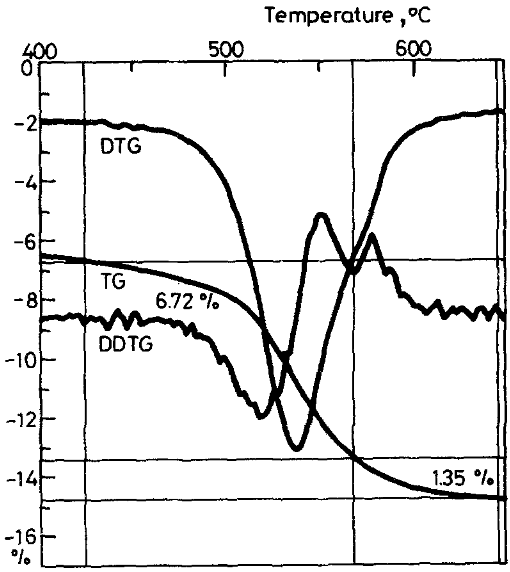

Fig. 4/b Thermogravimetric curves of the same sample between 400 and 650°C the reaction kinetics, but the procedure is probably suitable for the characterization of reactions and hence minerals [3].

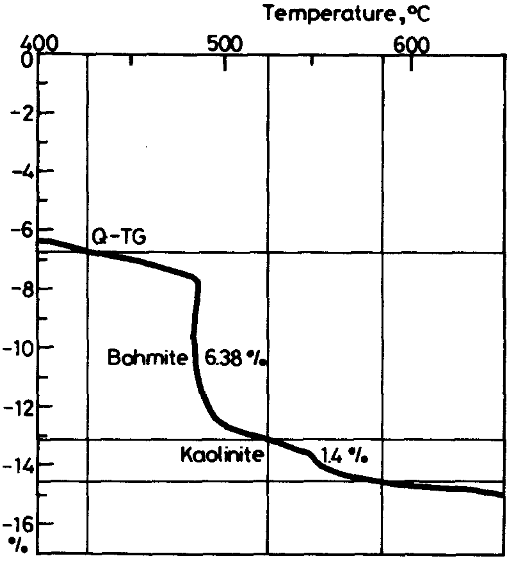

Fig. 4/c Q-TG curve of the same sample. Sample weight: 212.2 mg

There are many methods for measurement of the order of kaolinite by means of DTA (symmetry of dehydroxylation, half-width of dehydroxylation ratio to peak area, temperature of dehydroxylation, temperature of exothermic reaction, half-width of exothermic reaction, ratio of intensities of endothermic and exothermic reactions, ΔT (t_{OH} - 530°, etc.) (Fig. 5).

The Derivatograph-C software calculates the estimated kinetic parameters from the TG and DTG curves as a function of time (estimated order of reaction: by the method of Kissinger (4); activation energy: by the method of Arnold *et al.* [5], pre-exponential factor: by the method of Doyle (6) with a conversion of 0.2).

The estimated order of reaction of 18 kaolinite-bearing samples of different genetics and locations shows a correlation with the symmetry (calculated from the ratio of the peak areas before and after the peak maximum) (r = 0.93) with the ratio of the half-width and peak area (r = 0.75) and with the Smykatz-Kloss equation [7] (r = 0.63).

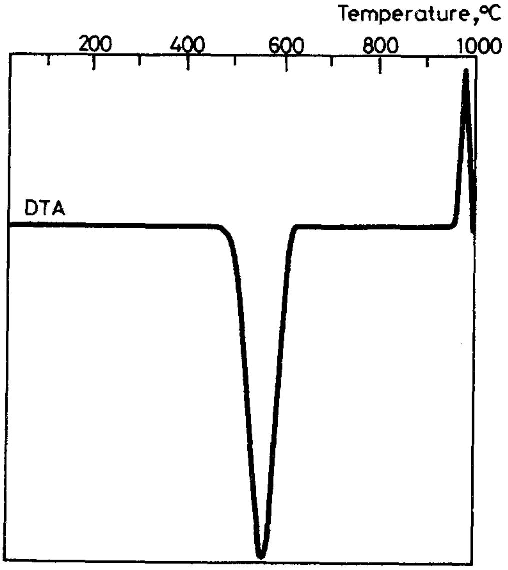

Fig. 5 Schematic DTA curve of the kaolinite

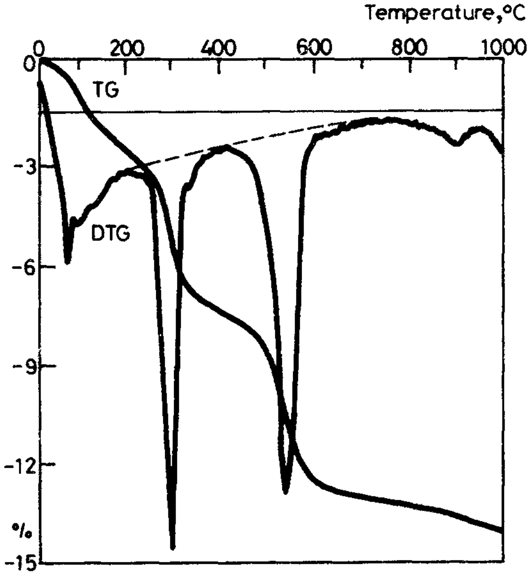

Fig. 6 Thermogravimetric curves of a bauxite sample with a large quantity of amorphous substance. Locality: Szöc (Hungary). Sample weight: 176.2 mg. Heating rate: 10 deg/min

7. Detection of amorphous phase. An example of a bauxite sample with a large quantity of amorphous phase besides the other minerals is shown in Fig. 6. Via the base line of the DTG curve and the constructed base line (dashed line), the water content on the amorphous phase can be taken into consideration in the quantitative determination of the composition. A comparison may be made with the bauxite sample in Fig. 4/a, which has a similar nineral composition.

References

1 J. Paulik, F. Paulik, M. Arnold, Thermochim. Acta, 107 (1986) 375.
2 F. Paulik, J. Paulik, J. Thermal Anal., 5 (1973) 252.
3 L. Stoch, I. Waclawska, J. Thermal Anal., 20 (1981) 291.
4 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
5 M. Arnold, P. Somogyvári, J. Paulik, F. Paulik, J.Thermal Anal., 32 (1987) 679.
6 C. D. Doyle, J. Appl. Polymer Sci, 15 (1961) 285.
7 W. Smykatz-Kloss, Chemie der Erde., 33 (1974) 358.

Zusammenfassung — In diesem Beitrag sind die Vorteile der letzten Generation thermoanalytischer Geräte (Derivatograph-c) der Ungarischen Optischen Werke zusammengefaßt. Es werden einige praktische Beispiele aus dem Gebiet der Phasenanalyse geologischer Proben beschrieben.