Journal of Thermal Analysis, Vol. 18 (1980) 111—115

APPLICATION OF WATER DETECTOR IN THERMAL ANALYSIS OF SOILS

J. Kristóf and J. Inczédy

Institute of Analytical Chemistry, University of Chemical Engineering, Veszprém, Hungary

(Received February 13, 1979)

A new detector was used for the continuous and selective detection of water vapour released during thermoanalytical investigations of soil samples.

For this purpose a derivatograph (MOM, Hungary) was directly combined with the water detector and the signals were simultaneously recorded. The gaseous products evolved in the reaction chamber of the derivatograph were passed through the detector cell by the carrier gas stream.

By comparison of the thermoanalytical curves and the trace of the water detector, further qualitative and quantitative information could be obtained, providing a better understanding of the thermoanalytical processes.

The solution of a problem by thermoanalytical methods often requires additional information along with the TG, DTG, DTA and T curves obtained under the same conditions. When two or more gaseous decomposition products are simultaneously liberated, the TG and DTG curves will not yield any information on the nature and the amounts of the individual decomposition products.

A new EGD method and a simple device for the continuous and selective detection of water vapour evolved during thermal decomposition reactions have been reported [1].

The continuous and selective water detector was used in this work to study the gases released during thermal investigations of soil samples.

The thermoanalytical curves produced by a derivatograph make possible the determination of moisture, the approximate organic content of the soil, the total weight loss up to 1000° and the amount of calcium carbonate.

However, it is very difficult to identify the decomposition stages of dolomite, magnesium carbonate and clay mineral components. By X-ray diffraction techniques crystalline materials can be evaluated only qualitatively, because their concentration in a highly amorphous system is too low.

Nevertheless, by comparison of the thermal curves and the trace of the water detector it became possible to identify the individual components and to determine their amounts, too.

Experimental

Measurements were carried out in an air atmosphere at a heating rate of 5° /min up to 1000°. The derivatograph was directly combined with the water detector. Air as carrier gas transported the gaseous decomposition products liberated from the sample. The carrier gas mixed with the gaseous decomposition products was passed through the detector cell at a flow rate of 10 liters/hour.

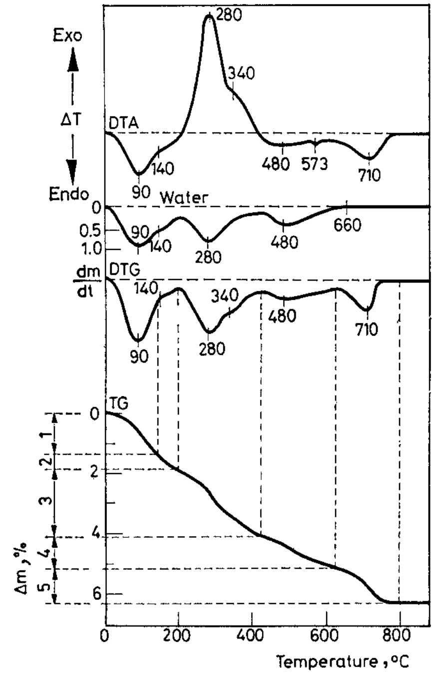

Fig. 1. Thermoanalytical curves of soil sample "A" and the signal of the water detector. 1 — Adsorbed water. 2 — Organic materials. 3 — Clay mineral. 4 — Magnesite. 5 — Clay mineral. 6 — Dolomite. 7 — Calcite

The thermal curves of 452.0 mg soil sample "A" and the simultaneously recorded signal of the water detector are shown in Fig. 1. From a comparison of the thermal curves and the signal curve of the water detector the following conclusions can be made.

The adsorbed water content of the sample is released with maximum rate at 90°. The signal of the water detector closely follows the changing water content of the carrier gas (i.e. the shape of the DTG curve). When the temperature is elevated, the organic content of the sample is combusted in three steps, at 280, 355 and 435°, respectively. The DTA curve indicates exothermic reactions. The signal of the water detector reveals that only the first combustion stage is accompanied by water production. In the second and third steps different types of decomposition products, e.g. carbon dioxide and others, are evolved. The decomposition step at 500°, as indicated by the detector, is due to the release of water. Hence, it can be assumed that the combustion of organic compounds is completed by 460° and at 500° the structural water of clay minerals is liberated. At 540° a separate step can be observed, accompanied by a weight decrease of 2.2 mg. In this stage the decomposition gases do not cause a detector reponse. It can be assumed with great probability that carbon dioxide originating from magnesium carbonate was liberated. In a wide temperature range, *viz.* between 560 and 690°, a horizontal plateau can be observed in the DTG curve. The signal of the detector also shows this plateau, but only up to 640°; above this temperature the signal returns to the baseline. By comparison of the DTG and the detector signal curves it was established that the structural water of clay minerals was liberated between 560 and 670°, while the thermal decomposition of dolomite took place from 640 to 690° The two different decomposition steps in the DTG curve can only be separated with the help of the water detector, because there is no inflexion point. Between 670 and 800° the characteristic decomposition curve of calcium carbonate can

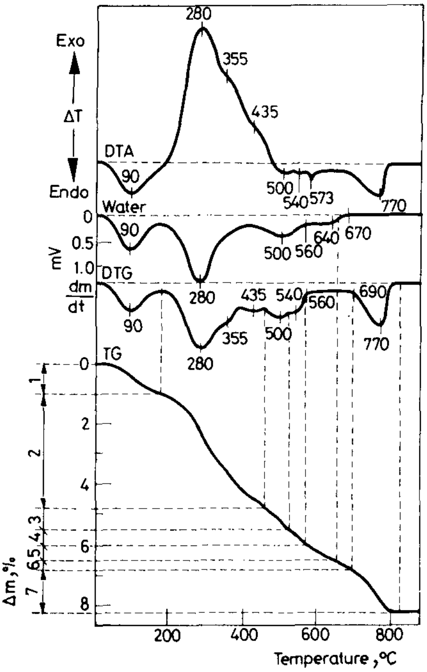

Fig. 2. Thermoanalytical curves of soil sample "B" and the signal of the water detector. 1 — Adsorbed water. 2 — Montmorillonite. 3 — Organic materials. 4 — Clay minerals. 5 — Calcite

be found. The amount of calcium carbonate can be divided into two parts; one part is originally present in the sample, while the other results from the decomposition of dolomite. At 800° the total weight loss is practically complete.

The thermal curves of 464.1 mg soil sample "B" and the signal of the water detector are shown in Fig. 2. From room temperature up to 200° two overlapping decomposition steps can be observed in the DTG curve. The shape of the curve produced by the detector is similar to that of the DTG. It can be concluded that the first step is due to the release of adsorbed water, and the second to the release of water originating from montmorillonite. The presence of montmorillonite in the sample was proved by X-ray diffraction, too. From 200 up to 430° the combustion of organic compounds takes place. Two steps at 280° and at 340° can be observed in the DTG curve. The water detector indicates that water is released only in the first reaction. In the second stage of the decomposition other types of gaseous products are liberated. The decomposition at 480° can be seen in the curve produced by the water detector, too. This mass loss is due to the release of structural water originating from clay minerals. The release of water is completed at 660°. The shape of the curve produced by the detector is similar to that of the DTG curve. At 760° the calcium carbonate is decomposed, the signal of the detector showing no change at all.

Table 1

Composition data of soil samples "A" and "B"

Sample	Adsorbed water %	Organic materials %	Structural water in clay minerals, %	Calcite %	Magnesite %	Dolomite %	Total mass loss up to 1000°, %
"A"	1.00	3.8	1.2	3.2	0.9	1.4	8.19
"B"	1.34	2.3	1.5	2.68	—	—	6.25

The composition data derived from the two sets of thermal curves are shown in Table 1.

Discussion

From the examples presented here it can be concluded that the continuous and selective water detector is a very useful source of further qualitative and quantitative information. When a complicated system such as soil is studied, the selective response of the water detector contributes to the better interpretation of the decomposition processes and the identification of the different phases.

In order to obtain quantitative information of higher accuracy, the trace of the detector can be used advantageously, especially in the case of overlapping decomposition reactions with water as one of the products.

References

1. J. Kristóf, J. Inczédy, J. Paulik and F. Paulik, J. of Thermal Anal., 15 (1979) 151.

Résumé — Un noveau détecteur a été utilisé pour déceler en continu et de façon sélective la vapeur d'eau dégagée lors de l'étude thermoanalytique des prélèvements de sols. Dans ce but, un dérivatograph (MOM, Budapest) a été directement rélié au détecteur d'eau et les signaux ont été enregistrés simultanément. Les produits gazeux dégagés dans la chambre de réaction du dérivatograph ont été envoyés dans le détecteur par un courant de gaz porteur. En comparant les courbes thermoanalytiques et la courbe enregistrée par le détecteur d'eau, des renseignements supplémentaires qualitatifs et quantitatifs ont pu être obtenus qui permettent une meilleure compréhension des processus thermoanalytiques.

Zusammenfassung — Ein neuer Detektor wurde zum kontinuierlichen und selektiven Nachweis von im Verlauf thermoanalytischer Untersuchungen von Bodenproben freigesetztem Wasserdampf eingesetzt.

Hierzu wurde ein Derivatograph (MOM, Ungarn) direkt mit dem Wasserdetektor kombiniert und die Signale simultan aufgezeichnet. Die in der Reaktionskammer des Derivatographen entwickelten gasförmigen Produkte wurden durch den Trägergasstrom in die Detektorzelle geleitet.

Durch Vergleich der thermoanalytischen Kurven und der Aufzeichnung des Wasserdetektors konnten weitere qualitative und quantitative Informationen erhalten werden, welche ein besseres Verständnis der thermoanalytischen Vorgänge gestatten.

Резюме — Использован новый детектор для непрерывного и избирательного обнаружения паров воды, выделяющихся при термоаналитических исследованиях почвенных образцов. Для этой цели дериватограф (MOM, Венгрия) был прямо соединен с детектором для воды и сигналы одновременно регистрировались. Газообразные продукты, выделяющиеся в реакционной камере дериватографа, были пропущены через ячейку детектора струей газа. При сопоставлении термоаналитических кривых и данных детектора для воды, может быть получена дальнейшая количественная и качественная информация, что необходимо для лучшего понимания термоаналитических процессов.