APPLICATION OF A CONTINUOUS AND SELECTIVE WATER DETECTOR IN THERMOANALYTICAL INVESTIGATIONS *

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ABSTRACT

A method for simultaneous TG, DTG and DTA combined with a continuous and direct water determination has been developed. The applicability of the technique is shown by reference to several examples such as limestone-containing metamorphic rock, clay, soil, cellulose and an anion-exchange resin.

INTRODUCTION

Many thermal decomposition reactions are accompanied by the release of water. It is often necessary to know if water vapour has been formed in a reaction, to detect it selectively from other gases evolved, measure its amount and continuously record the water-releasing process.

EXPERIMENTAL

We have developed [1] a water detector cell which can measure water vapour evolved in thermal decomposition reactions. This detector can be connected with various thermoanalytical units. In the course of our research we have applied it to the derivatograph [2]. The operation of the equipment is demonstrated in Fig. 1.

From the gas collecting adaptor of the derivatograph the liberated gases

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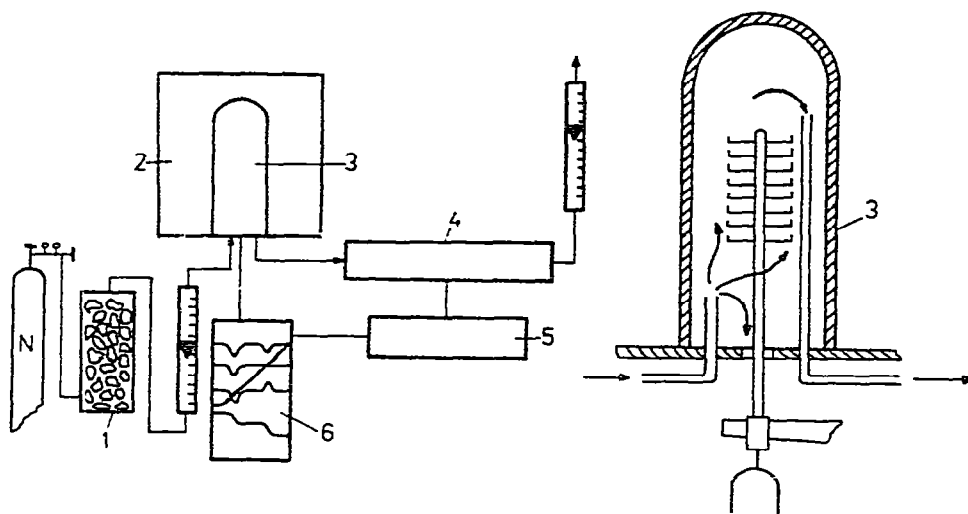
Fig. i Schematic structure of the device. 1, Gas cleaner column: 2, furnace of the derivato-graph. 3, gas collector. 4, detector cell: 5, Wheatstone-bridge, 6, recorder.

are transferred by a dry carrier gas stream (10 l/h) into the detector cell. The construction of this is illustrated in Fig. 2. The gas mixture enters the reaction vessel through tube (1) and leaves it through tube (2). The hygroscopic material carried on a glass sinter (4) absorbs the water content of the gas mixture: this is accompanied by the liberation of heat. The liberated heat of hydration changes the temperature of the coil of the resistance thermometer (6) and also its resistance, while the temperature and resistance of the reference cell coil (5) remain unchanged. The changes in the resistance difference are measured by a Wheatstone-bridge (7) and traced by a recorder. The curve obtained indicates the changes in concentration of the water vapour in the carrier gas. From the peak area conclusions can be
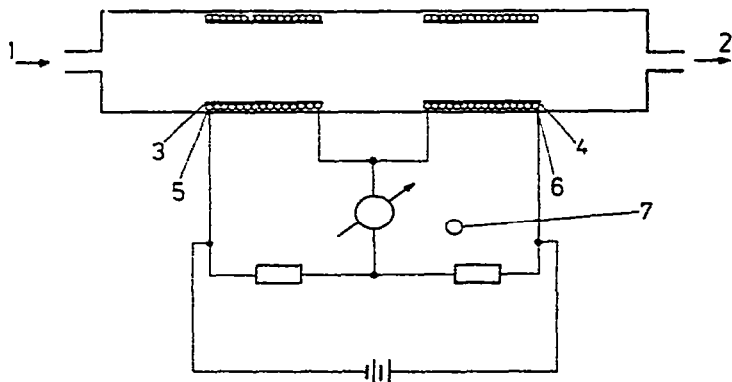

Fig. 2. Construction of the detector cell. 1 and 2, Inlet and outlet of the carrier gas; 3, glass texture without absorbent; 4, glass texture with absorbent: 5 and 6, resistance coil; 7, Wheatstone-bridge.

drawn regarding the amount of water. According to experience this correlation is linear.

RESULTS AND DISCUSSION

Figure 3 shows the TG, DTG and DTA curves for a few mg copper sulphate pentahydrate. The DTA (H_2O) curve demonstrates that the dehydration process was correctly followed by the device.

The second example is a limestone-containing metamorphic rock sample (Fig. 4). A comparison of the detector signal (H_2O) and the TG, DTG and DTA curves leads to the following conclusions. The thermal decomposition of calcium carbonate takes place at 850°C. This decomposition stage seems to belong exclusively to the release of carbon dioxide because no inflection point can be observed in the DTG curve. A very small amount of adsorbed water is liberated at 50°C. The detector signal, however, reveals four other overlapping decomposition stages at 280, 600, 680 and 810°C, respectively, due to the release of the structural water of various minerals. X-Ray diffractometry indicated that the sample contained calcite, muscovite and quartz and small amounts of chlorite, goethite and rutile minerals.

Figure 5 shows the thermoanalytical curves of a clay sample. By comparing the corresponding curves, it can be concluded that adsorbed water is released at 80°C, closely overlapping with the release of the structural water of montmorillonite at 120°C. At 310 and 440°C the organic contaminants of
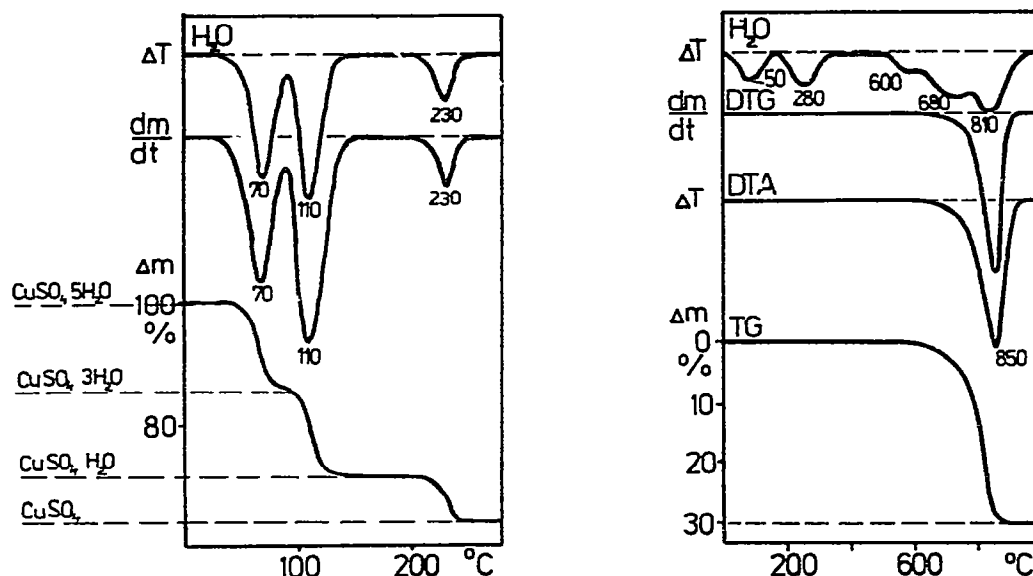

Fig. 3. Thermal decomposition of copper sulphate pentahydrate.

Fig. 4. Thermal decomposition of a limestone-containing metamorphic rock.

the sample are burnt off in two steps. The detector signal reveals water formation only in the first combustion stage. At 500°C structural water is evolved. The release of water continues up to 800°C at a constant rate. However, this process is not observed in the DTG curve, being masked by the decomposition of calcium carbonate.

In Fig. 6 the decomposition stages of a soil sample are very similar to those described above. Adsorbed and structural water are released at 110 and 180°C, respectively. The first combustion stage of the organic contaminant at 300°C is accompanied with water formation. At 500°C structural water is evolved. The release of water continues up to about 900°C.

Synthetic Y-zeolites are widely used as catalysts in alkylating reactions of hydrocarbons. HY-type catalysts are produced by calcination of the NH_4Y-type zeolites [3]. During the calcination process ammonia and water are released from the sample. The proton formed reacts with the oxygen of the lattice and forms hydroxyl groups, which can be considered as Brönsted acid sites. Above 500°C the activity of the catalyst dramatically decreases. According to Ward's theory [4], above this temperature the Brönsted acid sites are converted into Lewis acid sites. In this scheme two Brönsted acid sites form one Lewis acid site with the release of one molecule of water. Figure 7 shows the water detector trace of NH_4Y zeolite. Most of the water content is released until about 300°C. Above this temperature structural water is evolved. At 600°C the detector trace indicates the formation of Lewis acid sites, supporting the validity of Ward's theory.

The thermal decomposition of cellulose is considered to be an extremely complex process, e.g. 37 decomposition products were isolated by Schwenker.
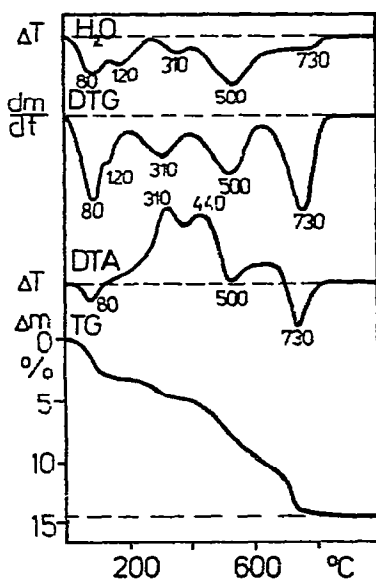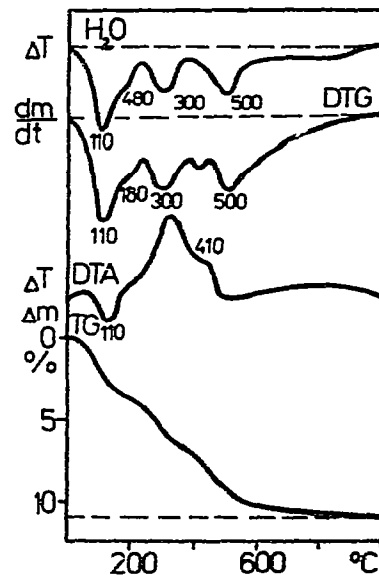

Fig. 5. Thermal decomposition of clay.
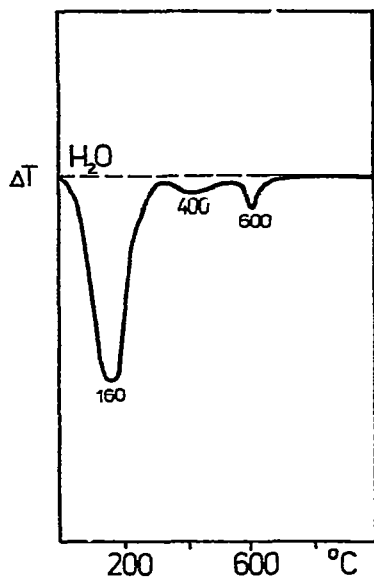

Fig. 6. Thermal decomposition of soil.

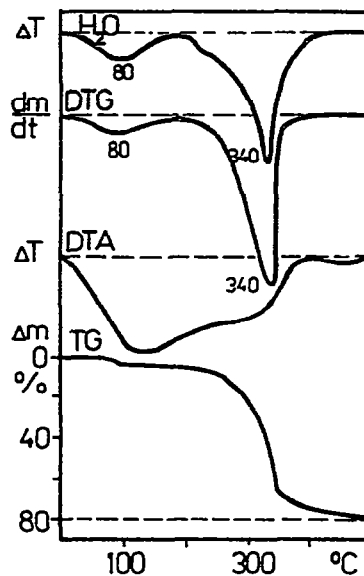Fig. 7. Thermal decomposition of NH$_4$Y zeolite.

Fig. 8. Thermal decomposition of cellulose in nitrogen

Different decomposition theories have been developed concerning the dehydrating process. In the main decomposition stage there is a competitive process between dehydration and depolymerization. The thermoanalytical curves of an industrial cellulose sample in nitrogen are shown in Fig. 8.
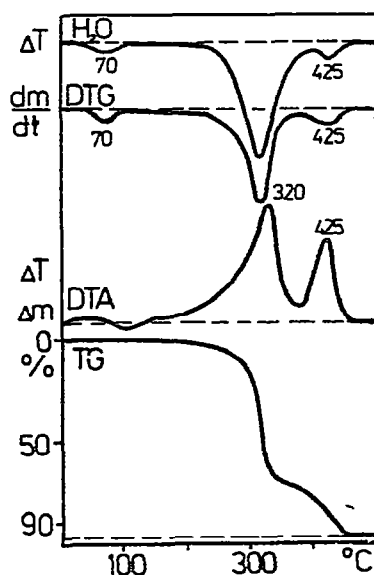

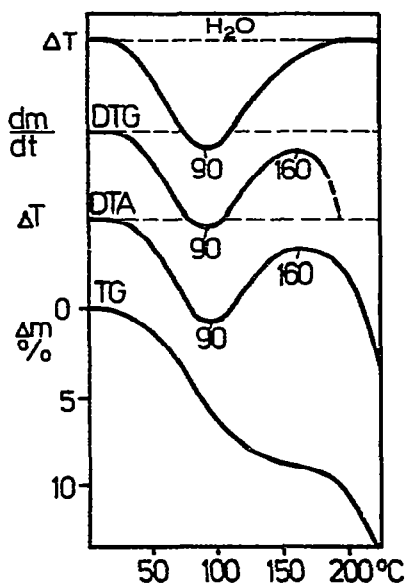Fig. 9. Thermal decomposition of cellulose in air.

Fig. 10. Thermal decomposition of the Cl form anion-exchange resin.

According to the detector trace, water is evolved stepwise throughout the entire decomposition range. The amount of water was determined by calibration and found to be 27%. The thermal decomposition of cellulose in air
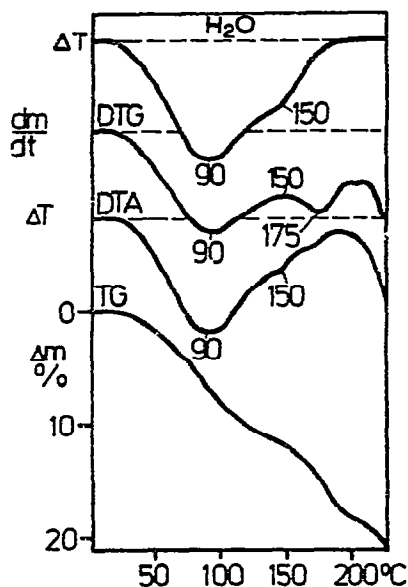

Fig. 11. Thermal decomposition of the SO_4 form anion-exchange resin.

(Fig. 9) is quite different from the former scheme. Combustion takes place in two separate stages at 320 and 425°C, respectively. The peak temperatures in the DTG and water detector curves are seen to almost coincide.

Figures 10 and 11 show the thermal decomposition curves of a DOWEX AG Ix8 type anion-exchange resin in the Cl and SO_4 forms. In the case of the Cl form resin, however, two types of bound water can be distinguished at 90 and 150°C, respectively. The release of water and the partial decomposition of the resin matrix takes place simultaneously. In the DΓG curve, the presence of strongly bound water cannot be detected at all. The only way to determine the amount of water released is by calibration and use of the water vapour detector [1].

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