*Journal of Thermal Analysis, Vol. 15 (1979) 151–157*

# A SIMPLE DEVICE FOR CONTINUOUS AND SELECTIVE DETECTION OF WATER VAPOUR EVOLVED DURING THERMAL DECOMPOSITION REACTIONS

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(Received November 16, 1977)

A technique developed for the continuous and selective detection of water vapour formed during thermal decomposition reactions is described.

The device can be connected to different types of thermoanalytical instruments without any difficulties. The detector can closely follow changes in the amount of water released during decomposition reactions, with negligible time delay.

The signal curves obtained by the detector can be compared to the simultaneously recorded thermoanalytical curves and used to determine the step in which the water was released.

The device as a free standing unit can be used to detect water plugs in different gas flows as well.

The different techniques of evolved gas detection (EGD) and evolved gas analysis (EGA) are widely used in thermal analysis to detect the volatile products, if any, and to determine the nature and amount of the volatile products formed during the heating process.

Different types of thermoanalytical equipment (thermobalance, DTA apparatus, dilatometric equipment) are connected to gas chromatographs [1], mass spectrometers [2], thermo-gas-titrimetric equipment [3], infrared spectrophotometers [4], heat conductivity cells [5] and others.

Compared to the simple thermoanalytical methods, these complex methods give additional and detailed information on the decomposition processes.

During thermal decomposition processes it is often necessary to know exactly whether or not water vapour has been formed in the reactions, to detect it selectively in the evolved gases, and continuously to record the change in the amount of water released and to measure its approximate amount.

In practice a number of techniques are used to determine the water contents of different flowing gases. However, the number of techniques available for determination of the time-dependent water contents of flowing gases is much lower. For example, there are different well-known methods to measure the water contents in flowing gases, based on conductivity [6], coulombmetry [7], piesoelectricity [8] and dew-point determination [9].

The above methods are not suitable for thermoanalytical purposes for various reasons: their characteristic curves are non-linear, the instruments are sensitive ot corrosive gases, or the response time is too high.

A simple, cheap and easy-to-handle device has been developed for the continuous detection of water evolved during thermal decomposition processes.

The detector has to meet the following requirements:

1. Selective response. This is important because in most cases the decomposition reactions take place in more then one stage and different gaseous products are released simultaneously.
2. Appropriate response time to indicate the appearance and disappearance of water in the carrier gas at a flow rate of 5 – 10 l/h, following closely the changes in water content.
3. A signal proportional to the actual water content.
4. The detector signal can be recorded simultaneously along with the TG, DTG and DTA curves.

In the method developed by the authors, the $H_2O$ evolved in the course of examination is transported by a carrier gas through a detector (Fig. 1: 2). The electric signal is measured in comparison to a reference signal.

## Experimental

Preliminary experiments were carried out by injecting water-saturated air samples. The schematic diagram of the device is shown in Fig. 1. Nitrogen gas flows through the detector cell (2) from the carrier gas supply (1) at a constant flow rate of 5 l/h. The water content of the gas is preliminarily adsorbed in a drier filled with dried silica gel. The flow rate of gases passing the detector cell is controlled by a rotameter (6). A "*T*" element (4) is connected to an aspirator bottle (5)

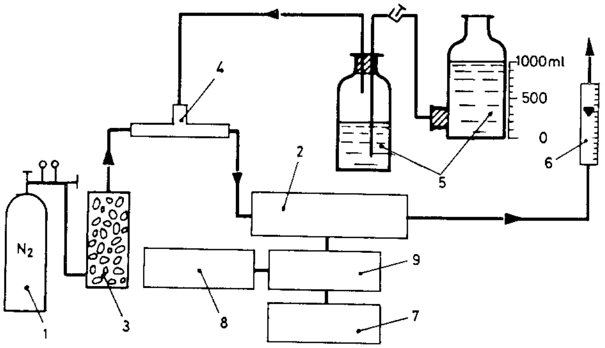

Fig. 1. Schematic diagram of the apparatus used for continuous detection of water vapour in water-saturated air samples. 1: Gas bomb, 2: detector cell, 3: drier (silica gel), 4: *T*-element, 5: aspirator bottle, 6: rotameter, 7: D. C. power supply, 8: recorder, 9: Wheatstone bridge

containing the water-saturated air. The detector is fed by a D.C. power supply (Type TR-9253, FOK-GYEM, Hungary (7) and the signal of the detector is registrated on a four-channel $\mu$V recorder (MOM, Hungary) (8).

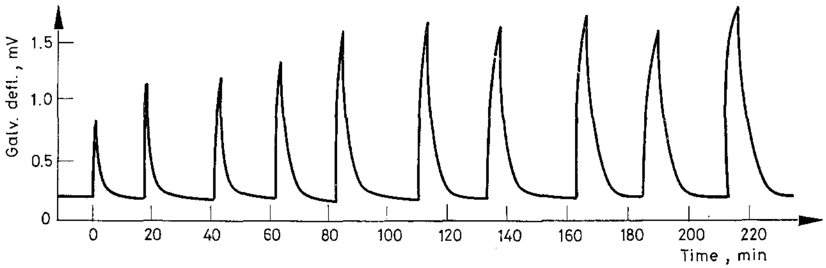

Fig. 2. The curves obtained with the detector. Initially 50 cm$^3$ water-saturated air sample was injected, and its amount was increased in equal steps of 50 cm$^3$ up to 500 cm$^3$

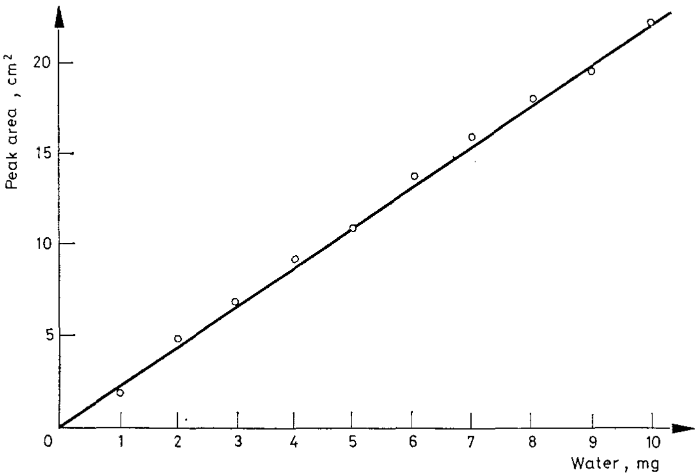

Fig. 3. The areas enclosed by the curves plotted against the water content of the air samples saturated with water

Initially, 50 cm$^3$ air sample saturated with water was introduced into the dry carrier gas stream, and its amount was increased in equal steps of 50 cm$^3$ up to 500 cm$^3$. Ten curves were recorded, as shown in Fig. 2. The rising parts of the curves represent the addition of water-saturated air samples. The addition was stopped at the peak. The areas enclosed by the curves were determined by a planimeter and plotted against the water content, as shown in Fig. 3. A linear relationship was found between the curve peak area and the water content. The results were evaluated by the least-square method. The constants of the linear regression line are as follows:

$$a = 2.19 \pm 0.14 \quad (1)$$

$$b = 0.17 \pm 0.24 \quad (2)$$

The regression coefficient ($h$) is:

$$h = 0.998 \quad (3)$$

For further tests the detector was connected to a derivatograph (Type 3427–1100°, MOM, Hungary) The schematic diagram of the apparatus is shown in Fig. 4. The sample is surrounded by a silica chamber, which can be flushed with an inert carrier gas [10]. The evolved gases are removed from the furnace chamber of the derivatograph and transported through the detector at a constant flow rate of 10 l/h by the carrier gas. The flow rate of the mixture of the evolved gases and the carrier gas was controlled automatically.

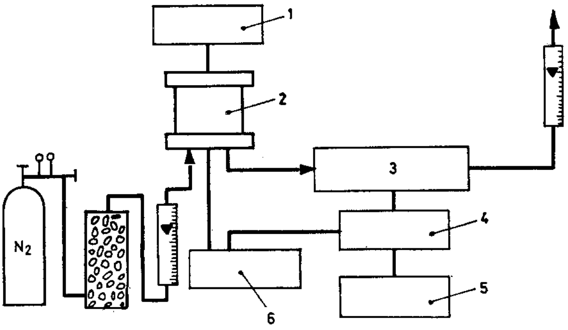

Fig. 4. Schematic diagram of the apparatus connected to the derivatograph. 1: Furnace temperature programmer, 2: furnace, 3: detector cell, 4: Wheatstone bridge, 5: d. c. power supply, 6: recorder

The thermal decomposition curves of 50.0 mg $CuSO_4 \cdot 5H_2O$, including the signal of the water detector, are shown in Fig. 5. The sample was heated at a heating rate of 5°/min.

Compared to the decomposition curves the following conclusions can be drawn as regards the signal of the detector:

1. The signal of the detector closely follows the change in the water content of the carrier gas (i.e. the shape of the DTG curve) with a negligible time delay.
2. All the points of the curve produced by the detector are proportional to the actual concentration of water in the carrier gas and are very close in time to the thermoanalytical curves.

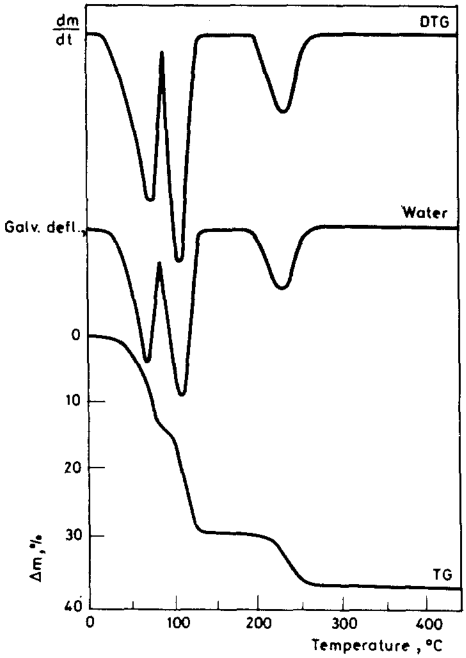

Fig. 5. Thermal decomposition curves of 50.0 mg $CuSO_4 \cdot 5H_2O$, including the signal of the water detector

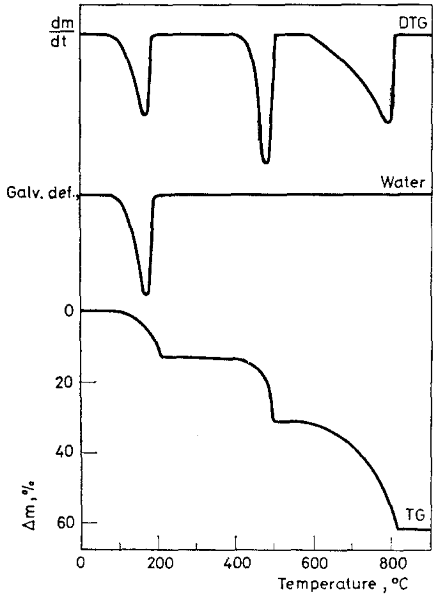

Fig. 6. Thermal decomposition curves of $Ca(COO)_2 \cdot H_2O$ in a nitrogen atmosphere, and the signal of the water detector

The measurements were repeated with different amounts of $CuSO_4 \cdot 5H_2O$. The relationship between the curve peak area and the mass of water was similar to that shown in Fig. 3.

The lowest detectable amount of water can be estimated as 2–3 mg. The standard deviation of the method is not worse than 2 rel. per cent.

### *Selectivity tests*

For investigation of the application of this technique to detect water in the presence of other gaseous thermal decomposition products, a known amount of $Ca(COO)_2\ H_2O$ in a nitrogen atmosphere was examined and the curves recorded (see Fig. 6). It was found that the signal of the detector indicates the release of water during the reaction in accordance with the DTG curve. Carbon monoxide and dioxide formed in the second and third stages of the reaction do not influence the response of the detector.

The thermal decomposition curves of an air-dry anion exchanger resin sample (AG 1 × 8 Bio-Rad, USA) in chloride form, heated in a nitrogen atmosphere, and the signal of the detector are shown in Fig. 7. The thermal decomposition takes place in three separate steps. The detector records only the water released in the first stage of the decomposition and the other gas products evolved do not disturb it.

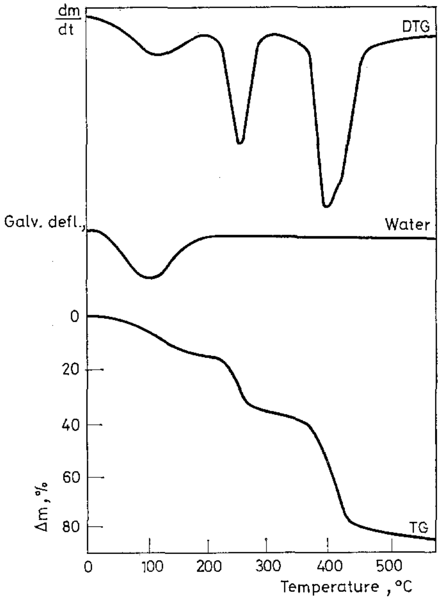

Fig. 7. Thermal decomposition curves of an air-dry anion exchanger resin sample (AG 1 × 8 Bio-Rad, USA) in chloride form, heated in a nitrogen atmosphere, and the signal of the detector

Similar investigations were carried out to examine the influence of sulphur dioxide, sulphur trioxide and ammonia. It was found that these compounds have no effect on the selective response of the detector either.

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Résumé — L'article décrit une technique mise au point par les auteurs pour déceler de façon continue et sélective la vapeur d'eau formée au cours des réactions de décomposition thermique.

L'appareil peut être raccordé sans difficultés à différents types d'instruments d'analyse thermique. Le détecteur permet de suivre étroitement et avec un retard négligeable les variations des quantités d'eau dégagée pendant les réactions de décomposition.

Les courbes obtenues par le détecteur être comparées aux courbes d'analyse thermique enregistrées simultanément et permettent de déterminer l'étape pendant laquelle l'eau s'est dégagée.

L'appareil peut être utilisé comme unité indépendante pour déceler les "bouchons" d'eau dans les différents circuits de gaz.

Zusammenfassung — Dieser Artikel beschreibt eine von den Autoren zum kontinuierlichen und selektiven Nachweis von im Laufe thermischer Zersetzungsreaktionen entstandenem Wasserdampf eingesetzte Technik.

Die Vorrichtung kann mit verschiedenen Typen thermoanalytischer Geräte ohne Schwierigkeiten verbunden werden. Der Detektor kann Änderungen der während der Zersetzungsreaktionen freigesetzten Wassermenge mit zu vernachlässigender Verspätung verfolgen.

Die durch den Detektor erhaltenen Signalkurven können mit den simultan aufgenommenen thermoanalytischen Kurven verglichen und zur Bestimmung der Stufe, in welcher das Wasser freigesetzt wurde, eingesetzt werden.

Das Gerät kann als frei stehende (selbständige) Einheit auch zum Nachweis von Wasserpfropfen in verschiedenen Gasströmen verwendet werden.

Резюме — Описана техника, развития авторами для непрерывного и селективного определения паров воды, образующихся во время реакций термического разложения.

Приставка может быть приспособлена к различными типам термоаналитических инструментов без каких-либо трудностей. Детектор может тщательно проследить изменения количества воды, выделяющейся во время реакций разложения с незначительным временем задержки.

Полученные детектором кривые сигналов могут быть сопоставлены с одновременно регистрируемыми термоаналитическими кривыми и могут быть использованы для определения стадии, на которой выделяется вода.

Приставка также может быть использована и самостоятельно для обнаружения водяных пробок в различных газовых потоках.