*Thermochimica Acta*
Elsevier Publishing Company, Amsterdam
Printed in Belgium



# COMPLEX THERMOANALYTICAL METHOD FOR THE SIMULTANEOUS RECORDING OF T, TG, DTG, DTA, TGT, DTGT, TD AND DTD CURVES

## PART I. DEVELOPMENT AND CHARACTERIZATION OF EQUIPMENT

J. PAULIK AND F. PAULIK
*Institute for General and Analytical Chemistry, Technical University Budapest (Hungary)*
(Received March 3rd, 1971)

ABSTRACT

A new complex thermoanalytical method is described for the simultaneous recording of the temperature (T), the differential thermoanalysis (DTA), the thermogravimetric (TG), derivative thermogravimetric (DTG), thermo-dilatation (TD), derivative thermo-dilatation (DTD), thermo-gas-titrimetric (TGT) and derivative thermo-gas-titrimetric (DTGT) curves.

---

As a result of the continuing development of the derivatographic method[1–4] a complex method has recently been elaborated with the help of which the thermal transformations taking place within a sample can be examined simultaneously from four different points of view on the basis of eight thermoanalytical curves. The four different processes recorded by the device are weight change, dilatation, enthalpy change and evolution of gas.

The equipment, of which the operating principle is shown in Fig. 1, is suitable for the recording of the temperature (T), the differential thermoanalysis (DTA), the thermogravimetric (TG), derivative thermogravimetric (DTG), thermo-dilation (TD), derivative thermo-dilation (DTD), thermo-gas-titrimetric (TGT) and derivative thermo-gas-titrimetric (DTGT) curves.

In order to measure the dilatation of the powdered sample, it is compressed into the shape of a hollow cylinder. This test piece is placed on the end of a silica tube which is connected to one arm of the balance. This silica tube is surrounded by another silica tube which rests with its stirrup-shaped end on the sample (see insert of Fig. 1). If the length of the test piece changes, the two concentric tubes will move in relation to each other together with the two diaphragms mounted on them. The diaphragms, behind which a light cell is situated, are illuminated with a parallel light beam. As a result of the movement of the diaphragms, light beams of different diameter will pass through the slits, generating in the light cell an electric signal whose voltage is proportional to the change in length of the test piece. A galvanometer records the changes in this electric signal. In this way the thermo-dilatation (TD) curve is obtained.

*This paper was presented at the 3rd Conference on Analytical Chemistry Budapest, August, 1970.

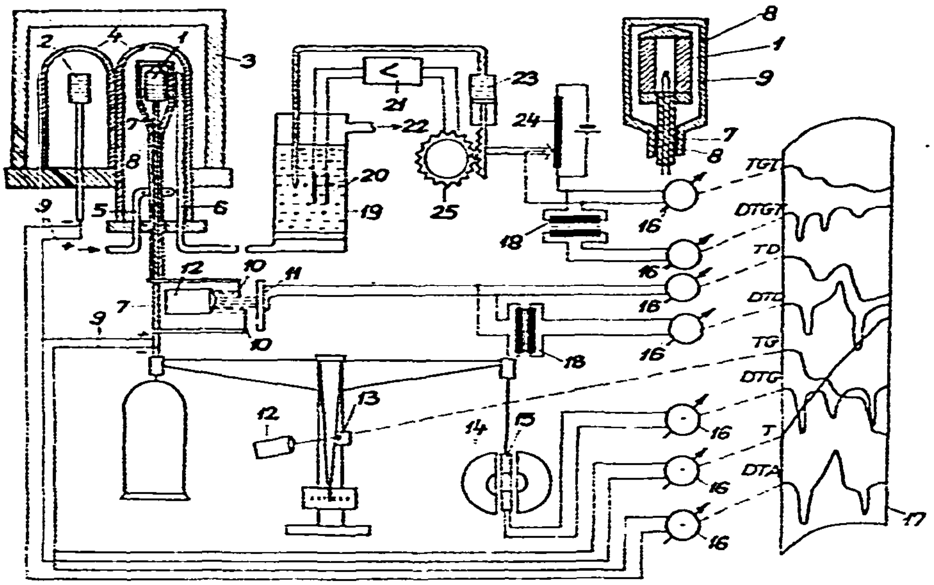

Fig. 1. Device for the parallel recording of DTA, T, TG, DTG, TD, DTD, TGT and DTGT curves. 1, Compressed test piece; 2, compressed reference substance; 3, furnace; 4, silica bell; 5, inlet tube for carrier gas; 6, tube for gas extraction; 7, silica tube; 8, silica tube with stirrup-shaped end; 9, thermoelement; 10, diaphragms; 11, light cell; 12, lamps; 13, optical slit; 14, magnet; 15, coil; 16, galvanometer; 17, photographic paper; 18, deriving transformer; 19, absorber; 20, electrodes; 21, amplifier; 22, vacuum pump; 23, automatic burette; 24, potentiometer; 25, servo-motor.

For the derivation of the light signal induced we have used our earlier method for the derivation of polarographic curves[2]. If a direct current of changing voltage is applied to the primary coil of a transformer, then the derivative of the primary current will appear in the secondary coil. Thus if the primary coil of a so-called deriving transformer is connected to the light cell, and the secondary coil to the galvanometer, then the derivative thermo-dilatation (DTD) curve is obtained.

The device described does not interfere with the free operation of the balance. Therefore, the derivatograph measures in the usual way the change in weight of the test piece (TG), the rate of the weight change (DTG), the temperature change (T) and the enthalpy change (DTA).

Independently from these measurements the equipment can also simultaneously measure by a continuous scheme the amount of the evolved gases. This section of the device operates according to the principle of our earlier thermo-gas-titrimetric method, but in its present form works automatically. In order to collect the evolved gases quantitatively, the sample is surrounded by a silica bell. At the bottom an inert carrier gas streams into this through a silica tube. The carrier gas transporting the released gases is exhausted at the top of the bell and led into the absorber vessel which generally contains water as absorption solution.

If for example, besides water, sulphur trioxide is also released from the sample under examination, then the pH of the absorption solution will change. This will be sensed by the indicator electrodes immersed in the solution, since an electric signal proportional to the pH change will be induced in them. This signal amplified can be used for the control of the rotational speed of the servo motor of an automatic burette; the automatic burette will add titrant, in the present case sodium hydroxide solution, to the absorption solution as long as the pH of this differs from the pH value selected, in the present case pH 7. The amount of titrant consumed will be recorded as a function of time photographically by means of a potentiometer connected to the automatic burette and a galvonometer. The thermo-gas-titrimetric (TGT) curve obtained represents indirectly the process of evolution of the gaseous decomposition products.

By connecting the primary coil of a deriving transformer with the potentiometer, and its secondary coil with the galvanometer, the derivative of the thermo-gas-titrimetric curve (DTGT) can also be plotted.

With adequate modification the method can also be used in cases, among others, when $H_2O$[5], HCl, $NH_3$, $SO_2$, $CO_2$ or $Cl_2$ are released and redox or deadstop titrations are applied to the determination.

This method enables the problem under investigation to be approached simultaneously from different sides, which may be of advantage in the interpretation of the phenomena observed.

## REFERENCES

1 F. Paulik, J. Paulik and L. Erdey, *Z. Anal. Chem.*, 160 (1958) 241.
2 F. Paulik, J. Paulik and L. Erdey, *Talanta*, 13 (1966) 1405.
3 F. Paulik, J. Paulik and L. Erdey, *Microchim. Acta*, (1966) 699.
4 J. Paulik, F. Paulik and L. Erdey, *Microchim. Acta*, (1966) 886.
5 P. Marik-Korda, É. Buzágh-Gere, J. Inczédy, J. Paulik and L. Erdey, *3rd Proc. Anal. Chem. Conf. Budapest*, 2 (1970) 235.