

Short Communication

THE DERIVATOGRAPH-C

A microcomputer-controlled simultaneous TG, DTG, DTA, TD and EGA apparatus. I

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The latest type of derivatograph, operated by a microcomputer, is described. The equipment is suitable for simultaneous TG, DTG, DTA, TD and EGA measurements under dynamic, isothermal, quasi-isothermal and quasi-isobaric heating conditions. As practical examples, the decompositions of bauxite and manganese(II) sulphate pentahydrate are demonstrated.

Simultaneous thermoanalytical measurements date from about 30 years ago [1]. The derivatograph [1-4] was the first industrially produced instrument operating on this principle. A number of successive generations [2, 5-7] of this apparatus have been marked. The most recent development is the derivatograph-C [8, 9]. The first part of our present paper deals with a schematic description of the structure and operation of this instrument. In later parts we illustrate its versatility and original applicability on characteristic and practical examples.

This equipment is suitable for the simultaneous recording of thermogravimetric (TG), derivative thermogravimetric (DTG), thermogastitrimetric (TGT) [2, 10-12] and either differential thermoanalytical (DTA) or thermodilatometric (TD) [2, 13] curves. TGT is one of the evolved gas analytical (EGA) measuring techniques [1, 2, 5]. If necessary, the device can also display the DDTG, DDTA, DTGT [2, 5, 10] and DTD [2, 4, 5, 13] curves, i.e. curves obtained by differentiating the basic curves.

The results obtained with some other apparatus can also be processed simultaneously, as one of the channels can be kept free for the reception of a signal moving between 0 and 5 V.

In Fig. 1 the operating principle of the apparatus is illustrated schematically. The weight changes (TG curve) of the sample are measured by a null-type electronic semimicro balance. An initial small weight change causes the beam of the balance (13) to deviate somewhat from its null-position, which is sensed by a nulldetector

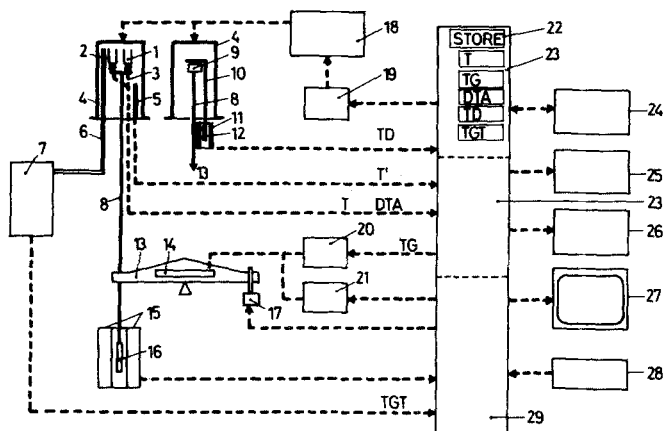


Fig. 1 1. Sample, 2. reference material, 3. counter-connected thermoelements, 4. furnace, 5. heating controller thermoelement, 6. gas exhaust tube, 7. thermogastitrimetric equipment, 8. corundum tube, 9. compressed sample for TD examinations, 10. corundum tube, 11. linear differential transformer, 12. iron core of linear differential transformer, 13. balance, 14. coil moving in magnetic field, 15. linear differential transformer, 16. iron core of linear differential transformer, 17. electromechanical device to perform rough taring, 18. heating controller system, 19. 8-bit D/A converter, 20. 15-bit D/A converter, 21. 12-bit D/A converter, 22. STORE part of memory, 23. memory of microcomputer (RAM and ROM), 24. floppy disk drive, 25. plotter, 26. printer, 27. display, 28. keyboard, 23. and 29. microcomputer

(15, 16). With the mediation of the 15-bit converter D/A (20), the microcomputer (23) intervenes with a speed proportional to the magnitude of the error signal generated in the detector (15, 16) and electromagnetically restores the balance to its original position with the help of a coil (14) moving in a magnetic field. Through recording of the control signal, the TG curve is obtained.

The rough taring of the balance is performed automatically by an electromechanical device that places a balance rider (17) into the appropriate point of the balance arm. For the fine taring, the microcomputer with the mediation of a 12-bit D/A converter (21) switches a current of appropriate voltage onto coil 14 and keeps the voltage at a constant value until the end of the experiment. For optimal accuracy of the weight change, it is necessary to change the measuring range of the balance to 5, 10, 20, 50 or 100 mg.

The temperature of the sample (curve T) and changes (DTA curve) in the difference (ΔT) between the temperatures of the sample (1) and reference material (2) are measured in the conventional way [2-4] with two counter-connected thermoelements (3).

There is a possibility to transport the gaseous decomposition products (SO_2 , SO_3 , CO_2 , HCl , Cl_2 , etc.) quantitatively with a carrier gas through a capillary tube

(6), into the absorption vessel of the thermogastitrimetric device (7), where the gases absorbed by water can be titrated continuously with a suitable reagent. In this way the various liberated gaseous decomposition products can be separated and the processes of the partial reactions can be determined selectively [2, 5, 10–12].

The construction of the equipment allows the simultaneous recording of the curves [2, 4, 5, 13]. In this latter case the powdery sample must be compressed into a tablet (9), which is placed on top of the corundum rod (8) fastened to the balance arm. On top of the test piece, a bridle (10) must be suspended. If the test piece changes its dimensions, the iron core (12) fastened to the bridle moves in the interior of a differential transformer (11). Since the simultaneous measurement of the weight change is achieved by means of a null-balance, the electric signal generated in the differential transformer (11) must be corrected for the error signal of the differential transformer (15). Recording of the corrected electric signal gives the TD curve, while recording of control signal gives the TG curve.

Experiments can be carried out in pure gas atmospheres of different kinds. The apparatus is equipped with two furnaces. One of them has Kanthal and the other graphite heating elements. The former can be heated up to 1200° and the latter up to 1600°. By means of the heating controller (18) and the intermediation of an 8 bit D/A converter (19) the furnaces are similarly controlled by the microprocessor.

For the measurements, three different kinds of heating techniques can be applied: linear, isothermal and quasi-isothermal heating.

In the case of linear heating, any heating rate up to a limit of 20 deg min⁻¹ can be applied, while any cooling rate can be achieved which is permitted by the spontaneous cooling of the furnace.

Within a single isothermal heating program, eight isothermal periods of any temperature and length can be attained. These isothermal levels can be reached with various heating and cooling rates [8].

The essence of the quasi-isothermal heating technique [2, 6, 7, 14, 15] lies in the condition that the sample temperature is raised at the usual rate (2–5 deg min⁻¹) until transformation begins in the sample. Thereafter, until the end of the transformation, the microprocessor establishes a difference between the sample and furnace temperatures such that the given transformation should take place with a weight change [2, 6, 7] (0.05–1.0 mg⁻¹), an enthalpy change [2, 6, 7], or a linear dimension change [2, 7, 14], at a very low and constant rate. The simultaneous recording of Q-TG and Q-TGT curves is also possible; experience [2, 7, 15] indicates that this further increases the resolution and selectivity of the examinations. The information content of the Q-TG, Q-DTA, Q-TGT or Q-TD curves obtained differs significantly from that of the conventional TG, DTA, TGT or TD curves [2, 6–9, 14, 15].

In the course of the examination, the periodical sampling of the signals observed,

the bunching of their values, the loading into the memory (23), and the continuous drawing of the curves on the display (27) are all performed by the microprocessor. After the measurement, the data can be recorded with a floppy disk drive (24) on a disk, from which they can be recalled at any time.

For data processing and data handling, a rich software program is designed, as summarized in Table 1. With the help of the software, for example the weight change, the linear changes in size, the consumed titrant, etc. can be given as functions of time or temperature. The curves can be multiplied, divided, increased or diminished by constant values, e.g. chemical factors (line *d*). Further possibilities: Addition or subtraction of curves of identical character (*o*) obtained in two different examinations (e.g. TG and TGT). Conversion of TG and TGT curves into percent (*g*) or mole number (*f*). Determination of on-set, off-set and peak temperatures, as well as peak areas and peak symmetry of the DTA curve (*m*). Differentiation (*b*) and smoothing (*a*) of curves. On-line correction of the base line of DTA and TG curves (*o*), necessary in the case of very small samples [8]. Calculation of virtual kinetic parameters (1). Curves can be shifted along the *x* and *y* axes (*i*). Selected sections of the curves can also be enhanced separately according to choice, as well in the direction of the *x* or the *y* axis.

The curves transformed by means of these operations can be ordered side by side and so the diagram can be constructed on the display (27) before it is drawn by the plotter (25) in the wanted size. After drawing the curves, the plotter automatically draws the scale division and scale values of the *x* and *y* axes. By means of the plotter, inscriptions with number or text can be prepared at any position on the diagram.

By means of the printer (26), the data sheet can be printed. The measurement data for any curve can be prepared between the wanted limits and with the required fullness of detail.

Before every measurement, every circuit can be calibrated separately and the obtained factors can be noted on the data sheet. The bunched data multiplied by the factors can be loaded into the memory (23). The double floppy disk drive (24) allows tracing, handling and deletion of data stored on the disk.

The running of the apparatus is simple. The software of the device helps its users (in the form of question + answer) to establish the program of the experiment with the help of the keyboard (28). Handling of the apparatus does not require any previous computer-technical experience.

The versatile applicability of the equipment is demonstrated below on two examples selected at random.

Figure 2 shows the original thermogram obtained for a bauxite sample. This proves, for instance, that in cases when two or more gaseous decomposition products are formed simultaneously in the course of the examination, it is advisable to trace the TGT curve simultaneously [11] with the TG, DTG and DTA curves.

Table 1 Data processing facilities

	TG	DTA	TD	TGT	T	DTG	DDTG	DDTA	DTD	DTGT	Store
a) Smooth	+	+	+	+	+	+	+	+	+	+	+
b) Derivative	+	+	+	+	+	+					+
c) Min.-max.	+	+	+	+	+	+	+	+	+	+	+
d) Op. const.	+	+	+	+	+	+	+	+	+	+	+
e) Rel. step. h.	+		+	+							
f) Step. mol. conv.	+			+							
g) Step-s. weight	+			+							
h) Step-s. length			+								
i) Shift	+	+	+	+	+	+	+	+	+	+	+
k) TG corr.	+										
l) Kinetics	+										
m) Peak		+				+	+	+	+	+	
n) Base line corr.		+									
o) Op. stored	+	+	+	+	+						

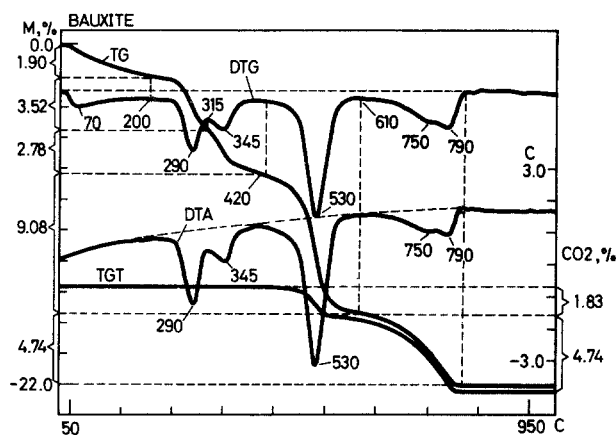
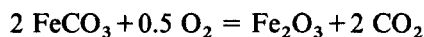


Fig. 2 Simultaneous TG, DTG, DTA and TGT examinations of a bauxite sample. Original diagram

In the given case, according to Table 2, on the basis of the weight changes alone, only the water (70° in the DTG curve), gibbsite (290°), goethite (345°) and dolomite (750°, 790°) contents of the sample could be determined with satisfactory accuracy, but not that of boehmite (530°), as the TGT curve showed that, besides the water originating from the decomposition of boehmite, 1.83% of CO₂ was also formed in the range 420–610°. It could be stated that the sample contained siderite. Therefore, the weight loss (1.50%) caused by the decomposition of siderite



had to be subtracted from the weight loss observed at 420–610° (9.08%).

Table 2 Composition of the bauxite calculated on the basis of curves illustrated in Fig. 2

Components	Decomposition		Calculated from			Amount of the components, %
	tem-perature range	peak temp., °C	TG	TG-TGT	TGT	
			curves			
			Δm , %	H ₂ O, %	CO ₂ , %	
Adhesive water	20–200	70	1.90	1.90	—	1.9
Gibbsite	200–315	290	3.52	3.52	—	10.2
Goethite	315–415	345	2.78	2.78	—	2.7
Boehmite + siderite	415–610	—	9.08	—	—	—
Siderite	415–610	(500)	—	—	1.83	4.8
Boehmite	415–610	530	—	7.58	—	50.5
Dolomite	610–820	750 790	4.74	—	4.74	10.8

Calculating with the corrected weight change (7.58%), it was found that the sample contained not 60.5%, but only 50.5% of boehmite.

Experience shows [2, 16] that the sulphide, sulphate, carbonate and organic material impurities in rocks and minerals can in general be determined with satisfactory accuracy in a similar way.

The weight of the bauxite sample placed into the open platinum crucible was 106.4 mg. The applied heating rate was 5 deg min⁻¹. Oxygen was used as carrier gas. The pH-stat titration was carried out at pH = 9.3 and at pH = 4.5. For the titration at pH = 9.3 1.59 ml of 0.1 N NaOH solution ($f = 1.000$) and at pH = 4.5 no titrant was consumed; consequently, no SO₃, but only CO₂ [16] was formed.

In Fig. 3 the Q-TG, Q-DTG and Q-DTA curves show the dehydration process of manganese(II) sulphate pentahydrate under quasi-isothermal and quasi-isobaric conditions, as functions of time (A and B) and temperature (C and D) respectively.

The weight of the sample was 249.1 mg. A conical crucible [7] was applied, inside which, according to experience, similarly to the labyrinth crucible [2, 7] pure

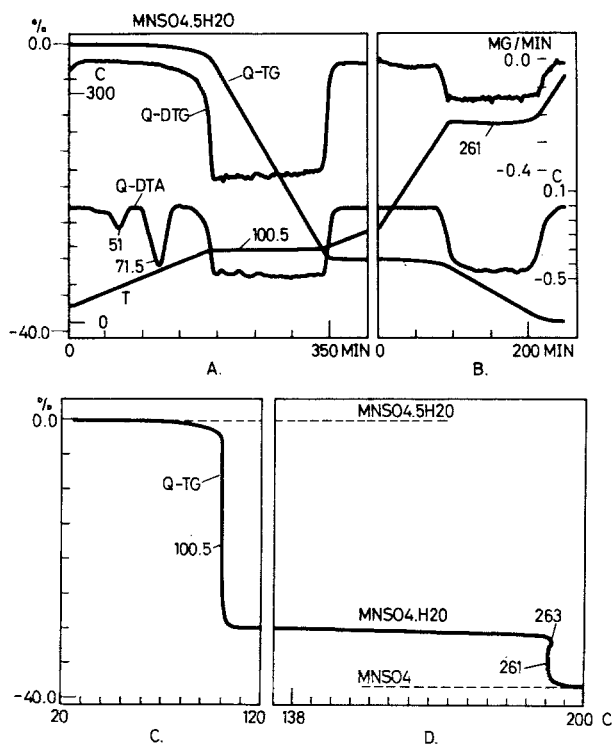


Fig. 3 Examination of manganese(II) sulphate pentahydrate under quasi-isothermal quasi-isobaric conditions. Original diagram

gaseous decomposition products with nearly 100 kPa partial pressure were formed. The examination was carried out in two parts (*A* and *B*) because, due to the different characters of the two dehydration processes, two different heating programs had to be applied. In the first part of the examination (*A*), in the dynamic heating period a heating rate of 0.4 deg min^{-1} was applied, while in the isothermal period a difference was established between the sample and furnace temperatures such that the transformation should take place at a rate of 0.4 mg min^{-1} . In the second part of the examination (*B*), the heating rate was 1.5 deg min^{-1} and 0.15 mg min^{-1} , respectively. The examinations were performed in the presence of air.

The literature contains divergent views regarding the possible composition of manganese(II) sulphate hydrates. We have investigated this problem, but we shall report our results in detail later. Our experience to date suggests that the course of the curves shown in Fig. 3 can be interpreted as follows. The pentahydrate decomposes under given conditions at 51.0° (Q-DTA curve), and the tetrahydrate and a solution phase corresponding to one mole of water are formed. At 71.5° (Q-DTA curve) the tetrahydrate decomposes and the amount of the solution phase increases. Despite the increasing temperature, the solution cannot evaporate up to 100.5° , since this is inhibited by the conical crucible. At 100.5° the solution begins to boil and departure of the water vapour starts at a rate of 0.4 mg min^{-1} (Q-TG, Q-DTG curves). The temperature of the system does not change until the 4 moles of water have departed from the crucible. The decomposition of the monohydrate took place at 261.0° . Here no solution phase was formed.

* * *

On the basis of our instructions, the prototype of the apparatus was developed in the Institute for General and Analytical Chemistry, in cooperation with the Hungarian Optical Works, in 1985. The software was designed by P. Somogyvári, G. Veress and T. Domokos, members of the Mathematical Group of our Institute. The computer hardware was prepared by the Institute for Process Control of the Technical University. The equipment is produced by the Hungarian Optical Works, Budapest, Hungary, 1525. P.O.Box 52.

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Zusammenfassung — Der neueste, von einem Mikrocomputer gesteuerte Typ des Derivatographen wird beschrieben. Mit der Apparatur können TG-, DTG-, DTA-, TD- und EGA-Messungen simultan unter dynamischen, isothermen und quasi-isothermen sowie quasi-isobaren Aufheizbedingungen ausgeführt werden. Die Arbeitsweise wird an Hand der Zersetzung von Bauxit und Mangan(II)-sulfat demonstriert.

Резюме — Описан новейший тип дериватографа в сопряжении с микро ЭВМ. Аппаратура позволяет одновременно проводить измерения ТГ, ДТГ, ДТА, ТД и АВГ в динамическом, изотермическом, квазиизотермическом и квазиизобарическом условиях нагрева. Действие прибора проказано на примере разложения бокситов и пентагидрата сульфата марганца.