AN AUTOMATED SYSTEM FOR THERMOGRAVIMETRIC ANALYSIS OF POLYMER MATERIALS

A. E. Vegner, M. S. Zheludkevich, T. R. Reyant, and Yu. E. Fraiman

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An automated system is described for thermogravimetric analysis in which the data are processed and the effective kinetic parameters of the thermal decomposition are calculated.

In thermogravimetric analysis of a material to determine the decomposition kinetics, the most laborious stage is represented by the data acquisition and processing. Automation with a microcomputer substantially reduces the time consumed in processing the data, and the computer can derive the kinetic parameters of the decomposition by means of special programs, which can substantially increase the accuracy and reliability of the results.

We have made an automated system on the basis of a comparatively simple and cheap microcomputer with equipment representing compact facilities for inputting the data and representing the results.

The following are the main components of this system (Fig. 1):

1) a TGS-1 thermogravimetric system made by Perkin-Elmer providing for measurements in the range 20-1000°C with heating rates of 0.3 to 320 deg/min;

2) an Shch 68,000 electronic digital voltmeter, in which the unit outputting the data to the printer has been replaced by a special interface board (interface to the microcomputer);

3) a 15VSM-5 control computing device in conjunction with a peripheral memory PM; and

4) a Konsul 260.1 printer with control unit CU.

The electrical signal proportional to the measured quantity (current mass of the specimen) passes from the thermogravimetric system to the recorder R and is parallel to the input of the voltmeter, which operates with internal triggering at a frequency of 25 Hz. The latter works with the interface board A and fanout unit FO to operate the 15VSM-5 computing device, which is also connected via the fanout unit to three peripheral memories. The 15VSM-5 receives the voltmeter signal, transforms it to normal form, and sends it for storage to one of the memories, and from this the data are extracted after the experiment for processing; this cycle is performed at strictly defined intervals corresponding to the temperature step Δt and which are monitored by means of computer-controlled pauses of fixed length.

The primary data, the intermediate calculations, and the results from the final processing are printed out through the control unit.

Figure 2 shows the block diagram of the interface board between the voltmeter and the 15VSM-5, which provides all the necessary control signals and the conversion of the parallel digital code from the instrument into serial code for input to the 15VSM-5. At the start, the computer accesses the digital instrument, and the decision potential from the output of the selection circuit 1 provides for signals to pass to the circuits that handle the control signals 2 and produce a synchronizing pulse 3.

The data are input to the 15VSM-5 in subsequent cycles. The synchronizing pulse inhibits repeat data reception up to the following measurement. The digital data are normalized on input to the computer by a firmware method involving the introduction of a constant into the most-significant digit, which is then subtracted in the 15VSM-5.

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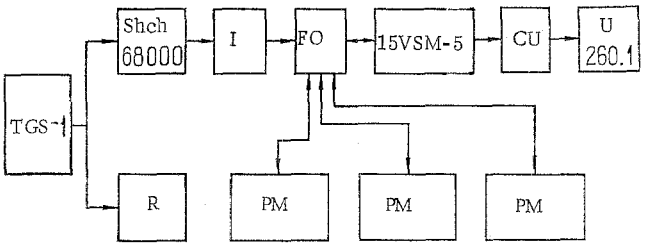

Fig. 1. Block diagram of the automatic system for thermogravimetric analysis.

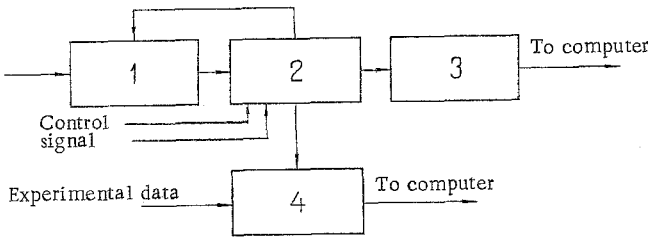

Fig. 2. Block diagram of the interface board: 1) circuit selecting number of interface board; 2) circuit producing control signals; 3) circuit producing synchronizing pulse; 4) data-input circuit.

Figure 3 shows the block diagram of the program for acquiring and processing the data and for calculating the effective kinetic parameters of the thermal decomposition. When the data have been received, the 15VSM-5 begins to process them. It smooths and differentiates the dependence of the specimen weight w on temperature t by a numerical method [1], with the width of the window varying in inverse proportion to the slope of the w(t) curve. For this purpose, the w(t) array is split up into zones, each of which is assigned a code providing information on the boundaries of the zone and the optimum window width. The arrays of values of t, smoothed w, and derivatives w' are printed out as a table and are stored in the memory, after which the machine analyzes the w'(t) array by means of turning-point criteria introduced into the program.

During the search for maxima and minima in w'(t), spurious turning points related to random unsmoothed deviations in w(t) are discarded and the numbers of the points corresponding to the true turning points are stored in the memory. The method of calculating the effective kinetic parameters for the process as a whole or the individual stages may be selected by the program in accordance with the character of the peaks on the w'(t) curve.

The calculation is performed by least squares for isolated peaks; the kinetic parameters are printed out and these are used in calculating theoretical curves for $w_T(t)$ and $w'_T(t)$, which are subtracted from the experimental ones and the calculation is continued.

Calculations on overlapping peaks (for multistage processes) are performed by successive elimination of the stages [2], where the criterion for selecting a working part is the minimum mean-square deviation S of the theoretical curve for w(t) from the experimental one. When the data have been analyzed, the remainders after subtracting all the calculated stages are printed out as the $\delta w(t)$ and $\delta w'(t)$ curves, while S(w) and S(w') are calculated and printed out, together with the combined graph for the observed and calculated w'(t) curves.

The program consists of 13 blocks of overall volume about 5 kbyte written in sequence on the 15VSM-5 magnetic tape, which is read automatically during the calculation; one of the peripheral memories is also used for temporary storage of certain blocks and subroutines. If necessary, the files of primary data, the smoothed values w, and the derivatives w' can also be written to magnetic tape for long-term storage.

Therefore, the thermogravimetric analysis and the data processing are completely automated. The specimen is placed in the oven, the heating is switched on with a certain rate, and the 15VSM-5 is started, after which no further intervention by the operator is required.

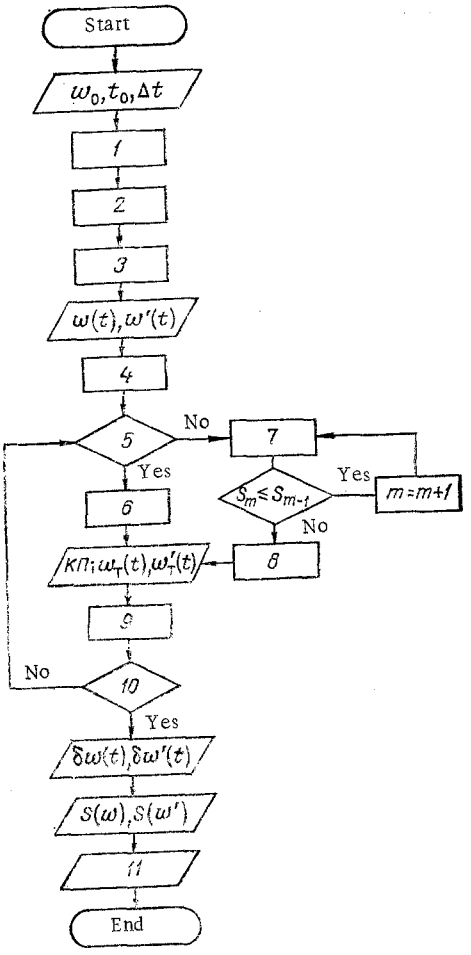

Fig. 3. Block diagram of the program for acquiring and processing thermogravimetric data: 1) reception, transformation, and writing to peripheral memory 001; 2) zone labeling; 3) smoothing and differentiation by zones, writing t, w, and w' into peripheral memory 002; 4) search for true turning points; 5) condition last peak isolated; 6) calculation of kinetic parameters and theoretical curves for isolated peak; 7) calculation of kinetic parameters and total mass loss for overlapping peak from kinetic parameters found from m − 1 points; 9) subtraction of calculated peak; 10) condition array analysis completed; 11) printing out combined graph for mass loss rate (experiment and calculation).

Figure 4a shows a computer graph obtained by calculation for three isolated stages in the thermal decomposition of calcium oxalate monohydrate with a heating rate of 160 deg/min for a mass of 0.864 mg in an inert atmosphere. The calculated curve agrees well with the experimental one (the mean-square deviation in mass in the temperature range 115-922°C is 0.4%, while in weight loss it is 4.2% of the maximum value), while the values for the kinetic parameters agree with published ones and values obtained by the authors previously, all of which indicates that the calculation method and program are reliable and give reliable results.

Figure 4b shows the analogous w'(t) graph obtained for the multistage pyrolysis of polyamide fiber in an inert atmosphere at 20 deg/min (specimen mass 1.471 mg). The main decomposition stage is one in which 20.2% of the mass is lost, and this is preceded by two isolated low-temperature stages, the first of which (5.6% by mass) is related to the release of water, while the second relates to the loss of 1.4% of volatile components.

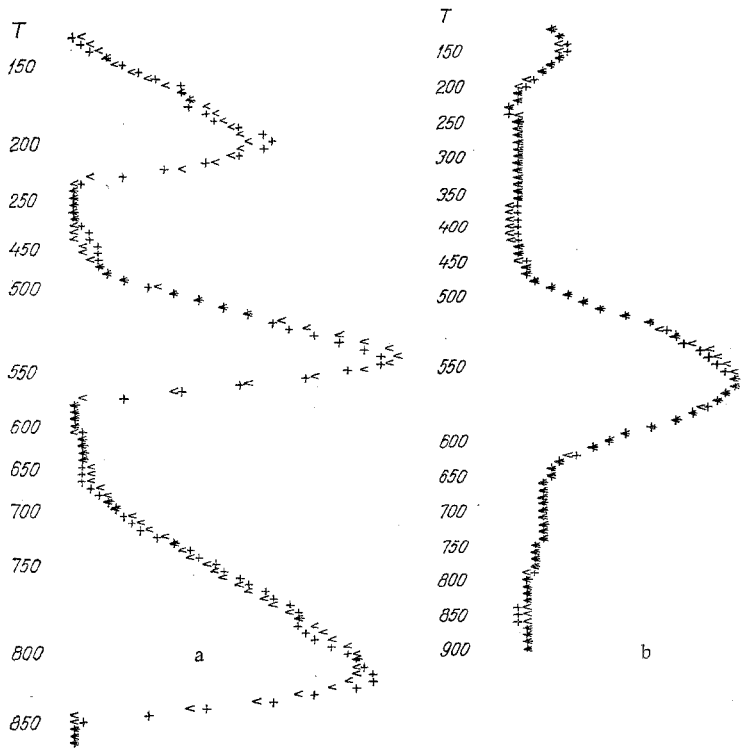

Fig. 4. Experimental (+) and calculated (<) curves for the mass loss rate for calcium oxalate monohydrate (a) and polyamide fiber (b); T in °C.

After the main stage and partly overlapping it there are two stages with mass loss of 8.4 and 4.6%. The standard deviation of the overall calculated curves from the experimental ones is 0.2% in mass or 1.3% in mass loss rate.

The entire procedure for calculating the multistage process, including the primary data processing, takes from 20 to 50 min in accordance with the number of stages.

LITERATURE CITED

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