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SOFTWARE FOR A MASS SPECTROMETER–THERMOBALANCE SYSTEM

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ABSTRACT

The questions of the computer control, data acquisition and data processing are treated for a TG–MS system built from a Perkin-Elmer thermobalance (TGS-2), a Balzers quadrupole mass spectrometer (QMG-511) and a small configuration of a DEC PDP-11 minicomputer. The aim of the computer software was to optimize the performance of the system for the requirements needed for the TG–MS analysis of solid fuels and other complex organic materials. The organization of the mass spectrometric measurement, the fast processing of the mass spectrometric peaks, the quick acquisition of time-averaged weight and temperature data and the problems of the concise data storage are treated. The outlined considerations may be applicable to other instruments. A method for the fast digital filtering of the mass spectrometric data is described in a separate Appendix.

INTRODUCTION

The study of the processes of thermal decomposition frequently requires the measurement of the nature and amount of the volatile products. When the results are needed as functions of the reaction time, mass spectrometry is more often used. The state of the art in this field is described in two recent reviews [1,2]. Mass spectrometric thermal analysis cannot be done effectively without a computer. The use of the computer is not limited to the collection, storage and processing of the data: the capacity of the measurement system itself can be improved by proper computer programs. This will be the subject of the present paper. The hardware, for which the described software was made, was built from well known and commonly used units: a small configuration of a DEC minicomputer, a Perkin-Elmer thermobalance and Balzers QMG-511 quadrupole mass spectrometer. According to the literature reviewed by the Thermal Analysis Abstracts, the QMG-511 seems to be the most frequently applied mass spectrometer in thermobalance–mass spectrometer systems. This may be due to the fact that a commercially available TG–MS system is also based on the QMG-511 [3,4]. Nevertheless,

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the considerations of the paper may be applicable also to other systems of mass spectrometric thermal analysis, especially in the "limited budget" category [5].

The software described is based on an experience of 12 years of TG–MS work [6–8].

EXPERIMENTAL

The detailed description of the TG–MS hardware and the coupling problems will be given in another publication. The following brief description is restricted mainly to those aspects which had to be considered for the computer programming.

The thermobalance was a Perkin-Elmer TGS-2 controlled by its own System 4 controller. It was operated under atmospheric conditions with carefully controlled and checked gas flow rates. The furnace was modified to ensure the proper flushing out of the volatile products. A portion of the volatile products is led to the ion source in a two step pressure reduction through a heated capillary and a molecular leak. To check the system continuously, the pressure was monitored before and after the molecular leak by a Baratron capacity manometer and a Balzers ionization gauge, respectively. The mass spectrometer used was a Balzers QMG-511, equipped with a cross beam electron impact ion source, an electron multiplier and an electrometer based on an 8-bit voltmeter. The scan speed of the mass spectrometer varied between 0.1 ms/u and 10 s/u, but the higher scan speeds (from 0.1 ms/u to 0.1 s/u) proved to be too noisy for the measurement of the minor decomposition products.

The parameters of the mass spectrometric measurement could be set and changed by computer. In the programming, special attention had to be given to the electrometer ranges. Three ranges were used with overflow limits of 10^{-5}, 10^{-7} and 10^{-9} A, respectively. The ranges slightly overlap each other: they allow measurement with a sufficient precision in intervals 0.25×10^{-11}–10^{-9}, 0.25×10^{-9}–10^{-7} and 0.25×10^{-7}–10^{-5} A, respectively. The change from one electrometer range to the other required some time-delay, especially if range 10^{-9} A was set after the measurement of a higher current.

The computer was a DEC PDP-11/34 with a 64 kbyte memory and a dual floppy disk. The TG data and the monitored control parameters (pressures and gas flow rate) were acquired by 12-bit analogue-to-digital (A/D) converters (DEC AR-11). The communication between the computer and the mass spectrometer was made by digital I/O channels provided by Balzers. A FORTRAN subroutine library was also obtained from Balzers, allowing the control of the mass spectrometer and the corresponding data acquisition through simple FORTRAN subroutine calls. The software we developed for the TG–MS measurements was written in the FORTRAN language of the PDP-11/34 computers. The computer was used under the RT-11 operating system.

The requirements of the study of solid fuels and other complex organic materials

The above-described TG–MS systems were used mainly for the study of coals and lignites [7,8]. Other applications included special polymers and polymeric ion-exchangers. For this type of application the following requirements arose.

(1) Almost all ions in the range where volatiles may arise have to be monitored since a priori data are not known on what products will be characteristic to the given problem.

(2) The major and the minor products have to be monitored simultaneously. In the case of coals, for example, the compounds produced in small quantities are sometimes more important than the greater amounts of water, carbon monoxide etc. Besides this, the various products may evolve at different temperatures, thus sometimes it is necessary to measure the highest values of the main components together with the smaller values of an important minor component. In this way the intensities of the measured ions may differ by more than 4 magnitudes.

(3) The carrier gas strongly dilutes the products to be measured. Thus the concentration of the minor products may be below 1 ppm. (High gas flow rate and low sample mass is needed for the elimination of the diffusion control and secondary reactions.)

(4) The time available for the mass spectrometric measurements is limited. Practically, the intensities of the monitored ions have to be measured at least at every 10 K of temperature increase. Usually one applies heating rates of 10–20 K min^{-1} which means a time limit of 30 s for the acquisition and storage of the monitored quantities.

The measured quantities and their recording

The quantities of primary interest are the temperature, the weight, and the peak intensities of the monitored ions. Besides these data, it is also of worth to record the monitored control quantities, since their recording allows the user to analyse the performance of the system and to observe and locate occasional malfunctions. These control quantities are the pressure in two points of the system, the gas flow rate, the zero voltage of the A/D converter and the distances of the m/e values of the mass spectrometric peaks from the nominal masses of the corresponding ions. If the system works well, the recorded control quantities should be reasonably constant.

The number of the monitored ions varies from task to task. In the case of, e.g., calcium oxalate, only three ions are measured. For the majority of applications, however, practically all masses are monitored up to a value of about $m/e = 180$. Higher masses are seldom studied since the molecules of higher molecular masses are usually not volatile under atmospheric conditions. A few meaningless ions, e.g., the ions from $m/e = 3$ to $m/e = 14$ may be omitted to speed up the measurement. The main isotopes of the carrier gas must be omitted since their enormous intensities would cause overflow and contamination problems. When an argon atmosphere is used, the argon isotope of mass 38 is always measured as an internal standard. (Its steadily constant concentration (0.6%) is comparable to the concentration of the main decomposition products.)

The continuous monitoring of the above-listed quantities produced rather voluminous data sets. It could be possible to reduce the size by storing only those values of the control data which differ significantly from their nominal values. The number of the mass spectrometric intensities could also be reduced by recording only those intensities which differ significantly from their background level. The definition of the "significant differences" before a TG–MS experiment, however, is a dubious process since the experimental parameters vary from task to task. It seems more advantageous to store all of the data in a sufficiently compact form and to select out the superfluous data only after the TG–MS experiment.

For the sake of compactness, the differences between the actual and the nominal m/e values of the mass spectrometric peaks were stored in bytes as 8-bit fixed point numbers. Quantities such as mass and temperature can be stored with sufficient precision in 16-bit fixed point words. The mass spectrometric intensities, however, are not suitable for fixed point storage hence they were stored as special 16-bit floating point numbers. There were several possibilities for this type of storage; we have chosen a form which can be converted very quickly to and from the normal 32-bit floating point form. The conversion was made by simple bit manipulation. The mantissa was stored with 10-bit precision.

Noise reduction and related questions

To achieve good signal/noise ratios, numerical operations have to be applied. The noise reduction of the non-mass spectrometric data were made by averaging during the mass spectrometric measurements: whenever the mass spectrometer required some settling time, the computer acquired data through the A/D converter and averaged them.

The mass spectrometric intensities were measured in small windows around the nominal mass of the ions. The size of the windows was an adjustable parameter, usually $m/e = \pm 0.2$ was applied. If considerably smaller windows were used, too much mass calibration work would have been necessary during the TG–MS measurement. A simple real-time mass calibration, based on the monitoring of the m/e values of a few selected ions, was part of our program. For smaller windows however, separate real

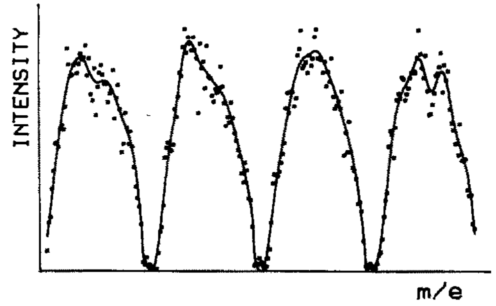

Fig. 1. Repeated scans of a small, noisy MS peak. Each square (■) represents an intensity value composed of the averaging of 16 intensity measurements. The solid line is the result of the numerical smoothing of the data. The "local maxima" on the smoothed peaks have no physical meaning, they are the low frequency components of the noise which cannot be filtered out without a loss in the resolution.

time calibration would be necessary for the low, medium and high masses, respectively.

Inside the windows the mass was increased by values of $m/e = 1/64$. At each m/e, several intensity values were acquired and averaged. The number of the averaged values is a user defined parameter. The intensity–mass functions obtained in this way were smoothed before the selection of the peak intensities. The numerical method worked out for this smoothing is described in the Appendix. The effect of the smoothing is illustrated in Fig. 1. The smoothing method has been carefully tested on simulated MS peaks in order to avoid the decrease of the resolution of the mass spectrometer. The resolution of the mass spectrometer is crucial for the measurement of small peaks in the neighbourhood of high peaks.

To speed up the computation, the averaging and smoothing was made by 16-bit integer data. Micro- and mini-computers process 16-bit integer operations far more quickly than the usual 32-bit floating point operations. Thus the acquired intensity data were converted from the special internal code of the mass spectrometer directly into 16-bit integer numbers and all numerical operations were carried out with these integer numbers. Only the peak intensities selected after the smoothing were converted into 32-bit floating point numbers for the display and into 16-bit floating point numbers for the storage.

The representation of the intensities as 16-bit integer numbers required scale factors: each intensity value of a given peak was multiplied by a scale factor to avoid overflow, underflow or loss of significant digits. To obtain proper values for these scale factors, the magnitudes of the peak intensities were predicted from the magnitudes of the peaks in the previous two measurement cycles. In this way, each peak had a separate scale factor in each measurement cycle.

The order of the mass spectrometric measurements

The monitored ions were not measured in a strict order of their mass. Instead of this they were divided into groups according to the magnitude of their peak intensities. These groups corresponded to the applied electrometer ranges, 10^{-9}, 10^{-7} and 10^{-5} A. The grouping was automatic and changed dynamically during the TG–MS experiment. It should be noted that it was easy to predict the magnitude of a given peak intensity from its previous values since the decompositions studied by TG–MS systems are usually continuous processes. Discontinuous processes, e.g., explosions, are seldom examined by thermobalance systems. There was no need for a very accurate prediction: a simple linear extrapolation from the data of the last two measurement cycles was sufficient. For safety's sake, the predicted intensity values were assumed to have high uncertainty. Thus if a predicted value achieves 51% of the given overflow limit of the electrometer, we assumed that the actual intensity value will be somewhat between 25.5% and 102% of the overflow limit and—to be sure of avoiding the overflow—we measured the corresponding ion in a less sensitive electrometer range. In this way the number of the time-consuming changes of the electrometer range was minimized: each range was set once only in a given measurement cycle. The longest settling time, about 1 s, was required by the change to the range of 10^{-9} A. During this time, the computer dealt with the output and display of the data.

Timing

In a given mass window of $m/e = \pm 0.2$, the scan required 18 ms if no averaging was made and about 200 ms if each intensity value was measured 16 times for averaging. (The actual number of averaging is a user defined parameter.) When the data acquisition in a given mass window was ready, the m/e value was moved to the beginning of the next mass window to be processed. The mass spectrometer required some settling time for this move. In our conditions, the settling time was about 50 ms. During the settling time the computer dealt with the digital filtering of the mass spectrometric data and with the collection and averaging of the non-mass spectrometric data through the A/D channels.

The digital filtering of the intensities of a given mass window required about 15 ms. In this way the acquisition and averaging of the non-mass spectrometric data was made in 35-ms intervals distributed evenly during the measurement of the mass spectrometric data. If only a few mass spectrometric peaks were measured, some additional time could be reserved for the acquisition and averaging of the non-mass spectrometric data before and after the mass spectrometric measurements. When the measurements in a given cycle were ready, the data were displayed in a concise tabular form

TABLE 1

Dependence of the run time and the deviation of the peak intensities on the averaging of the intensity values

Number of averaging	Run time[a] (s)	Deviation[b] (in arbitrary units)
1	15	1
4	23	0.7
8	34	0.5
16	53	0.4

[a] The time values belong to the measurement, filtering, display and storage of 200 mass spectrometric peaks and 7 other data.

[b] The deviations refer to small mass spectrometric peaks near to the detectability limit of the system.

on the videoterminal and output on the disk. Typical values of the overall elapsed time are given in Table 1. The last column of the table indicates the effect of the averaging of the intensity data on the standard deviation of the intensities of small noisy MS peaks. Note that the parameters of the digital filtering are not adjustable since slighter filtering cannot speed up the measurement and a stronger filtering would decrease the detectability of the small MS peaks in the neighbourhood of the bigger peaks.

OFF-LINE DATA PROCESSING

When the TG–MS measurement was ready, the data were processed with further programs. The first step of the processing was the scanning of the recorded peak intensity–time functions to select those which showed significantly greater changes than their noise level. Various corrections then followed, including the subtraction of the background values of the intensities and the multiplications by sensitivity factors. The subtraction of sloping base-lines and the formation of linear combinations of the corrected peak intensities are also possible. After the corrections, the user defines various subsets of the measured data and displays them on the videoterminal or plots them by a multicolour plotter coupled to the minicomputer. The details of the off-line data processing will be given in a separate paper.

APPENDIX

Fast digital filtering of mass spectrometric data

The method worked out for the fast numerical smoothing of the intensity–m/e functions can be used for the smoothing of any type of data in the range [0, 4095] by 16-bit integer arithmetics. Among others, it is suitable for the quick processing of data produced by 12-bit analogue-to-digital converters. The method is a modification of the well known and well established polynomial smoothing [9] when third order polynomials are pushed along the measured curve, and each smoothed value is the centre point of a polynomial approximating the surrounding raw data. This type of smoothing is frequently used in mass spectrometry [10]. Recently, Bush [11] pointed out that very favourable run times can be achieved by using simplified formulae with small integer coefficients, so that 16-bit integer arithmetics could be used without overflow or round-off problems. We did not follow Bush in constructing ad hoc formulae with arbitrarily chosen coefficients. Instead of this we solved the following optimization problem by computer. Find the coefficients minimizing the "noise amplification" [12] of the smoothing formula so that

(i) the formula would be exact for any third order polynomial
(ii) the coefficients would be small integer numbers suitable for integer arithmetics.

The length of the formula was fixed to 13 points since test calculations showed that our data can be approximated reasonably by third order polynomials in intervals of 13 points.

The result of the optimization was the following formula

$$\begin{aligned} y_i = \{ & x_{i-3} + x_{i-2} + x_{i-1} + x_i + x_{i+1} + x_{i+2} + x_{i+3} \\ & + [2(x_{i-4} + x_i + x_{i+4}) - x_{i-3} + x_{i-1} + x_{i+1} - x_{i+3} \\ & - 3(x_{i-6} + x_{i+6})]/6\}/7 \end{aligned} \qquad (1)$$

where x_i and y_i stand for the measured data and their smoothed counterparts, respectively. It can be shown that no integer overflow can occur in eqn. (1) if $0 \le x_i \le 4095$ for all i. The round-off error caused by the integer divisions is about 1 which means a relative error of about 0.0002. (Obviously this error can be halved by proper rounding: the half of the divisor should be added to the dividend before integer division.) If the x_i data have independent random errors with standard deviation σ, the standard deviation of the smoothed y_i is 0.419 σ. Note that a similar value, 0.418 σ, can be obtained also by the corresponding third order least-squares formula [9], thus the condition of the small coefficients does not increase the noise amplification to any significance.

Since central formulae cannot be used at the ends of the domain of the data, we carried out the optimization also for asymmetric formulae. The following two formulae were obtained

$$\begin{aligned} y_i = \{ & x_{i-1} + x_i + x_{i+1} + x_{i+2} + (x_{i-2} + x_{i+3} - x_{i+6})/2 \\ & + [2(x_{i+4} - x_{i+7} - x_{i+8} + x_{i+10}) + x_{i-1} + x_{i+1} + x_{i+5}]/6\}/5 \end{aligned} \qquad (2)$$

and

$$y_i = [2(x_{i-1} + x_i) + x_{i+1} + x_{i+2} + (x_{i+3} + x_{i+4} - x_{i+6} - x_{i+8} - x_{i+9} + x_{i+11})/5]/6 \tag{3}$$

Equations (2) and (3) are exact for any third order polynomial and do not cause integer overflow if $0 \leq x_i \leq 4095$ for all i. Their round-off error is also about 1. If the deviation of the x_i is σ, the deviation of y_i of eqns. (2) and (3) will be 0.486 σ and 0.533 σ, respectively. In their present form, eqns. (2) and (3) can be applied to the left end of the domain. The corresponding formulae for the right end can be obtained by reversing the order of the subscripts. Equation (3) serves for the smoothing of the second and the penultimate point of the domain. The first and last points are not smoothed.

On our equipment, a mass spectrometric window of $m/e = \pm 0.2$ contains 25 data and their smoothing takes place during 5 ms. There is more time available during the settling time of the mass spectrometer, so the smoothing is repeated three times. The effect of the repeated polynomial smoothing is treated in Hamming's book [12]. The frequency response of a polynomial filter contains considerable ripples in the stop band which means that a certain portion of the noise is not smoothed out in the filtering. If the filtering is repeated three times, the ripples disappear but the frequency response will have a flat transition between the pass band and the stop band. Nevertheless, there is no need for a sharp transition zone for the smoothing of Gaussian-type peaks since there are no sharp limits between the frequencies of the signal and the noise. We studied the effects of the smoothing process on actual measurements as well as on simulated Gaussian mass spectrometric peaks. In this latter case, the standard deviation in the central part of the mass window was found to be 0.355 times the standard deviation of the input data. The relative systematic error was only 0.02% on the peak tops.

If a small peak is measured on the tailing part of a large neighbour peak, the error of the (linear) digital filtering will be the sum of the errors on the peak top of the small peak and the tailing of the large neighbour. Thus it is important to determine the systematic error on the tailing parts of the peaks, at distances of $m/e = \pm 1$ from the peak tops. In our test calculations, this error was about 10% of the corresponding tailing values and a 10% deformation of the tailing parts of the peaks was considered acceptable. However, intervals longer than 13 points cannot be used in the smoothing formulae without jeopardizing the detection of the small peaks since the systematic errors of the third order formulae are proportional to the fourth power of their interval length.

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