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SOFTWARE FOR A COMBINED STA-QMS INSTRUMENT

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ABSTRACT

Based on a modern 16/32 bit computer system, versatile software for the programming, control and data acquisition of a combined TG-DTA/DSC-mass spectrometer instrument was developed. The evaluation of results is demonstrated in the MID-mode (multi ion detection for max. 16 different mass numbers) and scan mode (mass range variable according to hardware, 40 scans per test).

INTRODUCTION

The coupling of a mass spectrometer to a simultaneous TG-DTA/DSC instrument makes an extremely efficient analytical system. The simultaneous information of the kind and quantity of evolved gases as well as mass and enthalpy changes allow clarification in complex reactions. Various gas inlet systems for the mass spectrometer allow simultaneous gas analysis in the temperature range 25 to 2400°C (/1, 2/). Specially designed interfaces are necessary to guarantee unchanged gas composition and to prevent condensation phenomena in the inlet system.

However, the different kind of documentation of the TG-DTA/DSC results and of the mass spectrometer results frequently is a restriction for an optimum evaluation. In most cases two separate recording systems are used and the time/temperature correlation between the TA curves and MS results is not ensured. Based on only one modern computer system, a common software programme was developed for online programming, control and data acquisition of a simultaneous TG-DTA/DSC-quadrupole mass spectrometer instrument.

The very versatile software programme for the evaluation of results will be described. It was developed at Messrs. Netzsch-Gerätebau, FRG and is commercially available for use with Hewlett-Packard computers (series 3000).

INSTRUMENTATION

The simultaneous TG-DTA/DSC instruments, Netzsch model 409 STA and 429 STA, are coupled by capillary or double orifice systems to a quadrupole mass spectrometer, Balzers model QMG 420. The capillary coupling can be operated in the temperature range 25 to 2400°C, using an alumina orifice system the orifice coupling can operate up to 1500°C. The TG instruments offer a sensitivity

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for the mass change signal of 1 digit/1.25 µg and the simultaneous heat flux DSC has a sensitivity of 1.5 to 15 µV/mW.
The mass range of the QMG 420 is determined by the quadrupole massfilters and electronics; usually a mass range of up to 200 is used together with the capillary coupling and up to 512 with the orifice coupling systems.
The thermal analysis data is transferred from the data acquisition system 414/1 to the computer via an IEEE 488 parallel interface, the mass spectrometer data is picked up via a RS 232 C serial interface; in both cases buffers are available for intermediate storage of measured data.
The quadrupole mass spectrometer QMG 420 is a modular system with an universal quadrupole control unit (QMG 420). Sixteen channels allow individual programming of all control functions. The digital signal processing and filtering give optimum signal to noise ratio and allow also very fast scan speeds. All entries can be made via the keyboard or the computer interface. The quadrupole analyzers can be equipped with various ion sources and ion detectors.
A 16/32 bit computer, Hewlett-Packard model 310 C, is used for the online programming, control and data acquisition of the TG-DTA/DSC and mass spectrometer combination. The computer is equipped with a two megabyte RAM, a 20 megabyte hard disc (Winchester drive) and a 12 inch colour monitor. Also a two megabyte 3.5 inch floppy disc is integrated in the system. Peripheric units such as printers and plotters can be used to give text and graphical hardcopies. The software uses HP BASIC 5.1 programme language. Work can safely and easily be done by it, because for the main operations, the functions keys on the keyboard are utilized.

SOFTWARE DESCRIPTION

The software for programming of the combined equipment is clearly structured. The data input programme takes up the parameters for the test, i.e. the laboratory, the sample and reference description, the measuring ranges for TA signals and the temperature programme as well as the operating conditions for the mass spectrometer (table 1). Up to 40 scans can be programmed in one experiment. The scan width can be up to 256 amu (atomic mass units) each. To cover different mass ranges and to optimize the sensitivity according to expected ion intensity changes, 4 channels can be programmed individually for different scans. The start of a mass scan and the temperature or time interval between subsequent scans are also controlled by the computer.

CHANNEL	0	1	2	3	4	5	6	7
STATE	ENABLE	ENABLE	ENABLE	ENABLE	ENABLE	ENABLE	ENABLE	ENABLE
CH_MODE	SAMP-N	SCAN-N	SAMP-N	SAMP-N	SAMP-N	SAMP-N	SAMP-N	SAMP-N
FIRST	10	10	16	18	28	32	44	64
WIDTH	1	90	1	1	1	1	1	1
SPEED	1 s	50 ms	0.2 s	1 s	1 s	1 s	1 s	1 s
RESOLUTION	25	25	25	25	25	25	25	25
STEPS/AMU	n/1	n/1	n/1	n/1	n/1	n/1	n/1	n/1
RANGE	E-9	E-9	E-9	E-9	E-7	E-8	E-10	E-10
DETECTOR	SEM	SEM	SEM	SEM	SEM	SEM	SEM	SEM
FILTER	AUTO	AUTO	AUTO	AUTO	AUTO	AUTO	AUTO	AUTO
SEM	1700	1700	1700	1700	1700	1700	1700	1700
OFFSET	0	0	0	0	0	0	0	0
PAUSE	0	0	0	0	0	0	0	0
CALMAN	1	1	1	1	1	1	3	1

Table 1 Programming of the quadrupole mass spectrometer QMG 420

All relevant parameters are shown on a printer hardcopy. For repeated experiments all parameters can be taken from the previous test.
The incoming measuring signals are shown in the colour screen in an adjustment graphic before start of the temperature programme to check for the correct selection of preamplifier ranges and the background spectra of the mass spectrometer. After the start of the temperature programme in the data acquisition programme, the combined instrument is completely controlled by the computer. The TA curves and up to 6 channels of the mass spectrometer (MID mode) are shown on the screen online in a time scaled graphic. In the scan mode each scan is on the screen after completion until the next scan cycle.
The experiment is finished after reaching the programmed final temperature or the emergency reset temperature. The experimental data are already stored on the hard disc (Winchester drive). For the TA signals, a max. of 10 000 single measuring values per channel (e.g. TG, DTA, DSC) are recorded. Also for the MID curves, up to 10 000 values per channel (16 channels) are recorded. In the scan mode, a max. of 4096 points for each scan are picked up. A peak for a single mass number can be recorded by 64, 32, or 16 intensity values; therefore one scan can over a mass range of 64, 128, or 256 mass numbers (also depending on quadrupole analyzer hardware).

EVALUATION AND RESULTS

The numerous possibilities for the data evaluation (off-line) can be indicated by only a few examples.
For the thermal analyst, the MID mode is a more convenient way than scan mode

to interpret mass spectrometer results, as peaks in the MID curves normally indicate gas evolution when also TG changes and DTG peaks are found. But the MID mode requires some knowledge of the expected evolved gases as the mass spectrometer has to be programmed for the corresponding mass numbers. This selection of mass numbers is in many applications with organic materials not complete and information on unknown gaseous products or molecular fractions may be lost in such experiments. The evaluation of MID curves includes determination of characteristic temperatures (onset, extrapolated onset, peak, end temperature and inflection point) and graphic display in multigraphs as well as together with the TA curves and all evaluated results (fig. 1).

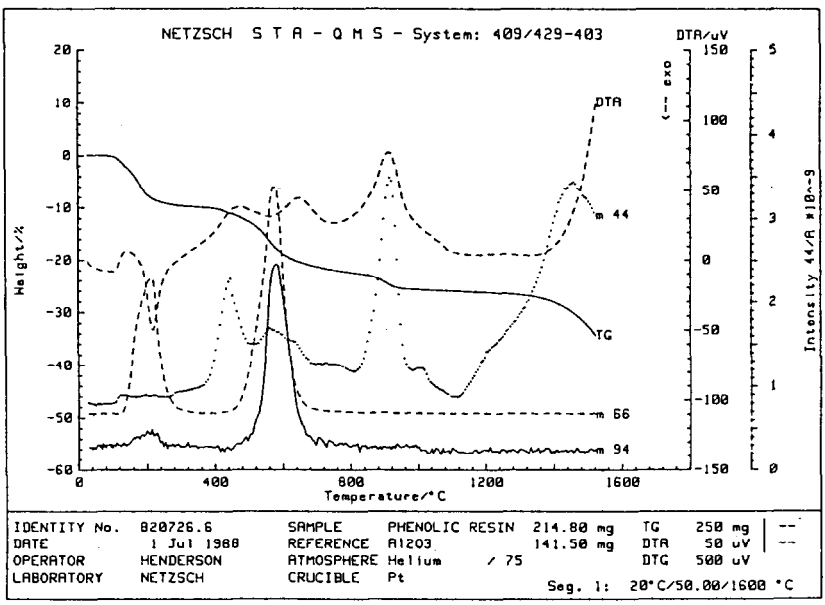

Fig. 1 Curing, degradation and carbon-silica-reaction in a talc and glass filled phenolic resin

The complex reactions in a phenol-formaldehyde resin with 60.5 % fillers (talc, glass fibres) are more easily explained by the information on evolved volatiles. The MID curves in fig. 1 show the evolution of phenol (m/z = 94, fraction at m/z = 66) during curing (200°C) and degradation (600°C) and carbon dioxide (m/z = 44) with main peaks at 400°C, 850°C and above 1300°C (carbon-silica reaction). Further MID-curves (16 channels) are not shown in fig. 1 for clarity. For complete interpretation of the simultaneous TG-mass spectrometer results see Ref 3.

The evaluation of scans offers further possibilities. The scans can be displayed separately or in multigraphs for comparison, and also together with the TA curves. Scan subtraction is used to eliminate the background in the evaluation. The sequence numbers of scans are indicated on the relevant TA curve (e.g. TG curve) for easier concentration on scans during a thermal effect. A comparable evaluation to the MID mode is possible with scans in a way that up to 6 peaks can be selected from a scan and their change during the temperature programme is shown (time or temperature scaled) (fig. 2). Even for the large number of scans (max. 40), a fast and complete evaluation becomes possible by this scan-M-graph.

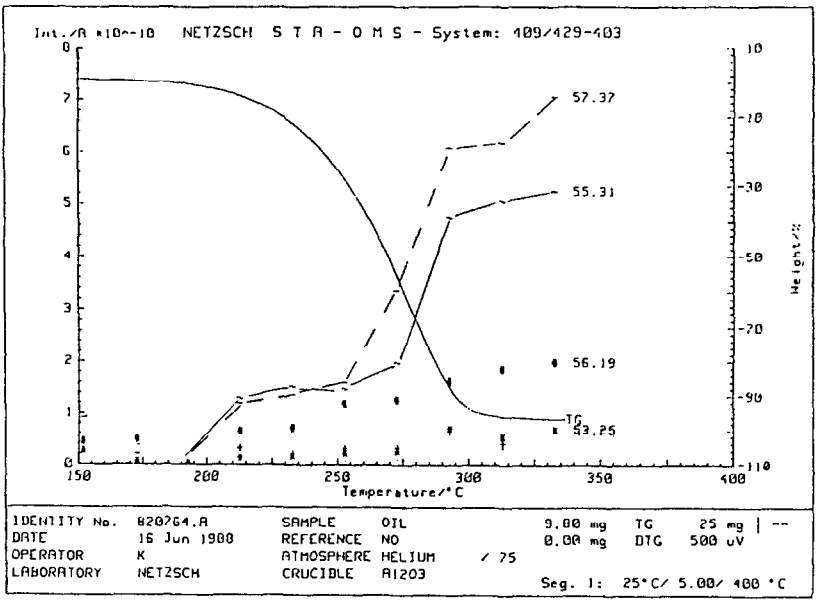

Fig. 2 SCAN-M-Graph for an oil sample

The evaporation of the oil is shown by some typical mass numbers, selected from subsequent scans.

Besides the comparison of MID curves or scans from one experiment, comparisons between curves from four different experiments are possible in one graph. The scales are freely selectable for TA and MS signals and different line types are used to distinguish between curves in black and white copies also.

CONCLUSIONS

The application of a coupled TG-DTA/DSC-mass spectrometer instrument becomes very easy under computer control using the newly developed software. Programming and data acquisition is done via the same computer. The evaluation

of results is done off line and the corresponding software offers all possibilities for the treatment of the TA and the mass spectrometer results.

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