Total analysis with DSC, TMA and TGA-EGA

The investigation of printed cicuit boards is used as an example to show how the results from different thermoanalytical techniques can be evaluated to make a comprehensive assessment of the product.

Introduction

Printed circuit boards

Printed circuit board (PCB) is the term used to describe nonconducting sheets of material that serve as supports for printed circuits of electronic components. The PCB is a laminate material made by pressing together several layers of a support material with a curable plastic as binder (the matrix resin). The outermost layer consists of a copper foil that forms the circuits after the redundant areas have been etched away.

Resin-bonded paper known as “FR2” is made using paper as the support material. For industrial electronics high performance PCBs known as “FR4” are used. These are made from fiberglass and a special epoxy resin as the matrix resin.

Requirements for a PCB

- A certain degree of structural rigidity and above all dimensional accuracy
- Low thermal expansion (soldering, operating temperatures): PCBs are anisotropic; they exhibit quite different coefficients of expansion of length (x), width (y) and thickness (z).
- Sufficiently high softening temperatures since the mechanical and dielectric properties deteriorate when the matrix resin softens (glass transition).
- Adequate thermal durability of the matrix resin to resist the soldering bath temperature and possible heat accumulation in later operation. Any initial degradation of the matrix resin is accompanied by the formation of gases which can force open the layers (delamination) and thereby destroy the laminate.
- Finally, the PCB must be flame resistant (FR). The high performance “FR4” standard material is flame resistant due to its brominated monomer building blocks (tetrabrom-bisphenol A). Because of this, corrosive decomposition products are formed on heating. Up until now, it has not been possible to achieve adequate flame resistance with ecologically more friendly additives.

The applications of interest in thermal analysis

Thermal analysis measures the physical properties of a sample that is subjected to a temperature program in a defined atmosphere.

Thermoanalytical technique	**DSC**	**TMA**	**TGA**
Physical property measured	Energy change	Dimen-sion	Mass
Effect, Information			
Specific heat	0		
Vaporization, drying	0		0
Glass transition, softening	0	0	
Thermal degradation, pyrolysis, depolymerization, “temperature resistance”	o	o	0
Delamination		0	
Reaction kinetics and etimates of reaction time or the stability at a particular temperature	0	0	
Analysis of gaseous decomposition products, EGA			0
Analysis of the composition	o		0
Linear expansion coefficient		0	
Swelling in solvents		0	

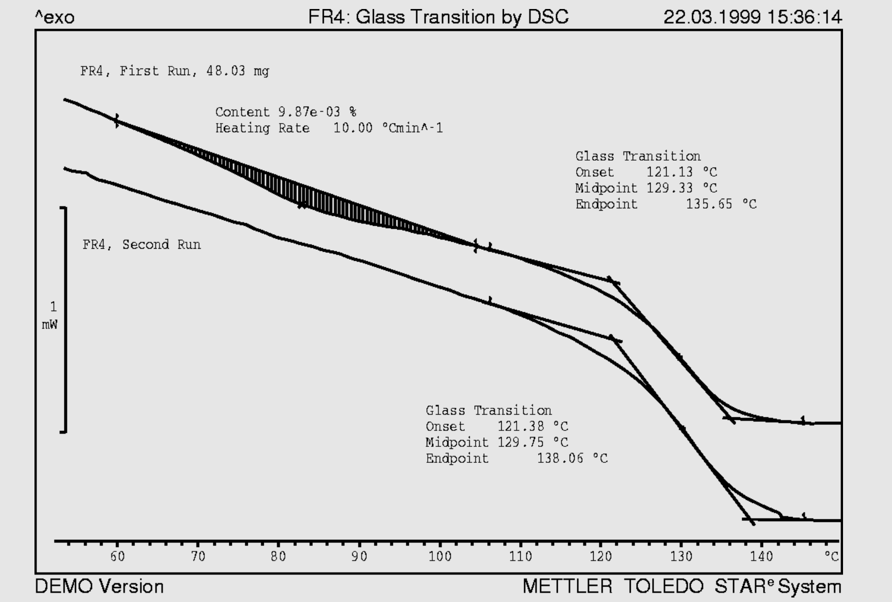


Fig. 1. DSC at 10 K/min: The first measurement exhibits an endothermic effect at about 90 °C. On the assumption that this is due to the vaporization of moisture, this yields a moisture content of 0.01% (heat of vaporization of water is taken to be 2400 J/g). This assumption is confirmed in the second measurement where no such peak is observed. The midpoint of the glass transition increases from 129.3 °C to 130.8 °C.

Experimental details

The following instruments were used for these investigations: METTLER TOLEDO **STAR**^{e} System; DSC821^e with air cooling and automatic sample changer; TMA/SDTA840; TGA/SDTA851^e LF 1100 °C, in some cases in combination with a Balzers ThermoStar quadrupole mass spectrometer or a Matson Genesis ll FTIR spectrometer with a gas cell; **STAR**^{e} SW Version 6.00 (Windows NT® operating system).

DSC measurements

DSC measures the heat flow to and from the sample and thereby detects any effect that is accompanied by a change in enthalpy.

As the table indicates, as far as PCBs are concerned, DSC is used mainly to determine the glass transition temperature (and if need be drying and postcuring after heat aging). If the glass transition temperature increases markedly in the second measurement, then curing was incomplete. The first DSC measurement curve is often affected by desorption of moisture or by traces of solvent and by enthalpy relaxation effects that occur during the course of long storage time (Fig. 1).

In addition, the specific heat c_p can also be determined from the DSC curve. In the case of FR4, it increases from 0.89 J/gK at 100 °C to 1.05 J/gK at 140 °C. Pure (glass fiber free) epoxy resin exhibits a typical c_p increase of about 0.35 J/gK.

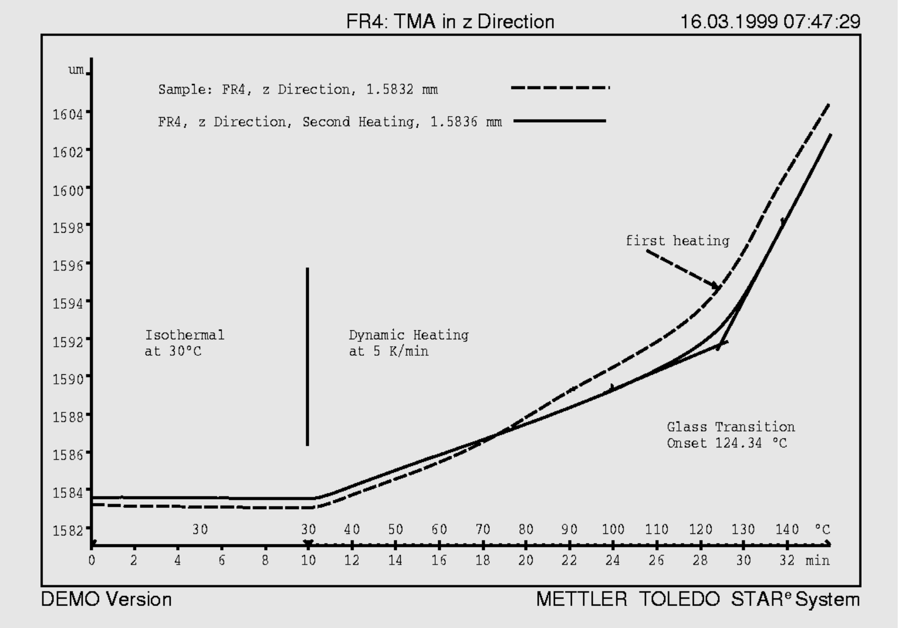


Fig. 2. TMA at 5 K/min: Once again the first measurement shows a different behavior around 80 °C. The increase in thickness due to themal expansion increases markedly at the glass transition point. After cooling to 30 °C , the sample is 0.4 μm thicker in the z-direction. The sample is covered with a quartz glass disk in order to distribute the load of 0.05 N uniformly.

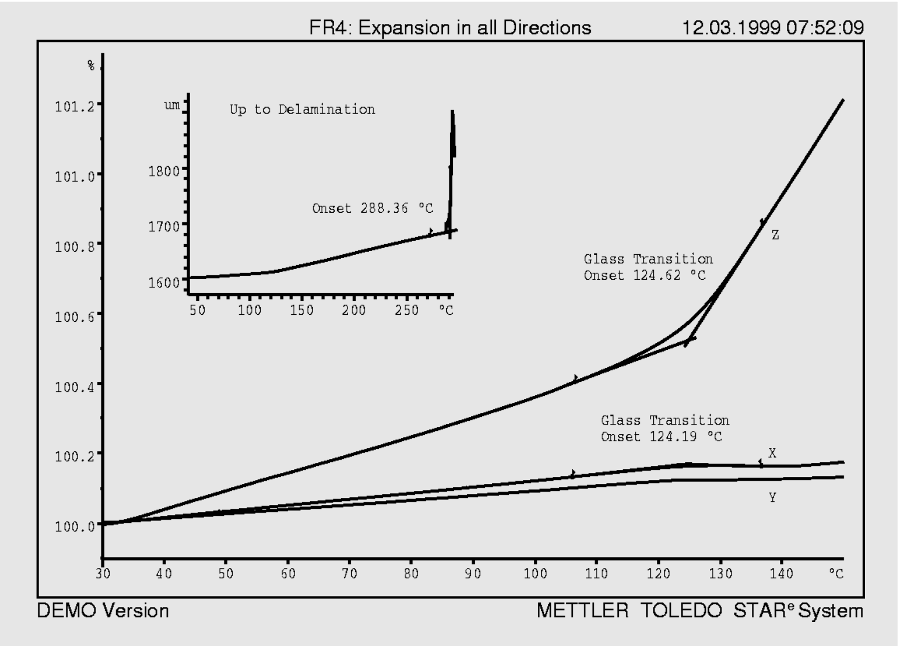


Fig. 3. The large diagram shows the normalized lengths in all three directions. The sample was prepared with plane-parallel faces using a diamond saw. The expansion of the matrix resin is hindered parallel to the glass fibers and is diverted into the z-direction. Normally the glass transition temperature is evaluated using the measurement curve in the z-direction. The evaluation is also possible in the other two directions but is less accurate due to the difficulty of drawing tangents.

The diagram shown in the insert up to 300 °C shows the bursting of the laminate (delaminiation) at 288 °C.

Thermomechanical measurements (TMA)

TMA measures the dimensional changes of a sample under almost zero loading (dilatometry) or the deformation under a definite load (true TMA). The resolution of a modern TMA instrument is 0.01 µm. This allows submicroscopic changes to be detected. The ordinate shown in Figure 2 is for example magnified about 3000 times! Figure 2 shows the first and second measurements in the z-direction. Initially the sample is held isothermally at 30 °C for 10 minutes (temperature equilibration). The first measurement curve often exhibits artifacts. These can include "memory effects" resulting from thermomechanical pretreatment such as residual effects originating from the pressure used in the manufacturing process, i.e. length changes resulting from the release of tension. Other possible causes have to do with volume relaxation or with the flattening of uneven parts of the surface on softening. In any case, the first curve is different from all successive curves. Normally the second curve is used for quantitative evaluations. The first derivatives of the curves shown in Figure 3, i.e. of the relative lengths with respect to temperature, yield the coefficients of linear expansion in all three directions: (see Fig. 4)

$$\alpha = \frac{dL}{dT}\,\frac{1}{L_0}$$

Expansion coefficients are given in units of ppm (parts per million) per degree Celsius (i.e. 10^{-6} °C^{-1}).

The volumetric expansion coefficient corresponds to the sum of the three coefficients measured at right angles to one another.

The glass transition in comparison

The STAR^{e} software allows the measured physical properties to be presented together (Fig. 5). The fact that the DSC measurements gave a glass transition temperature slightly higher than the TMA measurement has nothing to do with an incorrect temperature adjustment, but is systematic and due to the different heating rates used. The rather imprecise descriptions of the evaluation procedures given in the standards [1] also contribute to these differences.

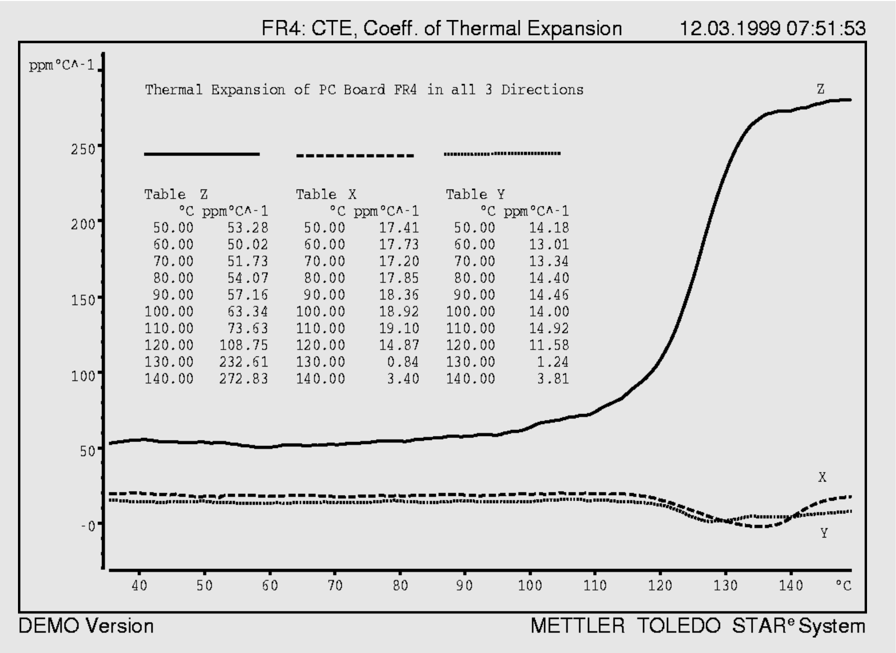


Table Z °C	Table Z ppm°C^-1	Table X °C	Table X ppm°C^-1	Table Y °C	Table Y ppm°C^-1
50.00	53.28	50.00	17.41	50.00	14.18
60.00	50.02	60.00	17.73	60.00	13.01
70.00	51.73	70.00	17.20	70.00	13.34
80.00	54.07	80.00	17.85	80.00	14.40
90.00	57.16	90.00	18.36	90.00	14.46
100.00	63.34	100.00	18.92	100.00	14.00
110.00	73.63	110.00	19.10	110.00	14.92
120.00	108.75	120.00	14.87	120.00	11.58
130.00	232.61	130.00	0.84	130.00	1.24
140.00	272.83	140.00	3.40	140.00	3.81

Fig. 4. The coefficient of linear expansion in all three directions displayed as curves and in tabular form. Up until about 120 °C, the expansion corresponds to that of copper, which is used as the conducting material (17 ppm/K). Anisotropic materials can also give negative values (in the x-direction at 135 °C).

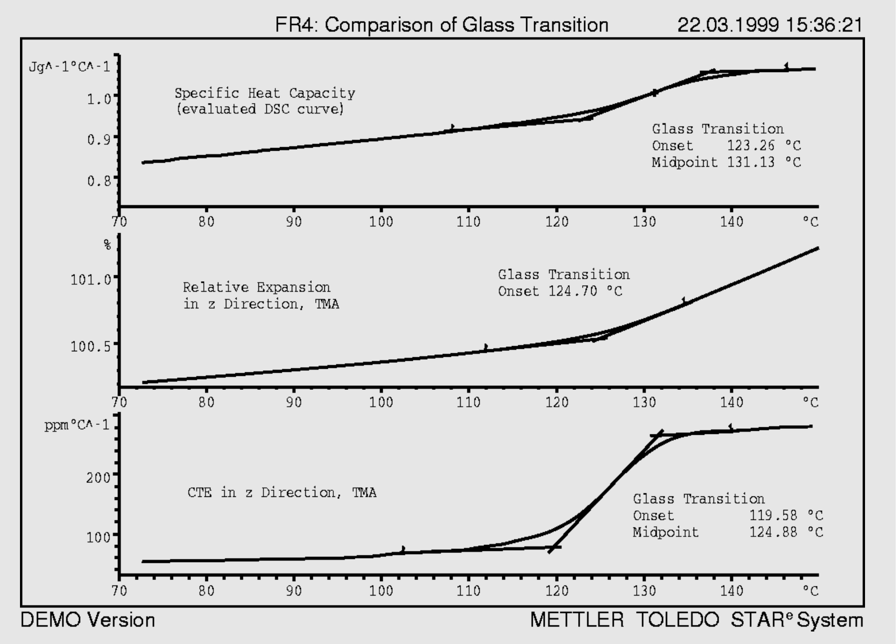


Fig. 5. The glass transition from DSC and TMA data. The three evaluation procedures yield somewhat different results. The TMA values measured at 10 K/min were also higher.

Thermogravimetric measurements

The thermobalance measures changes in the mass of the sample. Thermogravimetric analysis (TGA) allows the entire decomposition process of an organic substance to be measured. Volatile decomposition products are formed and soot or ash may be left behind as residues - depending on the sample and the atmosphere chosen for the measurement. Practical measurements where the onset of decomposition is of special interest are usually performed in air (Fig. 6). The first derivative of the TGA curve with respect to time or temperature is known as the DTG curve. The DTG curve is proportional to the rate of decomposition. The simultaneously measured SDTA curve, which shows exothermic and endothermic heat changes, is also very useful. The reactions that occur at about 300 °C are responsible for flame retardation and will be investigated later in more detail with EGA. The decomposition products formed burn in air between 450 °C and 550 °C leaving behind the fiberglass.

In Figure 7 the first 20% weight loss, i.e. the beginning of decomposition is shown. The three different heating rates yield three different onset temperatures. There is therefore no actual "decomposition temperature". Chemical reactions are characterized by their reaction kinetic data. Previously only "nth Order Kinetics" evaluation software was available, which could only describe ideal reactions. "Model Free Kinetics" [2] allows much more accurate predictions to be made, e.g. concerning the stability at a particular temperature. Unfortunately, it is of course still not possible to predict the long-term behavior at room temperature from a few short measurements at 300 °C. However extrapolations over 100 °C are usually quite reliable (Fig. 8).

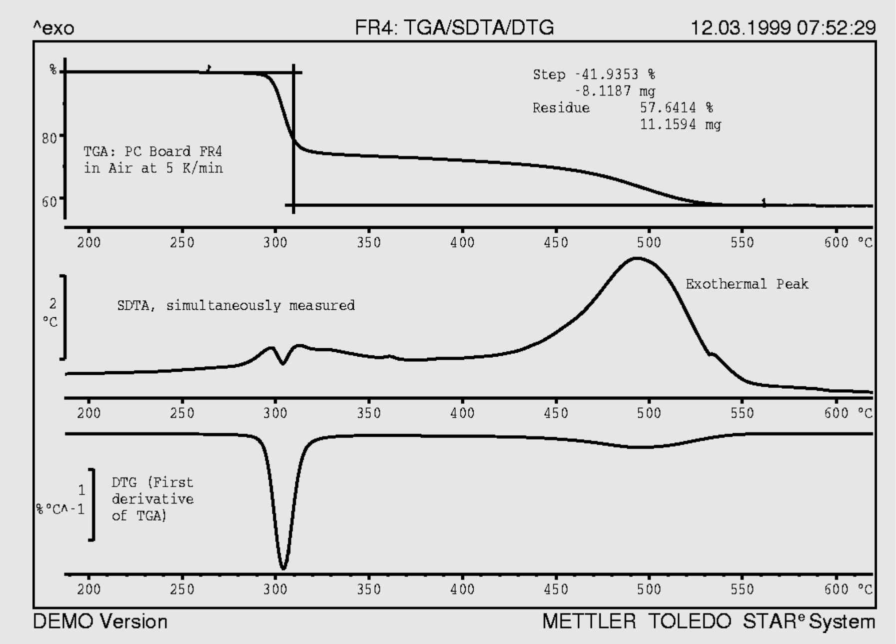


Fig. 6. The thermogravimetric behavior of the PCB. Uppermost curve: TGA, the decomposition of the matrix resin in air at 5 K/min occurs in 2 steps. The total weight loss of 41.9% corresponds to the resin content. The glass fibers remain behind (57.6%). The TGA curve does not tell us exactly what happens in this 2-step decomposition. The DTG curve shows that the decomposition is most rapid at about 300 °C . The largest exotherm occurs at 500 °C (SDTA curve). At 300 °C a sharp endotherm overlaps the exothermic reaction.

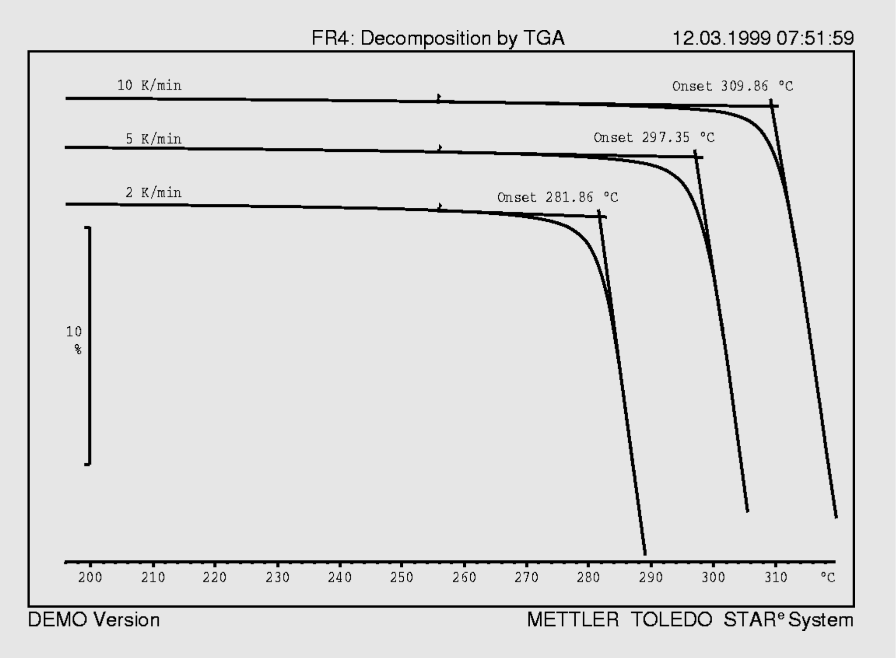


Fig. 7. There is no "starting temperature" for chemical reactions . The higher the heating rate, the higher the "onset of decomposition " appears to be.

Analysis of decomposition products with an MS combination

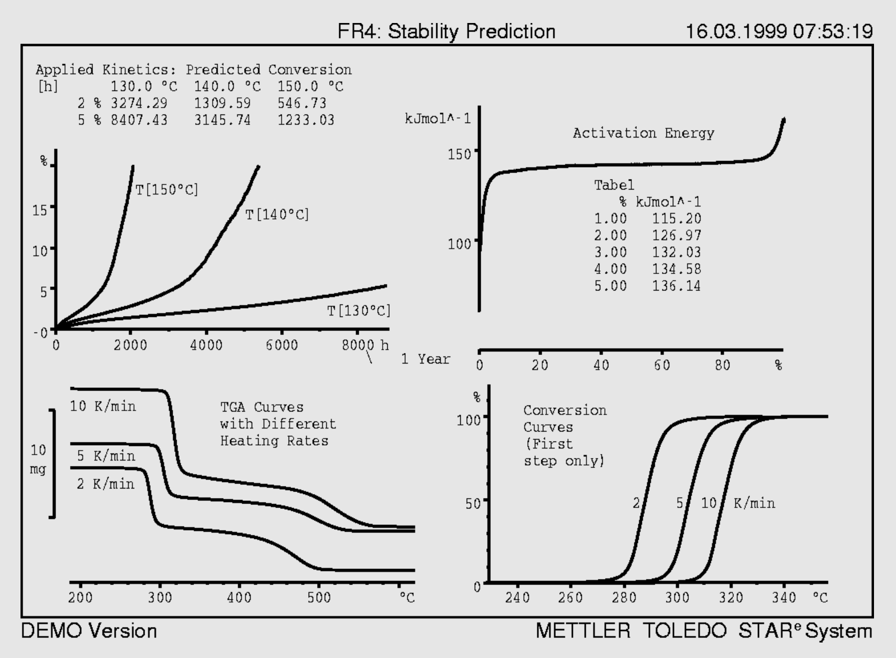
A mass spectrometer (MS) allows the qualitative and quantitative analysis of volatile compounds to be performed by analyzing fragments formed by ionization. In contrast to infrared spectroscopy (IR), chemical elements with sufficiently high vapor pressure can also be detected including the monoatomic and diatomic gases. Besides this, isotopes can also be separated. The two instruments are joined together by a heated quartz glass capillary, whose entrance is close to the sample undergoing decomposition. Excess purge gas is vented through a Y-piece.

During the TGA measurement, spectra are recorded at short intervals in a mass range that can be selected. After the measurement, the spectra are examined in a three dimensional presentation in order to locate points of interest. The PCB gives rise to fragment ions with mass numbers of 79, 81, 94 and 96. These can easily be assigned to the two isotopes of bromine 79 (abundance in bromine about 50.5%) and 81 (about 49.5%) as well as methyl bromide (Fig. 9).

If the mass number of interest is already known from preliminary experiments or from the literature, it can be continuously monitored and imported into the TGA curve by the **STAR^{e}** software.

Analysis of decomposition products with an FTIR combination

The IR gas cell is connected to the TGA by a heated transfer line. In contrast to MS, the entire flow of purge gas together with the decomposition products passes into the IR cell. The infrared spectrometer allows the qualitative and quantitative analysis of functional groups, although the positions of the absorption bands in the gaseous state do not coincide with those in the liquid or solid state.



```
Applied Kinetics: Predicted Conversion
[h]      130.0 °C  140.0 °C  150.0 °C
    2 % 3274.29   1309.59   546.73
    5 % 8407.43   3145.74   1233.03
```

```
Tabel
    % kJmol^-1
 1.00   115.20
 2.00   126.97
 3.00   132.03
 4.00   134.58
 5.00   136.14
```

Fig. 8. Below left: the three TGA curves that are to be evaluated in the range 250 °C to 350 °C (first step). Below right: the calculated conversion curves. Above right: the activation energy as a function of conversion predicted with Model Free Kinetics. Above left: stability predictions for temperatures of 130 °C, 140 °C and 150 °C. If, for example, 5% of this reaction step is acceptable, then the material would be regarded as "stable" for 8400, 3100 and 1200 hours. This corresponds to 11.7, 4.4 and 1.7 months at the temperatures concerned. The diagram shows the conversion for three isothermal temperatures calculated from the kinetic analysis data.

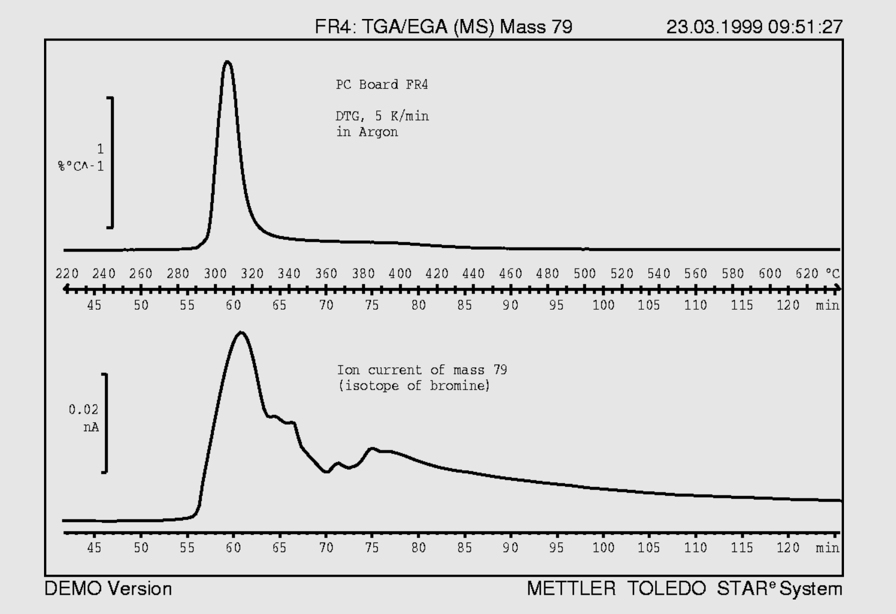


Fig. 9. In the upper diagram the DTG curve is shown in the reverse direction. The continuous monitoring of the ion current of mass 79 (below) shows that the formation of decomposition products containing bromine (hydrogen bromide, methyl bromide and other compounds) runs parallel to the first decomposition step.

Conclusions

This work shows that thermal analysis provides information on a wide range of thermochemical topics.

For "daily" quality assurance, a single thermoanalytical technique is usually sufficient. The intelligent combination of methods provides an overall picture of the sample.

Such comprehensive investigations are often necessary for R+D, damage assessment and the analysis of competitive samples and products.

Modern evaluation software allows the complex facts of an investigation to be clearly presented and helps to make the use of combined measurement techniques more widespread and popular.

Literature:

[1] DIN 51 007; NF T 51-507-1; IEC 1006, ASTM D 3418

[2] S. Vyazovkin, J. Thermal Analysis, 49, 1493-1499, 1997