USER COM

Information for users of
METTLER TOLEDO thermal analysis systems

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Dear customer

As you have no doubt seen, we have expanded the number of thermal analysis customer courses and seminars. These days hardly anyone has time to read the operating instructions in detail to find out all the possibilities that an instrument system offers. In our courses we show you everything that is available. This saves you time later on. A Tutorial kit applications booklet is now available for the new set of test substances. This enables you or a new colleague to become familiar with thermal analysis measurement techniques. We would nevertheless still be delighted to see you on one of our TA courses.

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TA TIP

General comments

Normally, phase changes of reference substances with known transition temperatures and transition enthalpies are used to calibrate and adjust DSC measuring cells. This leads immediately to the first problem: the literature values differ according to the source. Depending on the reference substance, the values can vary typically from 0.1 °C to 0.3 °C (transition temperature) or 0.5% to 1.5% (transition enthalpy). One should therefore only use substances whose literature values are reliably known.

In the following investigation, the reference substances listed in Table 1 were each measured at 4 different heating rates with a DSC821^e [1 - 6]. An instrument was used that had been adjusted neither for temperature nor for heat flow. The onset temperatures and the transition enthalpies were evaluated from the curves. From the data obtained, a number of temperature and heat flow adjustments were calculated and compared with one another.

Table 1 shows that many of the reference substances used in the low temperature range are volatile organic compounds at room temperature. For heat flow measurements, these substances must be measured in hermetically sealed crucibles.

Substance	Transition	Temperature[°C]	Enthalpy [J/g]
cyclopentane	solid-solid	-135.1	4.9
cyclopentane	melting	-93.4	8.6
n-hexane	melting	-94.0	151.8
n-heptane	melting	-90.6	138.6
adamanthane	melting	-64.6	24.8
octane	melting	-56.8	180.0
mercury	melting	-38.8	11.5
water	melting	0.0	335.0
gallium	melting	29.8	80.2
naphthaline	melting	80.3	147.0
indium	melting	156.6	28.5

Table 1. Selected reference substances for temperature and heat flow adjustment in the temperature range -140 °C to 160 °C.

We recommend that you use 40 µl standard aluminum crucibles that have previously been heated at about 300 °C for 15 minutes. This converts any hydroxides of aluminum that have been formed on the surface of the crucible to aluminum oxide. The crucibles can then be sealed “hermetically” without any difficulty using our crucible sealing press. Longterm investigations have shown that this pretreatment results in extremely low “evaporation” losses of about 2 µg/h. This is negligable with sample weights of 10 mg and typical experimental times of about 1 h.

Temperature deviations

Onset temperatures were determined from 10 individual measurements that were performed each time at 4 different heating rates. The differences between these temperatures and the literature values are given in Figure 1 above the individual temperatures. The figure shows that with the exception of cyclopentane the temperature differences can be described quite well by a linear temperature function. The large deviations shown by cyclopentane can be easily explained (see Fig. 2). The melting peak of cyclopentane at -93.43 °C is exceptionally broad making an exact determination of the onset temperature impossible. The peak at -135.09 °C is a solid-solid phase transition. For these types of transition the definition of the transition temperature (onset or peak) is the subject of debate. For this investigation we have used the onset temperatures. Since most users are probably not prepared to adjust their instruments with 10 reference substances, we considered what might be expected from an adjustment when 2, 3 or 4 reference substances randomly selected from Table 1 are used. In this respect, we calculated all the possible combinations of reference substances making sure that the transition temperatures differed by at least 20 °C (this excluded for example the combination of heptane and hexane in the same “reference set”). The root mean square temperature deviation of the reference substances lying within the temperature range defined by the reference substances (no extrapolations) served as the criterion for the quality of the adjustment performed in this way. Cyclopentane was excluded from the investigation for the reasons previously mentioned. Figure 3 shows the resulting frequency distribution for the 3 different sets of reference substances investigated. It shows that the probability of making a temperature measurement error no greater than ±0.4 °C is about 8% (0.08 on the normalized frequency axis), independent of the number of substances used (the differences between the values at 0.4 °C are not statistically significant). The sums of the probabilities are summarized in Table 2. This table shows the probabilty with which an error in the measurement of the onset temperature occurs (due to adjustment errors) that is smaller than the given uncertainty. If, for example, an accuracy of ±0.8 °C is specified, then this requirement is satisfied in 92% of the cases, when the instrument is adjusted with 4 reference substances. If, however, only 2 reference substances are used for the adjustment, then, for the same probability, an uncertainty of well over 1.0 °C results. If you perform the adjustment with only 2 reference substances, then make sure that their melting points differ by at least 150 °C. If you adjust the temperature range in discussion with heptane and indium,

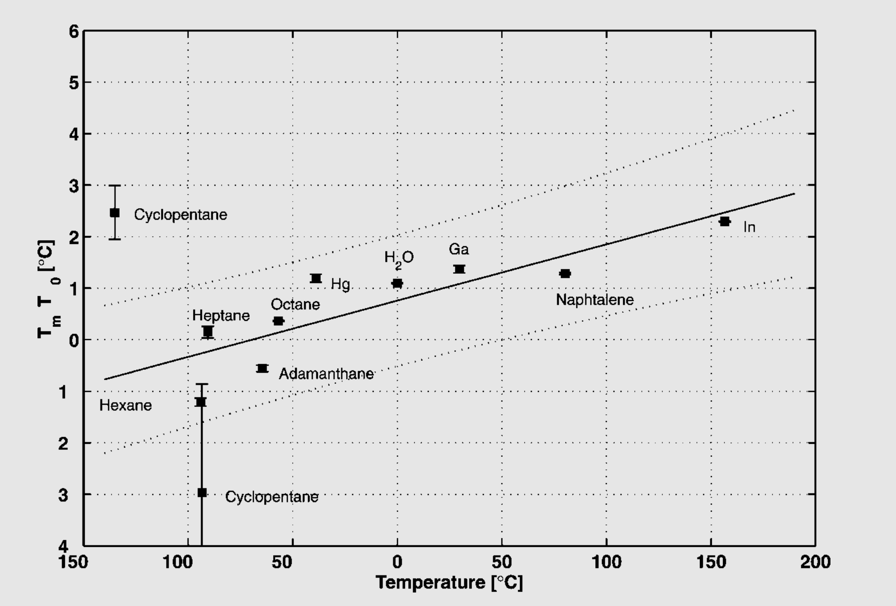

Fig.1. Temperature differences (measured onset temperature (T_m) – literature value (T_0)) as a function of temperature. Continuous line: straight line regression curve taking all reference substances except cyclopentane into account. Dotted lines: 95% confidence intervals.

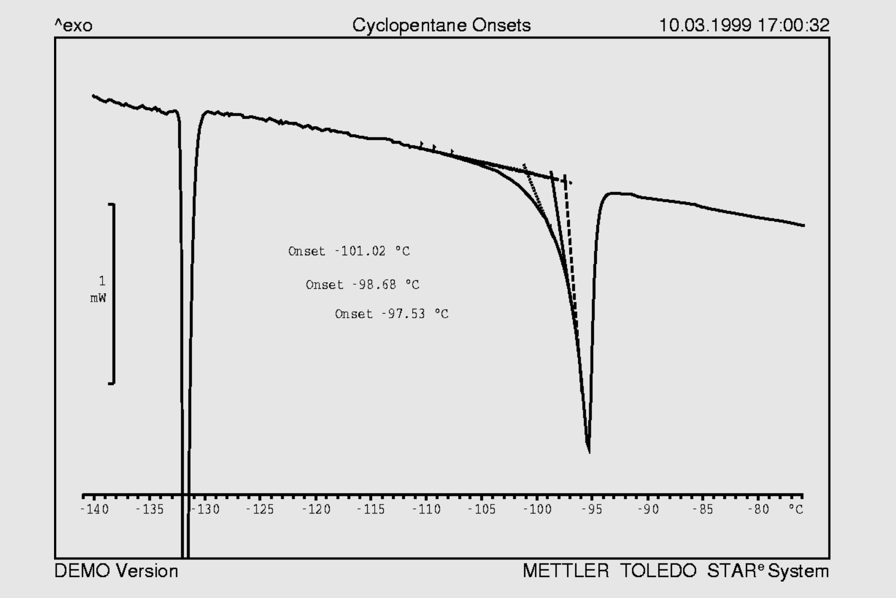

Fig. 2. Melting peak of cyclopentane. The onset temperature of the melting peak can not be clearly determined.

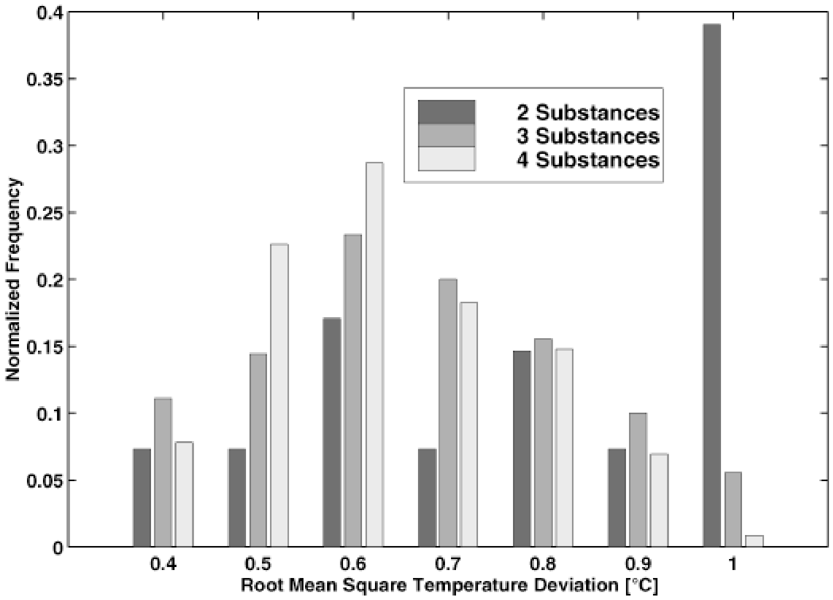

Fig. 3. Normalized frequency distribution of the root mean square temperature deviations for different temperature adjustments. The frequency at 1.0 °C corresponds to the probability that a temperature deviation >1.0 °C occurs.

Uncertainty [°C]	Probability with 2 RS	Probability with 3 RS	Probability with 4 RS
0.4	0.07 ±0.04	0.11 ±0.04	0.08 ±0.03
0.5	0.15 ±0.06	0.26 ±0.05	0.30 ±0.05
0.6	0.32 ±0.09	0.49 ±0.07	0.59 ±0.07
0.7	0.39 ±0.11	0.68 ±0.1	0.77 ±0.08
0.8	0.54 ±0.12	0.84 ±0.1	0.92 ±0.09
0.9	0.61 ±0.16	0.94 ±0.1	0.99 ±0.09

Table 2. Probability with which, for a certain number of randomly selected reference substances (RS), a particular uncertainty of the onset temperature of a transition results.

then you can achieve an accuracy of ±0.4 °C with 2 reference substances (compare also with Fig. 4).
The STAR^e software supports temperature adjustment with several substances. Depending on the number of reference substances, the correction function is described by a straight line or a parabola.

Heat flow deviations

The heat flow adjustment determines the proportionality factor with which the measured DSC sensor signal (voltage) can be converted to the heat flow. This proportionality factor or the calorimetric sensitivity is temperature dependent and must be adjusted accordingly. Just as in the case of temperature adjustment, the correction function for the heat flow adjustment is described by a straight line or a parabola, depending on the number of reference substances. This correction function is then added to the calorimetric sensitivity function given by the STAR^e software.
For this investigation, the relative deviations δ_i were plotted as a function of temperature (Fig. 4). The relative deviation is defined as follows:

$$\delta_i = \frac{\Delta H_m^i - \Delta H_0^i}{\Delta H_0^i}$$

where ΔH^i_m and ΔH^i_0 correspond to the measured and the “true” transition enthalpies.
Figure 4 shows that, with the exception of the values for cyclopentane and tetrahydrofuran, all the values lie to a good approximation on a straight line. The large deviations shown by cyclopentane can be explained as follows: The enthalpies of both transitions of cyclopentane are comparatively low (see Table 1) which leads to relatively small signals. Secondly, the choice of integration limits and a suitable baseline is somewhat difficult. All in all, this leads to the considerable errors and deviations from the literature values that are shown.

Following on from this, we investigated the accuracy that can be expected from heat flow adjustment when 2, 3 or 4 reference substances are used for adjustment. With similar restrictions to those applied for the temperature adjustment, all possible combinations of reference substances were calculated (minimum difference of the transition temperatures 20 °C, cyclopentane excluded). The root mean square enthalpy deviation of the relative deviations of the reference substances lying within the temperature range defined by the reference substances used for the adjustment was again used as a criterion for the quality of the adjustment. The resulting frequency distributions are displayed in Figure 5. It shows that the probability of a maximum error of ±2% occuring in a heat flow measurement is about 10% (0.1 on the normalized frequency axis), irrespective of the number of substances used (the differences between the values at 2% are not statistically significant). If the sums of the probabilities are examined, the values given in Table 3 are obtained. This table shows once again the probability with which an error in the measurement of the enthalpy occurs (due to adjustment errors) that is smaller than the given uncertainty. If, for example, an accuracy of 3% is required, then this is achieved in 92% of the cases when the instrument has been adjusted with 4 reference substances. If, however, only 2 reference substances are used, then for the same probability an uncertainty of well over 3.0% results. Once again, it should be realized that this result does not mean that an adjustment with only 2 reference substances is inaccurate. Rather in this case one should take care that the melting temperatures of the substances are as far apart as possible. For example, if the heat flow adjustment is performed with heptane and indium, the expected error in the temperature range -100 °C to 160 °C is about ±2%.

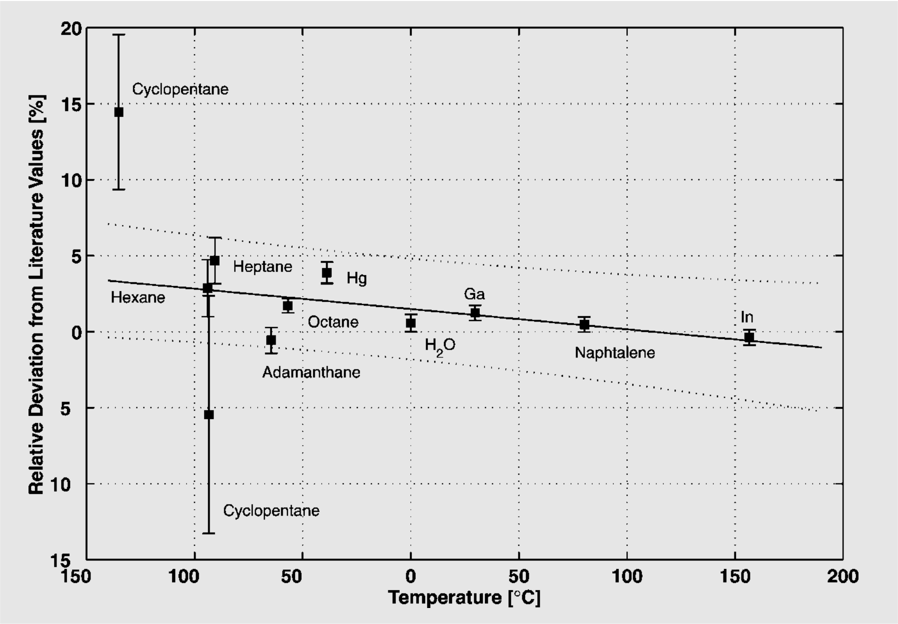

Fig. 4. Relative deviations of the measured transition enthalpies from the literature values for various reference substances. The data points for cyclopentane were excluded from the calculation of the of the regression curve (continuous line).

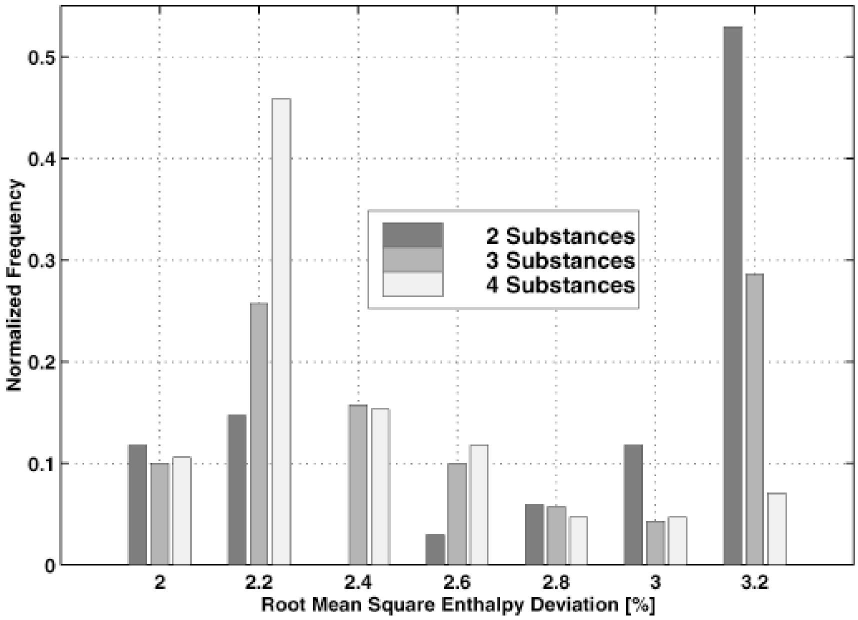

Fig. 5. Normalized frequency distribution of the root mean square deviations of the relative enthalpy deviations for different heat flow adjustments. The frequency at 3.2% corresponds to the probability that a deviation >3.2% occurs.

Uncertainty [in %]	**Probability with 2 RS**	**Probability with 3 RS**	**Probability with 4 RS**
2.0	0.12 ±0.06	0.10 ±0.04	0.11 ±0.04
2.2	0.26 ±0.09	0.36 ±0.07	0.56 ±0.08
2.4	0.26 ±0.09	0.51 ±0.09	0.72 ±0.09
2.6	0.29 ±0.9	0.61 ±0.09	0.84 ±0.10
2.8	0.35 ±0.10	0.67 ±0.10	0.88 ±0.10
3.0	0.47 ±0.12	0.71 ±0.10	0.92 ±0.10

Table 3. Probability with which, for a certain number of randomly selected reference substances (RS), a particular uncertainty of the enthalpy of a transition results.

Conclusions

The quality of temperature and heat flow adjustment is very dependent on the number of reference substances used. The expected uncertainty arising from adjustment errors is, for instance, doubled if only 2 instead of 4 reference substances are used. For the highest demands of accuracy, the use of at least 4 reference substances is recommended for both heat flow and temperature adjustment. In this case, accuracies of ±0.8 °C can be expected for temperature measurements and ±3% for the determination of transition enthalpies (90% confidence). As far as the choice of reference substances is concerned, it is apparent that this is not particularly critical for a "random" selection. With the exception of cyclopentane, any of the reference substances listed in Table 1 can be used both for the temperature and for the heat flow adjustment. The best results, however, are achieved when the transition temperatures are equally spaced and have the largest possible temperature differences between each other (e.g. with the 4 reference substances heptane, Hg, Ga and In). The investigation also showed that the use of cyclopentane as a reference substance is not recommended.

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[3] H. L. Finke et al., J. Am. Chem. Soc., 76, 333-341, 1954
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[5] ITS-90. H. Preston-Thomas, Metrologia, 27, 3-18, 1990
[6] J. Emsley, The Elements, Clarendon Press: Oxford, 1991

Low-mass platinum, sapphire and alumina crucibles

We have expanded our wide range of crucibles with 3 additional crucibles. The small, light-weight platinum and alumina crucibles increase SDTA sensitivity (shorter signal time constants). The smaller crucibles require less material and are therefore less expensive.
The sapphire crucible has been specially developed for high temperature applications. It protects the sample holder from contamination thanks to its very low porosity. With normal alumina crucibles it can sometimes happen that the molten sample passes through the crucible and contaminates the sample holder.

Crucible	**Order number**	**Number of pieces per set**	**Volume**	**Pressure**	**Material**	**Weight**	**Taulag**	**Signal time constant**
Light platinum crucible	51140842	4	30 µl	-	platinum	C: 180 mg L: 90 mg	3.6 s	3.9 s
Light alumina crucible	51140843	20	30 µl	-	alumina	C: 90 mg L: 60 mg	6.4 s	5.0 s
Sapphire crucible	51140845	4	70 µl	-	sapphire	C: 225 mg L: 65 mg	12.3 s	10.3 s

C: Crucible L: Lid

TA Poster

If you want to explain your thermal analysis system and the measurement principles involved to one of your visitors, then ask your local representative about the following posters (format A1):

- DSC (English: ME-51725032)
- TGA (English: ME-51725035)
- TMA (English: ME-51725038)

Each poster includes a cross-sectional diagram of the measuring cell with a brief description, as well as a measurement curve showing typical effects.

- DSC Sensor (English: ME-51725029)

The sensor poster shows in detail how the FRS5 sensor with its 56 thermocouples measures the heat flow with the highest sensitivity and why the baseline drift is so extremely low.

New DSC Sensor with 56 Thermocouples

Thermomechanical Analysis

Thermogravimetry

Differential Scanning Calorimetry

Fig. 1. DSC, TGA, TMA and DSC Sensor posters

New TA Tutorial Kit with Applications Booklet

The applications booklet to accompany the new Tutorial Kit with its 16 different test substances has now been available for several weeks. This book is very similar to the three existing applications booklets entitled Pharmaceuticals, Food and Thermoplastics (introduced in UserCom 5 and 6). For each sample, at least one interesting measurement and evaluation is described using the DSC, TGA or TMA. This booklet is especially valuable for training purposes; you can measure the samples on your own instrument and compare the curves and evaluations with the results given in the booklet. Order numbers:

German:	51140877
French:	51140 878
English:	51140 879

Thermal analysis of polyvinylchloride (PVC)

Dr. B. Benzler, METTLER TOLEDO GmbH, Giessen

In principle, three important properties of PVC samples can be investigated with thermoanalytical methods. They are:

- the thermal stability,
- the temperature and form of the glass transition
- the degree of gelation.

In practice two important methods of thermal analysis are used[1]: Thermogravimetric Analysis (TGA) and Differential Scanning calorimetry (DSC).

Thermogravimetry (TGA) [2] measures the change in weight of a sample that is subjected to a temperature program (usually a linear heating rate). Sometimes the weight change is measured as a function of time at constant temperature. It is usually displayed in units relative to the initial sample weight (in %). The first derivative of this TGA curve with respect to time or temperature, i.e. the DTG curve, is often useful because it makes changes in the curve much clearer. It presents the rate of weight change in units of %/min or in %/°C.

Figure 1 shows the TGA and DTG curves of a PVC window frame measured at a heating rate of 20 K/min under nitrogen (50 ml/min).

As can be seen from the DTG curve, thermal degradation occurs in two steps. In the first step, dehydrochlorination, i.e. the elimination of hydrogen chloride occurs up to about 378 °C. The weight loss in this step is 52%. Often plasticizers or other additives vaporize at the same time. The remaining polymer dedrades further in the second step. Up to 600 °C the sample loses a total of 78% of its weight. The temperature at which dehydrochlorination begins is used as a measure of the thermal stability of the PVC. It depends on the degree of stabilization of the PVC with additives and also on possible previous degradation. In this example, an "onset" can be observed in the DTG curve at 254 °C.

The weight loss data supplied by the thermogravimetric measurement is completely unspecific and gives no information about the nature of the degradation products. This type of information is only obtained when a TGA instrument is connected via a suitable interface to a device capable of analyzing gases. This can be an infrared spectrometer with a gas cell, or a mass spectrometer. Another, less expensive, detection method is to absorb the evolved gases in a liquid and to use titration techniques [3].

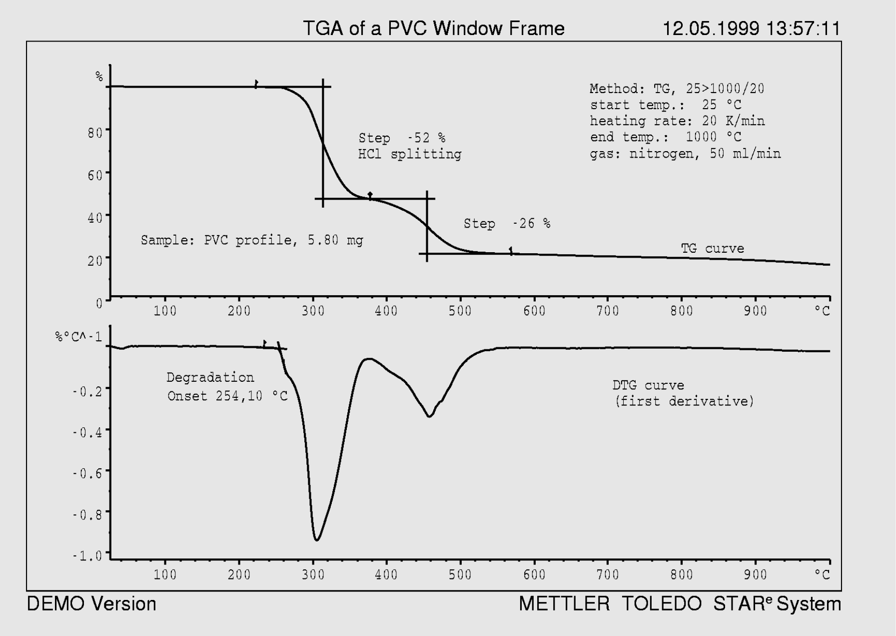

Fig. 1. TGA and DTG curves of PVC degradation

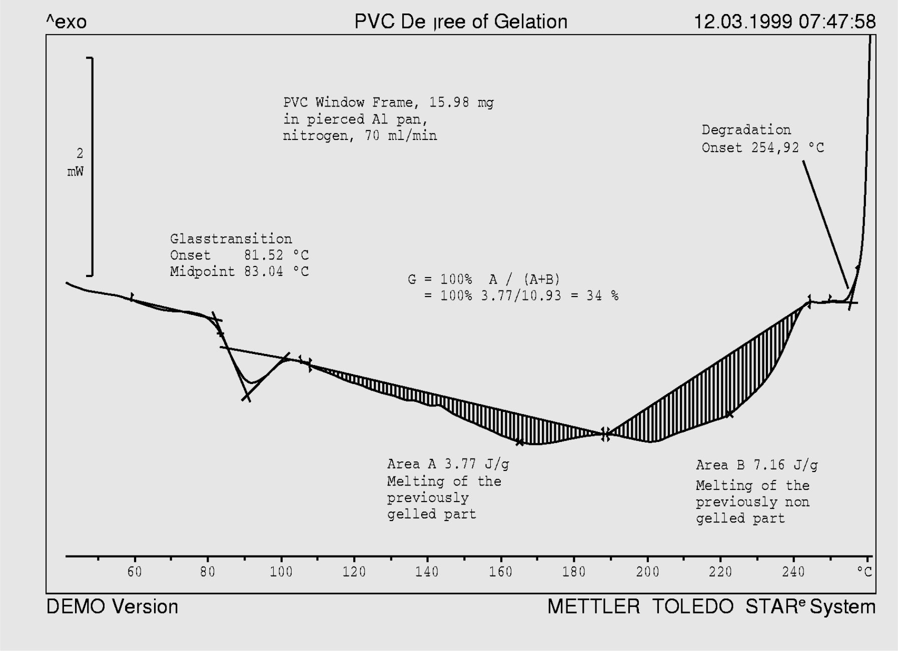

Fig. 2. DSC curves of PVC samples showing the four thermal effects.

Differential Scanning Calorimetry [4] measures the heat flow between a sample and its surroundings when the sample is subjected to a temperature program (heating or cooling), i.e. the heat absorbed (endotherm) or liberated (exotherm) by the sample. The physical and chemical processes that occur on heating are coupled with a loss or gain in energy or with a change of the specific heat capacity of the sample. Such processes are therefore shown as peaks or steps in the measurement curve. The integration of a peak (peak area) yields the transition energy or the heat of reaction.

Figure 2 shows the DSC curve of the same PVC window frame at a heating rate of 10 K/min under nitrogen (70 ml/min). Four consecutive effects are apparent:

- the glass transition with the relaxation peak. This depends on the thermal history of the sample. Plasticized PVC can exhibit a glass transition temperature, T_g, below 0 °C, while plasticizer-free PVC typically has a T_g of about 80 °C.
- a broad endothermic effect with an area A between the glass transition and about 190 °C. This temperature corresponds to the processing temperature. According to [5], the endothermic peak corresponds to the melting of the partially gelled PVC.
- a further broad endothermic effect with an area B between 190 °C and 240 °C. According to [6], this corresponds to the melting of the previously nongelled part during the measurement.
- above 250 °C the beginning of degradation of the PVC. The reaction of the hydrogen chloride formed and the aluminium crucible could be the reason why degradation almost always begins exothermally. The measured onset temperature is in good agreement with the temperature determined by thermogravimetry.

The degree of gelation of the PVC is calculated as the ratio of A to the total area. With this empirical method, the choice of the straight baseline is rather surprising. It is namely (at least for the area B) not formed tangentially to the DSC curve, as is usually the case.

Literature

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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	

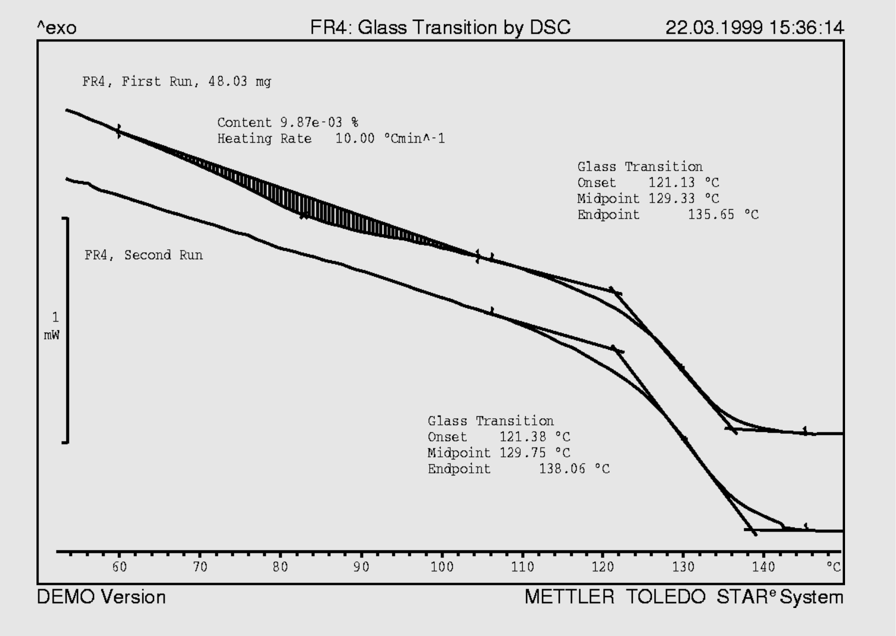


Fig. 1. DSC at 10 K/min: The first measurement exhibits an endothermic effect at about 90 °C. On the assumption that this is due to the vaporization of moisture, this yields a moisture content of 0.01% (heat of vaporization of water is taken to be 2400 J/g). This assumption is confirmed in the second 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.

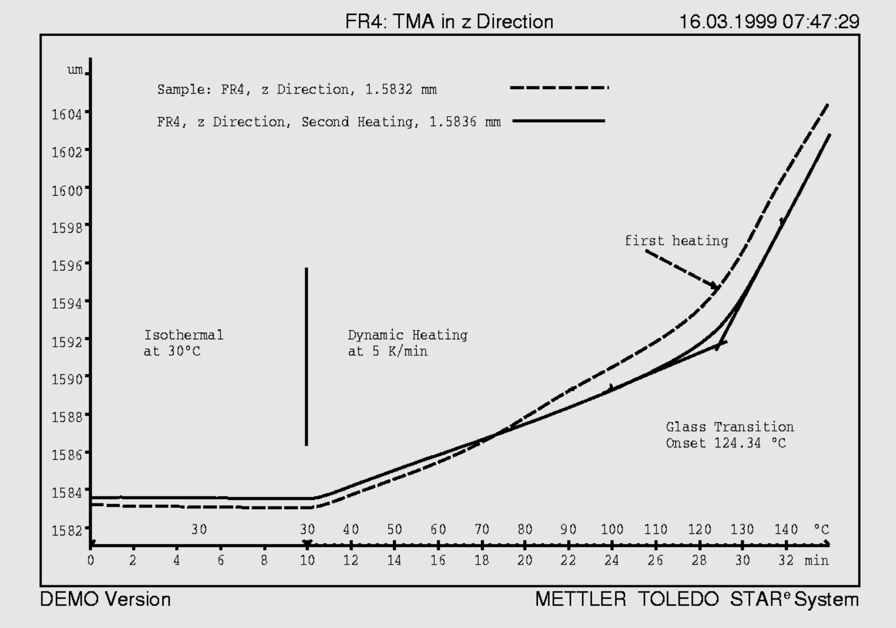


Fig. 2. TMA at 5 K/min: Once again the first measurement shows a different behavior around 80 °C. The increase in thickness due to themal expansion increases markedly at the glass transition point. After cooling to 30 °C , the sample is 0.4 μm thicker in the z-direction. The sample is covered with a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

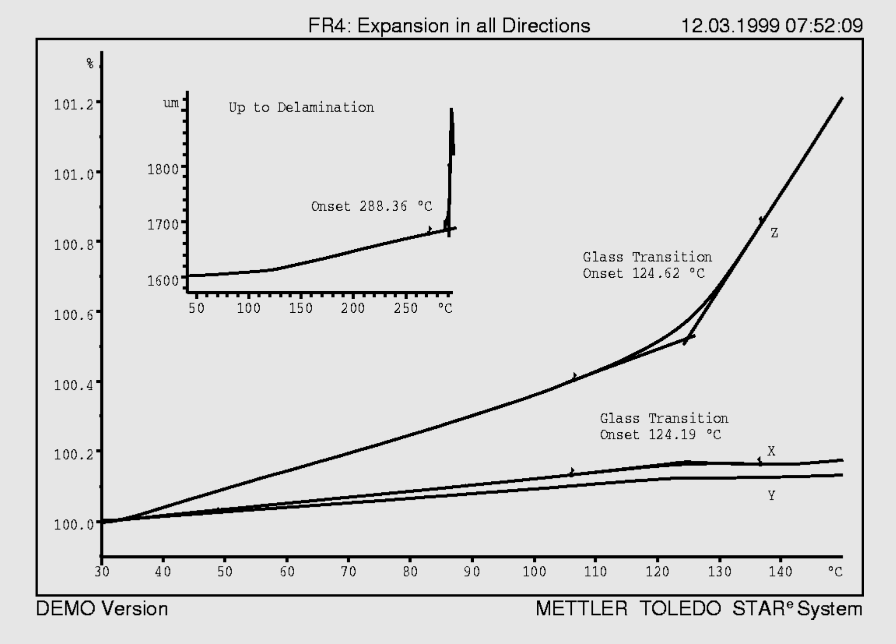


Fig. 3. The large diagram shows the normalized lengths in all three directions. The sample was prepared with plane-parallel faces using a diamond saw. The expansion of the matrix resin is hindered parallel to the glass fibers and is diverted into the z-direction. Normally the glass transition temperature 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.

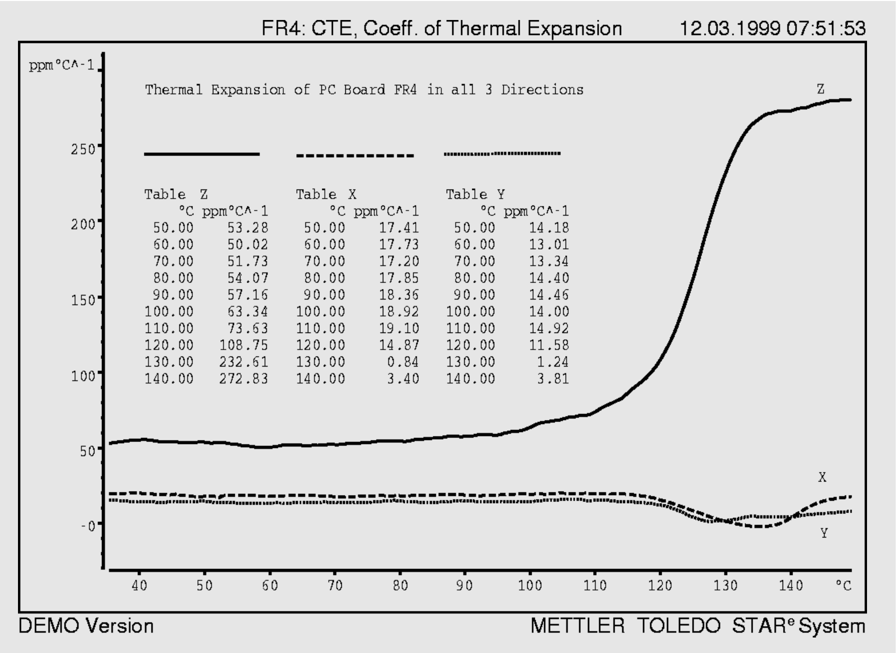


Table Z		Table X		Table Y	
°C	ppm°C^-1	°C	ppm°C^-1	°C	ppm°C^-1
50.00	53.28	50.00	17.41	50.00	14.18
60.00	50.02	60.00	17.73	60.00	13.01
70.00	51.73	70.00	17.20	70.00	13.34
80.00	54.07	80.00	17.85	80.00	14.40
90.00	57.16	90.00	18.36	90.00	14.46
100.00	63.34	100.00	18.92	100.00	14.00
110.00	73.63	110.00	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).

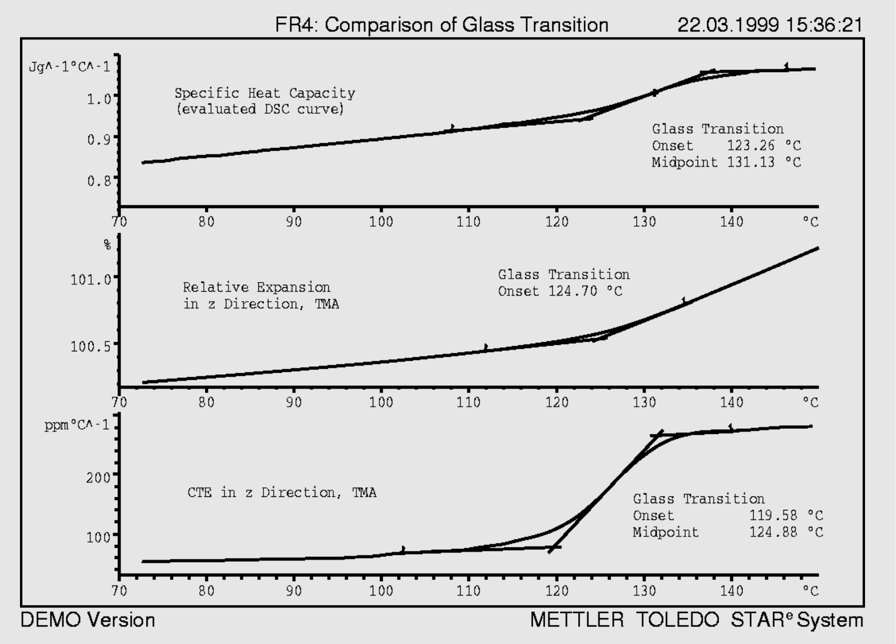


Fig. 5. The glass transition from DSC and TMA data. The three evaluation procedures yield somewhat different results. The TMA values measured at 10 K/min were also higher.

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).

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).

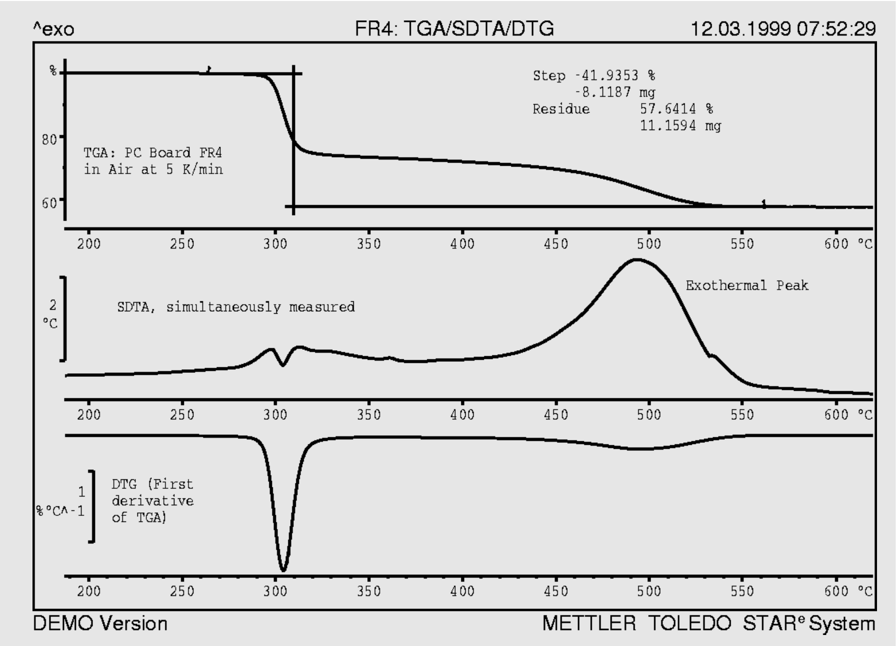


Fig. 6. The thermogravimetric behavior of the PCB. Uppermost curve: TGA, the decomposition of the matrix resin in air at 5 K/min occurs in 2 steps. The total weight loss of 41.9% corresponds to the resin content. The glass fibers remain behind (57.6%). The TGA curve does not tell us exactly what happens 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.

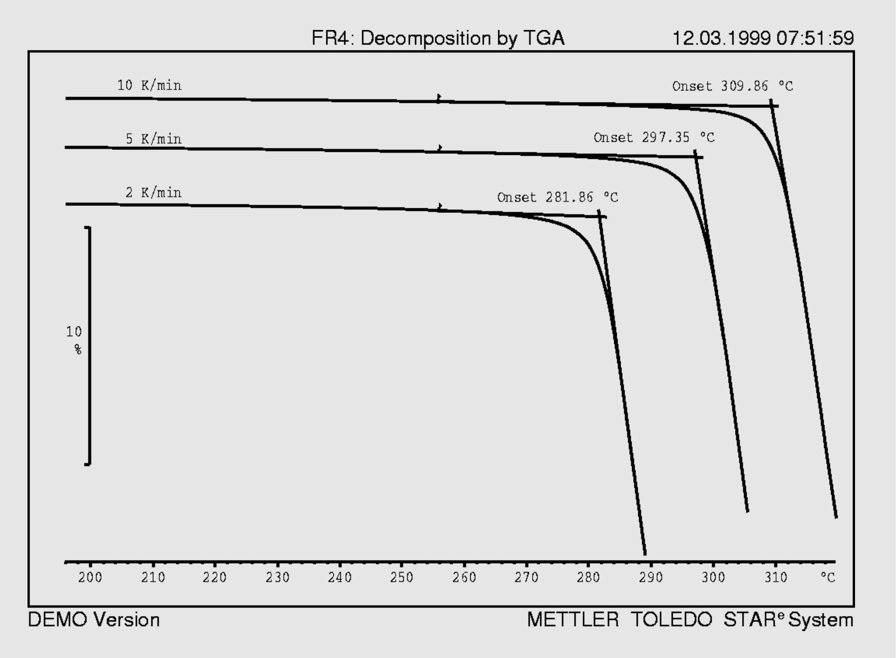
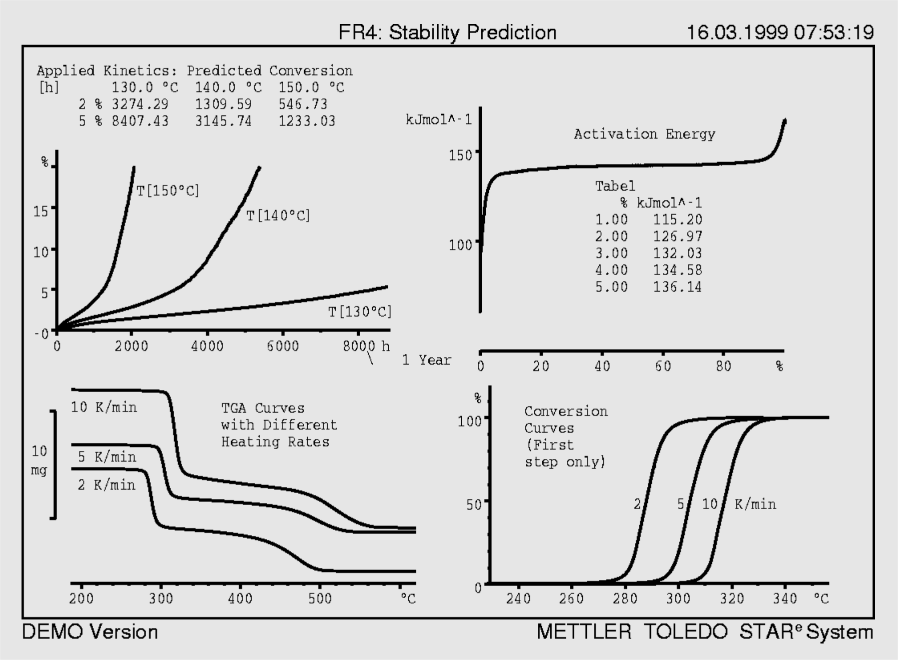


Fig. 7. There is no "starting temperature" for chemical reactions . The higher the heating rate, the higher the "onset of decomposition " appears to be.

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.

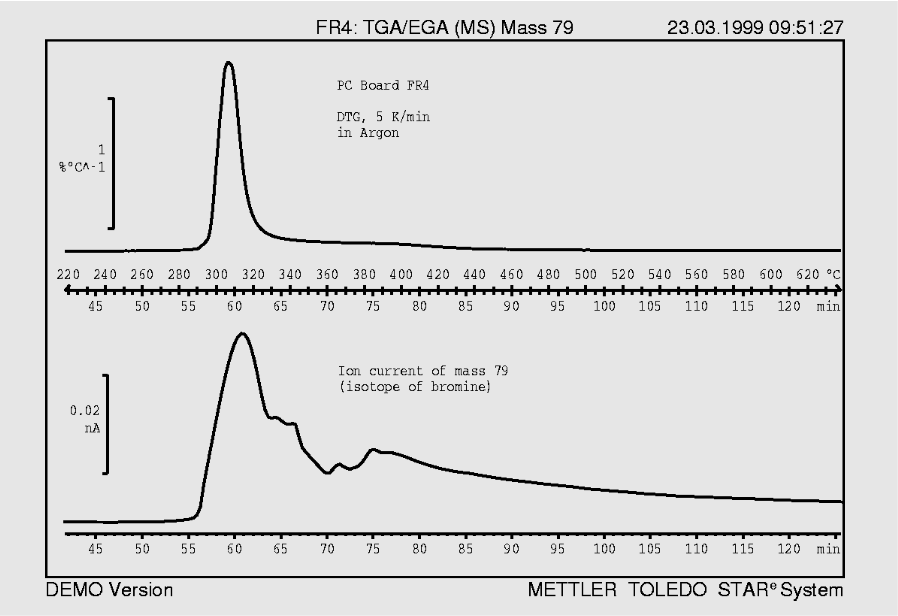


Fig. 9. In the upper diagram the DTG curve is shown in the reverse direction. The continuous monitoring of the ion current of mass 79 (below) shows that the formation of decomposition products containing bromine (hydrogen bromide, methyl bromide and other compounds) runs parallel to the first decomposition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

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DSC of butter fats and margarine

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Introduction

Butter is made by the mechanical blending of droplets of fat from cow's milk. Household butter is a water-in-oil emulsion containing about 15% water. Water-free butterfat is not only used for roasting but also for the manufacture of foodstuffs. Besides its typical buttery taste, the rheological properties, the texture and the appearance of the foodstuff are also influenced by the seasonal variation of its composition.

In contrast to many fats of plant origin, which consist mainly of three or four fatty acids (as glycerides), butter contains about 10 important fatty acids with 4 to 24 carbon atoms. The changing fatty acid content originating from the seasonal variations in the animal feed influences the crystallization of butter and through this its physical properties. For example, summer butter (at the same temperature) is appreciably softer than winter butter, which is the reason why butter taken directly from the refrigerator in winter is more difficult to spread. The foodstuffs industry in particular is very interested in standardized butterfats. These can be produced by fractional crystallization. The water-free molten butter is cooled down with gentle stirring until crystallization begins. The (high melting) crystals are filtered off and the remaining melt cooled further. The next crystal fraction is then obtained in the same way. Finally, the native butter has been separated into several fractions, which, depending on market requirements, can be mixed to give standard products. Such special products are required for the manufacture of ice cream, chocolate and pastry, to mention just a few.

Margarine is produced by emulsifying water with plant fats (formerly also with animal fats).

The crystalline composition of butter and margarine can be investigated using various analytical techniques:

- Isothermal NMR at different temperatures*)
- Isothermal X-ray diffraction at different temperatures*)
- Differential Scanning Calorimetry

*) normally from 0 °C to 40 °C in steps of 5 °C

Of these methods, DSC is the most important since almost any temperature program (heating, cooling or isothermal) can be performed automatically and reproducibly. Crystallization is observed as an exothermic peak and melting as an endothermic peak.

Polymorphism

Often when molten fats begin to crystallize, metastable α crystalls of low melting point are formed, which then change more or less rapidly to the more stable β' modification. In the course of time, the more stable β crystals are formed with the highest melting point (Fig. 1). The heat of fusion also increases with increasing stability.

Polymorphism is an important reason why the DSC curves of premelted butter differ markedly from those of untreated butter (stable modification) (see Fig. 2).

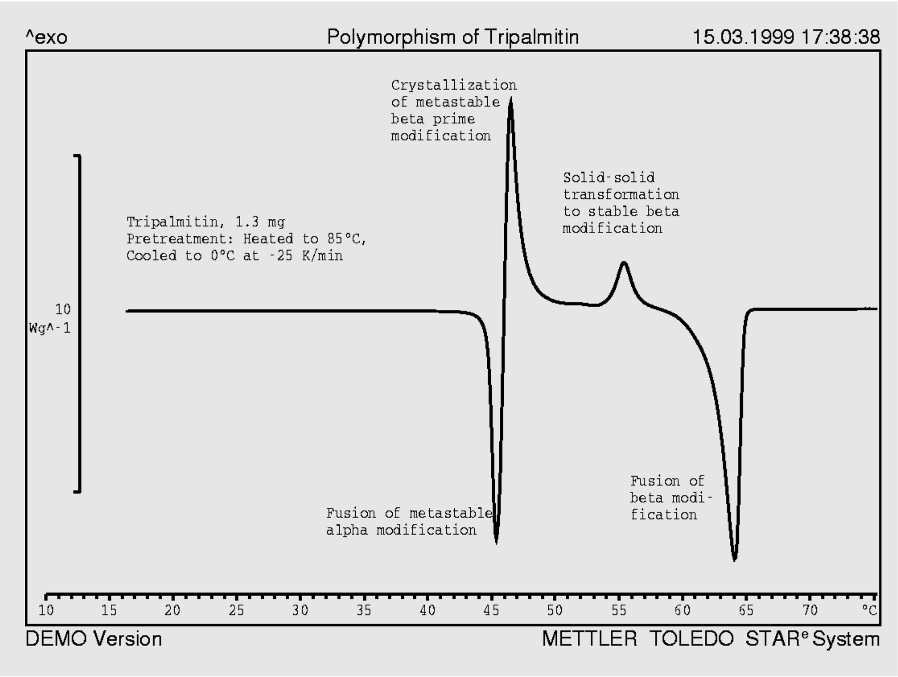

Fig. 1. DSC curve of tripalmitin that had been premelted and then cooled at 40 K/min. The metastable α phase melts at 45 °C. The more stable β' modification crytallizes from the melt and then at 55 °C undergoes a solid-solid transition to the stable β phase.

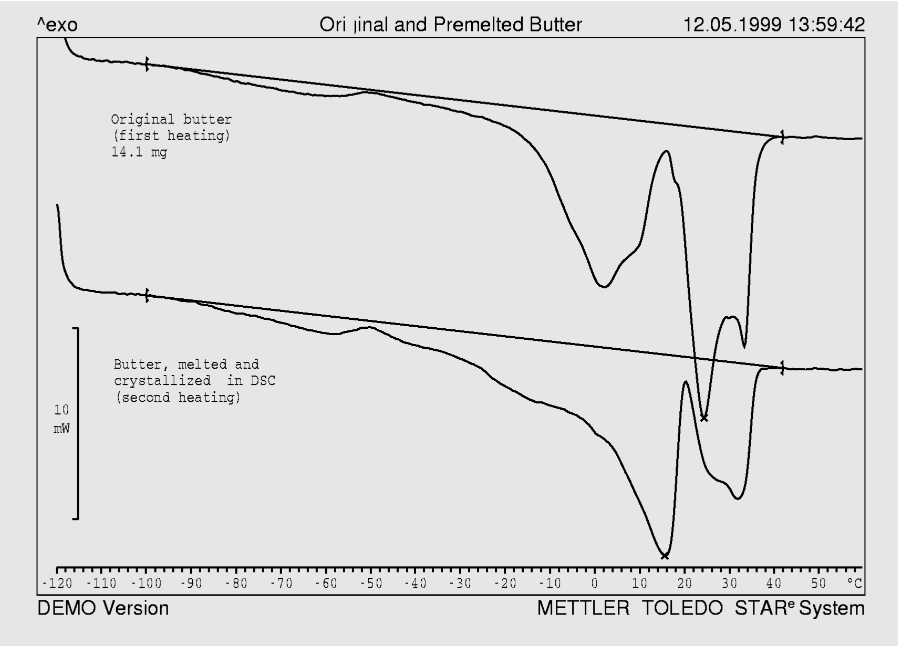

Fig. 2. The first measurement of a butterfat (concentrated butter) that had been stored at 15 °C (1st run) differs markedly from the DSC curve of the sample that had been melted and then cooled at 40 K/min.

Phase diagrams

The various fatty acid glycerides are soluble in each other both in the liquid and in the solid states. Two randomly chosen samples with appreciably different melting points make up the schematic 2-component phase diagram shown on the left in Figure 3. When the mixed melt of concentration $x_{B,0}$ is rapidly cooled, mixed crystals are formed with a melting point in between. If, however, the sample is annealed at a temperature of T_{temp}, then mixed crystals that are enriched in B (i.e. fractional crystallization, see above) crystallize out. This leaves behind a melt rich in A, which on cooling also crystallizes. The DSC heating curve of this crystal mixture therefore shows two melting peaks. The gap between the two melting peaks in the region of the former annealing or storage temperature is known as the melting gap. It occurs in almost all DSC curves of butter.

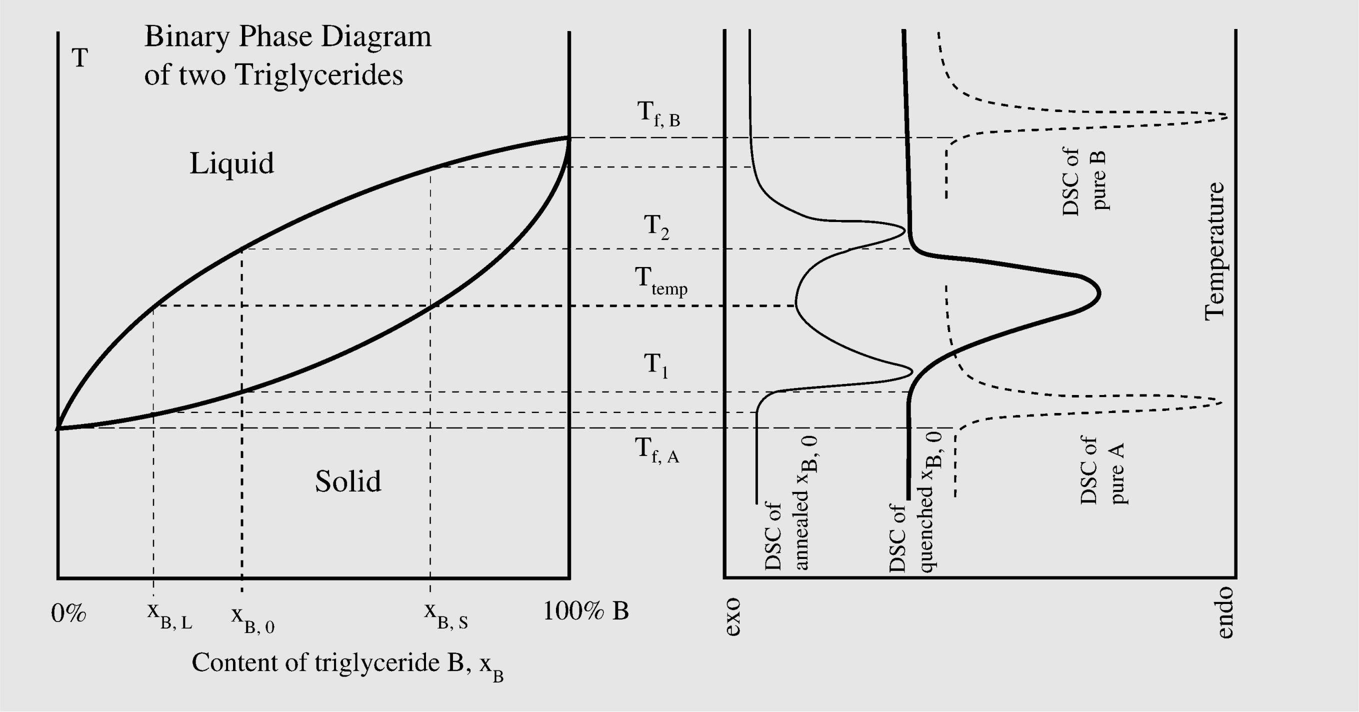

Fig. 3. On the left: 2-component phase diagram of a low melting triglyceride A with a higher melting triglyceride B. The abscissa shows the content of B from 0% to 100%. We start from the mixture $x_{B,0}$, which on annealing at a temperature of T_{temp}, forms the solid phase of composition $x_{B,S}$. Below the solidus line everything is solid, above the liquidus line everything is liquid. Solid and liquid phases coexist between the lines. On the right: the DSC curves of the annealed mixture, the rapidly cooled mixture (quenched) as well as the pure substances A and B are shown.

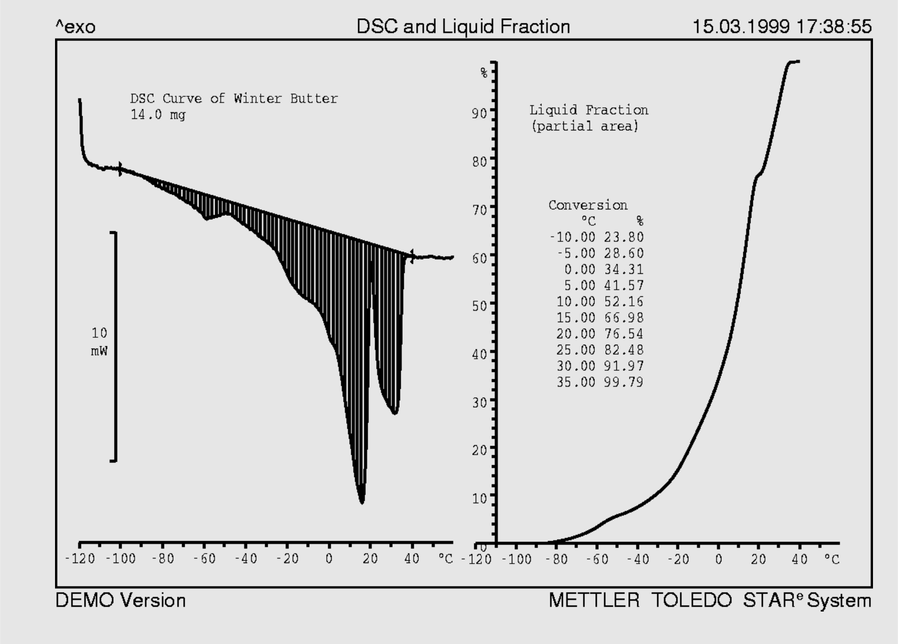

Fig. 4. The solid fraction can be determined at any temperature by partial integration. In Figure 5 the solid fractions of butter and margarine determined in this way are shown.

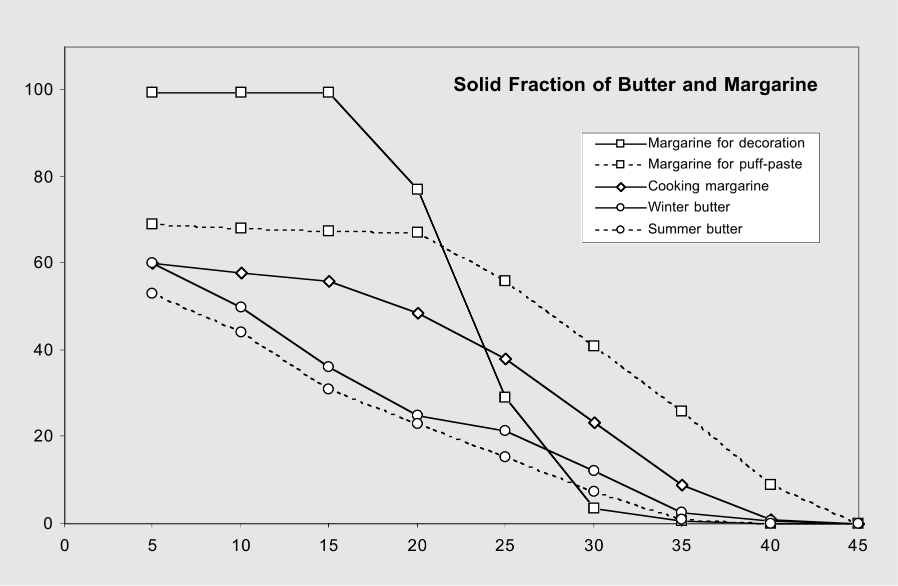

Fig. 5. The solid fraction of various butter and margarine samples are compared as a function of temperature (margarine for decoration, for pastry and for cooking, winter and summer butter).

Liquid/solid fraction

If the specific heat of fusion of the various fat fractions is assumed to be constant, then the area under the melting curve is proportional to the amount of crystalline material melted. The liquid fraction (also known as melt conversion or molten fraction) at a particular temperature corresponds to the partial integral up to this temperature divided by the total peak area. The solid fraction is equal to 100% less the liquid fraction (Fig. 4).
Such curves are ideal for the quantitative comparison of different fats or their fractions (Fig. 5).

Conclusion

Butter and margarine are mixtures of triglycerides whose melting behavior is additionally complicated by polymorphism. Differential Scanning Calorimetry together with suitable evaluation programs allow the samples to be easily characterized.

DSC with the TGA/SDTA851^e taking weight loss into account

Introduction

Heat flow measurements in a thermogravimetric measuring cell should also allow simultaneously measured changes in mass to be taken into account in the calorimetric result. To do this a temperature dependent adjustment factor is determined that converts the SDTA signal into a heat flow curve (DSC curve). The SDTA signal is the temperature difference between the temperature measured directly at the sample and the program temperature that serves as the reference [1, 2]. Analagous to the DSC, it indicates for example whether a decomposition process is exothermic or endothermic and shows in addition where phase changes or reactions with no change in mass occur.

Another way to measure transition enthalpies is to determine the specific heat capacity (c_p) of samples[3]. It is then better to perform the c_p measurement according to the sapphire method [4,5] with isothermal intervals, which however means an interruption in continuous heating.

In contrast to this, an adjustment curve allows the heat flow to be measured directly with SDTA at different heating rates and continuously over the entire temperature range without multiple measurements and without a comparison with sapphire. In this way, heats of reaction and phase transition enthalpies can also be determined by TGA/SDTA measurements even when changes in mass occur.

Experimental details

The measurements were performed with a METTLER TOLEDO **STAR^e** System (software version 6.00 under Windows NT®) and the TGA/SDTA851^e module (small furnace up to 1100 °C). Other experimental parameters: 70 µl platinum crucible, heating rate 10 K/min, nitrogen purge gas at 40 ml/min. In order to prevent metal samples from forming alloys with platinum at higher temperatures, about 15 mg of alumina powder were uniformly distributed in the bottom of the crucible and the metals placed on top.

Deviations from the above mentioned conditions are noted in the relevant sections.

Note: The adjustment curve can also be determined up to 1600 °C; the new sapphire crucibles should then be used for the metal melts. Platinum crucibles together with a sapphire disk should be placed on the crucible support.

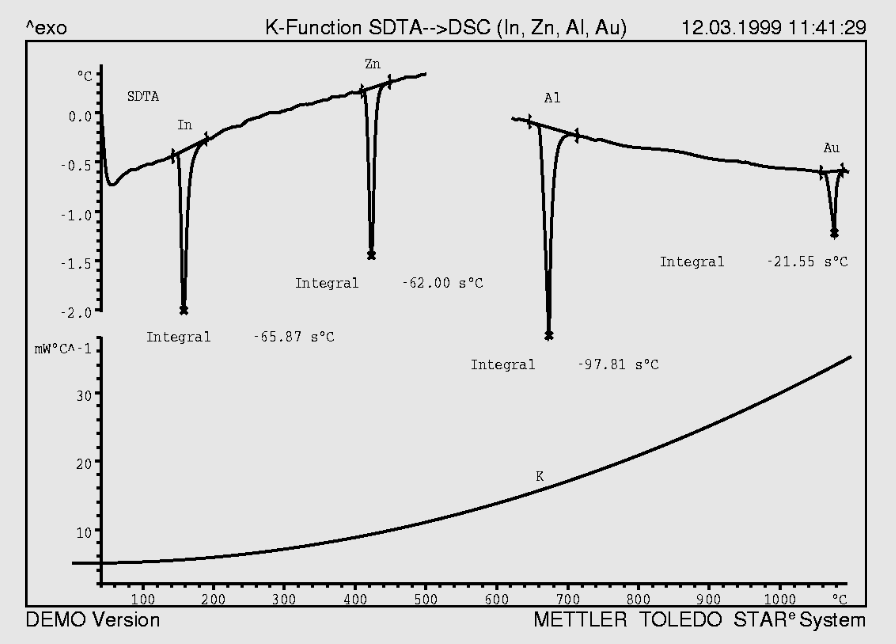

Fig. 1. SDTA melting curves of indium, zinc, aluminum and gold (two metals each in the same platinum crucible, speparated by alumina powder). See Table 1 for sample weights. Each peak was integrated with respect to time. The lower curve shows the adjustment factor K, which was calculated from these and other measurements.

Determination of the adjustment curve

Melting point standards are used for the adjustment of temperature. Since not only the melting temperatures but also the heats of fusion are known for these materials (Table 1), the same measurements can be used for the temperature and the heat flow adjustment. As an example, Figure 1 shows the SDTA melting curves of four high purity metals. The calorimetric sensitivity of the SDTA signal is determined by comparing the measured SDTA peak area (F_{peak}) with the theoretical heat of fusion (ΔH_{Lit}) for the sample. The corresponding adjustment factor K is calculated as follows:

$K\ [mW/°C] = (m_0 \cdot \Delta H_{Lit}) /(F_{peak})$

where m_0 is the sample weight used for the measurement of F_{peak}.

Example for aluminum (see also Table 1):

$$K_{Al} = 3.792\ mg \cdot 397\ J/g\ /\ 97.8\ s°C$$
$$= 15.4\ mW/°C$$

Several such measurements are now performed to determine the adjustment factors at different temperatures. Just as for the accurate temperature adjustment, we recommend that you perform several measurements for each substance. The entire temperature range can be covered with the four metals. If only a certain temperature range is of interest, then it is sufficient to measure just two heats of fusion, e.g. of indium and zinc. The temperature dependence of K can be described to a good approximation by a quadratic polynomial function. The

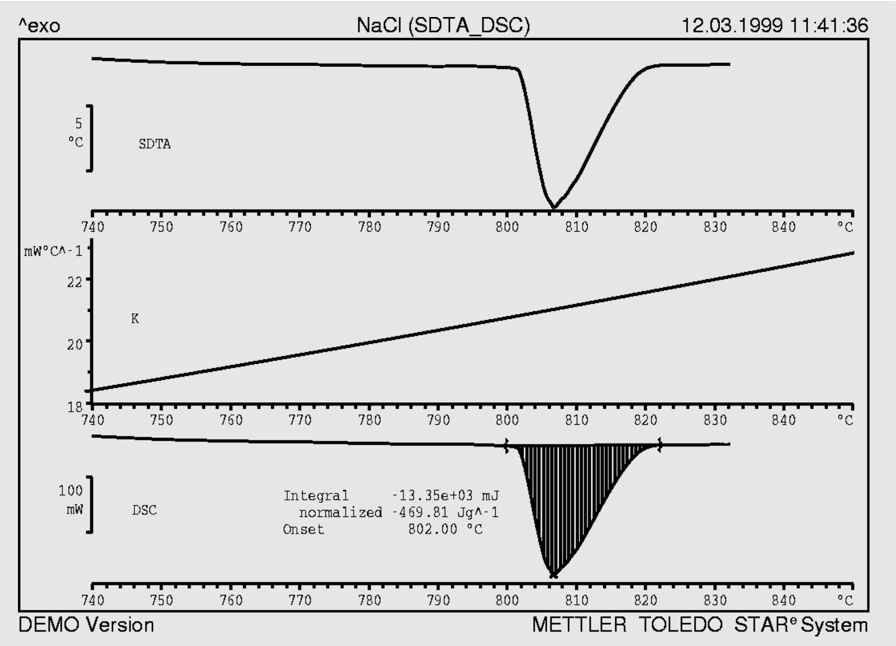

Fig. 2. The determination of the heat of fusion of sodium chloride (NaCl) by a TGA/SDTA measurement. Upper curve is the SDTA . The middle curve shows the course of the adjustment factor from 740 °C to 840 °C (see also Fig. 1). The lower curve shows the DSC curve determined by multiplying the SDTA curve by K. Theoretical heat of fusion : 480 J/g [database in http://www.nlci.com/users/gundlach/]. Sample weight: 28.412 mg, platinum crucible with lid to reduce vaporization which begins at this temperature.

Mathematics evaluation software option includes this calculation function. The polynomial regression function yields a curve that can be saved directly as an adjustment curve with the correct units. This permits the simple and direct conversion of the SDTA curves into heat flow curves (DSC curves). Here again the Mathematics option is used to multiply the SDTA curve by the adjustment curve, at the same time taking account of the units. Figure 2 shows an example of this: the melting of sodium chloride produces an endothermic peak in the SDTA curve. Multiplication with the adjustment curve in this temperature range leads directly to the the DSC curve, which, as usual, when integrated with respect to time, yields the heat of fusion of the substance.
The TGA/SDTA module therefore makes DSC measurements possible.

Factors affecting the adjustment factor

K increases relatively rapidly with temperature, i.e. the calorimetric sensitivity is at least six times lower at 1000 °C than at room temperature (see Fig. 1). Other effects are in contrast of little importance: the affect of sample weight as measured with 1 to 30 mg indium lies within the accuracy of the evaluation (position of the baseline for integration) [6]. No dependence was observed on changing the heating rate from 5 to 20 K/min and even small changes in the nitrogen purge gas flow rate of 10 to 30 ml/min had no effect on the value of K. The change from air or nitrogen to helium resulted in a marked deterioration of the the calorimetric sensitivity by a factor of 3 (measured at 156 °C) due to the better thermal conductivity of helium. However the type of crucible had hardly any effect on the adjustment curve K. The same curve can therefore be used for different types of crucible (e.g. platinum and alumina crucibles).
In general, calorimetric effects can be quantitatively determined by SDTA with an error level of less than 10%.

Mass-independent DSC (SDTA)

DSC results such as the heat of fusion or reaction enthalpy are usually related to the sample mass. However, if changes in mass occur, then results are obtained that are incorrectly normalized. The combination of TGA and DSC curves makes it possible to normalize the heat flow to the correct mass. The TGA/SDTA851^e module provides directly all the necessary measurement values as is shown in the example of aspartame (Fig. 3 and 4) [see also 7]. When the sweetening agent is heated from room temperature, the absorbed moisture (about 1%) vaporizes up to 100 °C, the water of crystallization is liberated at 125 °C, and then at 185 °C the first decomposition step with the elimination of methanol occurs. Finally the resulting

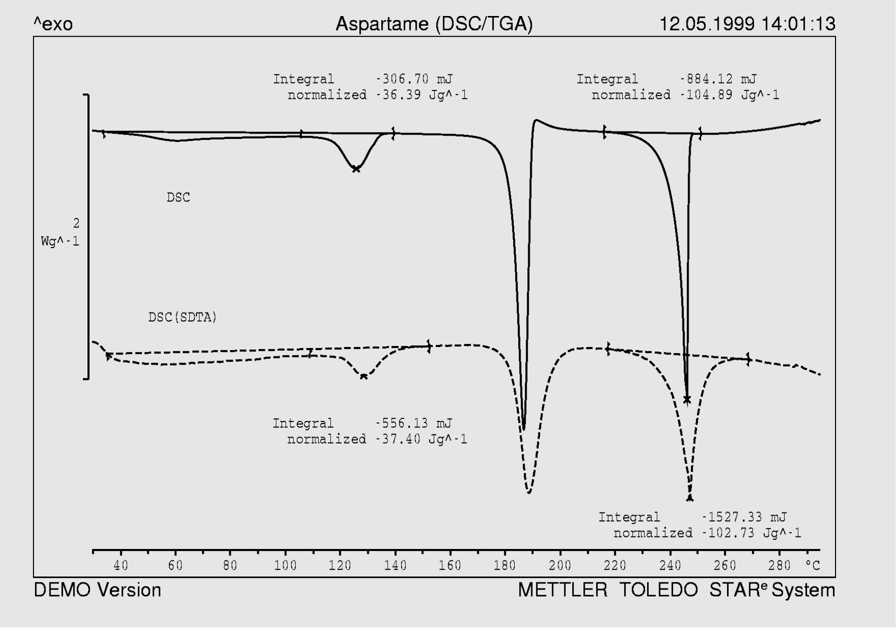

Fig. 3. The thermogravimetric and DSC measurements of aspartame up to 300 °C at a heating rate of 5 K/min. TGA/SDTA: 14.868 mg in a 70 µl alumina crucible. The SDTA curve was converted to a DSC curve as described above (in this case with the K curve for alumina crucibles). DSC821^e: 8.429 mg in a 40 µl aluminum crucible with a hole in the lid. Both DSC curves were normalized with respect to sample weight.

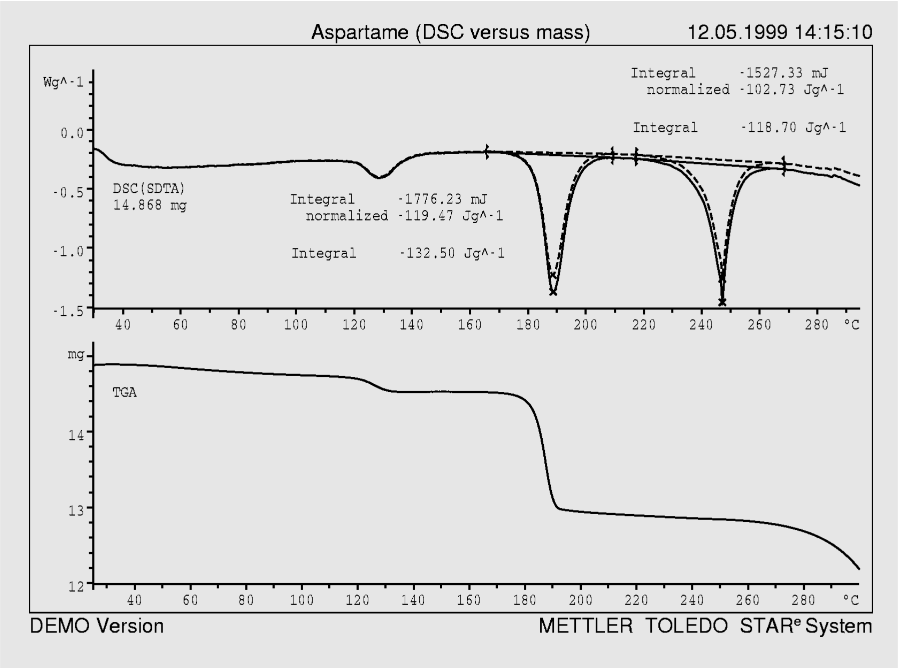

Fig. 4. DSC curve of aspartame (SDTA measurement as described in Fig. 3) normalized with respect to the sample weight (constant reference weight), upper curve (as in Fig. 3). In the lower curve the DSC signal has been normalized with respect to the changing sample weight (TGA curve).

product melts. As shown in Figure 3, the aspartame was measured once with TGA/SDTA and once with the DSC821^e. The comparison of the two DSC curves shows good agreement between the resulting heats of fusion and the decomposition enthalpies, although it is noticeable that the SDTA signal shows an appreciably longer time constant than the standard DSC. The correct transition enthalpies, i.e. the values that refer to the actual sample weights, are only obtained when the weight changes are taken into account. This effect is shown in Figure 4. The heat of fusion of the decomposition product thus increases by 15.5% to 118.7 J/g. The division of measurement curves is an option in the Mathematics evaluation software. If this possibility were not available, the sample weight would have to be determined before each individual effect, which would mean several measurements with reweighing.

Substance	**Melting point [°C]**	**Heat of fusion [J/g]**	**Sample weight [mg]**	**F_{peak} [s°C]**	**Adjust. factor K [mW/°C]**
Indium (In)	156.6	28.4	12.544	65.9	5.4
Zinc (Zn)	419.5	107.5	55.347	62.0	9.2
Aluminum (Al)	660.3	397.0	3.792	97.8	15.4
Gold (Au)	1064.2	63.7	11.133	21.6	32.9

*Table 1. Reference values and measurement data for the substances used (Literature values from the **STAR^e** database)*

Conclusions

The TGA/SDTA851^e module allows DSC measurements to be performed that can be normalized not only with respect to the initial sample weight, but also to the changing weight of the sample. The adjustment curve can be determined with a good degree of accuracy for the entire temperature range and then saved. The Mathematics option in the evaluation software provides the necessary functions for the multiplication and division of curves as well as for polynomial fitting to determine the adjustment curve.

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DSC of human stratum corneum

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Drug penetration and penetration acceleration

The passage of drugs though the skin barrier, the human stratum corneum (HSC), is often too slow for local, regional or systemic therapeutical purposes. This outermost layer of cells of the epidermis (thickness 10-15 µm) consists of dead, flattened and keratinized cells, embedded in a lipid matrix. The penetration can on the one hand be accelerated by increasing the solubility of the particular drug in this barrier. The mechanism for this would be through penetration of the ointment excipients (vehicle) or through additional penetration accelerator in the HSC. Alternatively, the penetration can be accelerated by increasing the diffusion coefficient of the drug in the barrier. In general, this results through interaction of the vehicle or the penetration accelerator with the HSC lipids in the sense of a fluidization leading to a lower state of order of lipid double layers, i.e. a loosening of the packing through increased mobility of the lipid chain [1].

DSC investigations of isolated humanem stratum corneum

Measurement of the effects of penetration accelerating substances on HSC by DSC

Specific interactions between vehicles or penetration accelerators and components of the HSC that change the structure of the horny layer and affect penetration, can be detected with the aid of DSC [2, 3, 4]. If isolated HSC is examined, four main characteristic endothermic peaks can be identified in the DSC curve (Table 1). The interactions mentioned lead to changes in the phase transitions with regard to peak position, peak area and peak width (Table 2, Figs. 2 - 4).

Peak 1: ~ 40 °C	is generally regarded as the transition (melting) of the sebum lipids; this peak is not always visible (in the 2nd heating run: Ta).
Peak 2: 70-75 °C	reversible phase transition of the stratum corneum lipids from a lamellar gel state to a liquid crystalline state through the melting of hydrocarbon chains of the free lipids inside the double layers.
Peak 3: 80-85 °C	T3 corresponds to the irreversible rupture of associations between lipids and proteins of the corneocyte membrane. When heated a second time, peak 3 is displaced to lower temperatures and is then overlapped by peak 2 (Tb). The area or enthalpy of Tb is consequently increased by the same amount. The previously associated lipids now behave as free lipids.
Peak 4: 105 °C	Denaturization through an irreversible conformational change of the proteins (transition from α- to β-Keratin in the corneocytes); they are usually only detectable above a water content of about 15%, can no longer be observed in the second heating run.

Table 1. Phase changes in human stratum corneum [2 – 13]

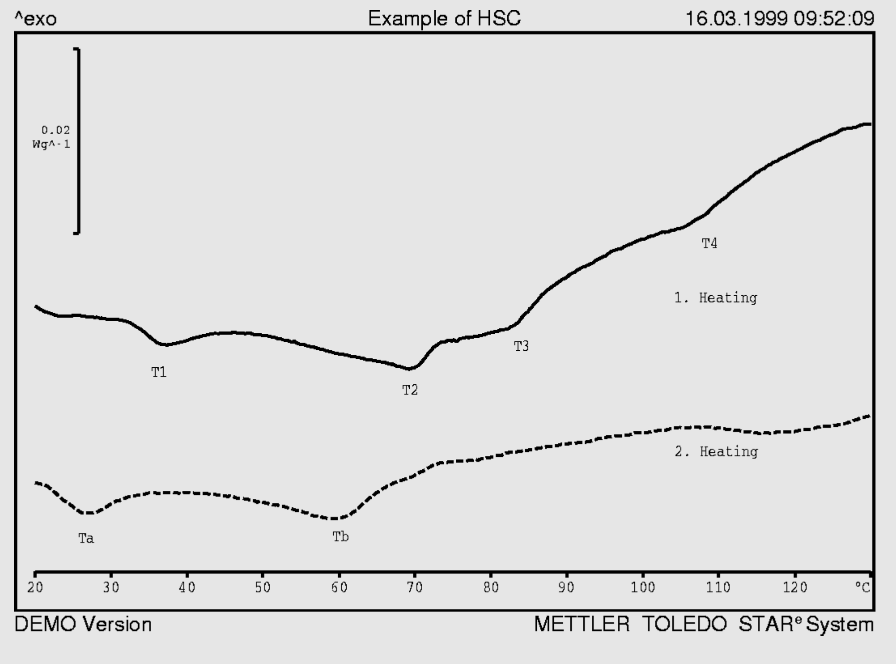

Fig. 1. Typical DSC curves of HSC, 1st and 2nd heating runs

Evaluation of the DSC curve

The lipid phase transitions are characterized using the positions of the peak maxima, which are treated as being equal to the phase transition temperatures. The peak areas or phase transition enthalpies vary appreciably. The values for double peaks are determined from the sum of the individual peak areas and are given per mass unit. The data determined in this way are compared with the values for the untreated horny layer of the relevant skin section and the difference given in °C (peak maximum) or in % (enthalpy).

Practical limits of significance (Table 3) for the assessment of changes in the phase transition temperatures and enthalpies are then applied. These limits result from the repeated measurement of untreated samples of horny layer from the same skin section and determine the degree of variation of the quantity measured.

Investigation material

The isolation of the HSC was done according to the method of Kligman and Christophers [14].

The samples of horny layer were stored until measurement on wire mesh at room temperature in a dessicator over silica gel. This guaranteed that the samples could be stored for a long time [7].

Besides HSC, similar horny layer samples of mammals such as pigs, mice or cows are also suitable for DSC studies [12].

Sample preparation

- untreated:
  conditioning for at least 4 days over silica gel at room temperature (~ 10% relative humidity) ➞ ~ 4% H_2O in the sample
- higher relative humidity (approximation to in-vivo conditions):
  conditioning for 3 days in hygrostats over saturated NaCl solution at 32 °C (~ 75% relative humidity) ➞ ~ 15% H_2O in the sample
- incubate with vehicle or penetration accelerator:
  - wet the sample, store at 75% relative humidity at 32 °C for 12 hours
  - press out the sample between cellulose
  - condition the sample at higher relative humidity as descibed above.

Measurement parameters

Instrument:	DSC821^e
Crucible:	medium pressure, 120 µl
Measurement range:	-20 °C – 140 °C
Heating rate:	2 K / min
Purge gas:	nitrogen, 80 ml/min
Sample weight:	15 – 20 mg

The samples were folded several times and pressed firmly into the crucible; the contact with the bottom of the crucible is of decisive importance for good heat flow transmission.

Examples of investigations

Change	**possible causes**
A T_{Peak} constant, decrease of ΔH	Dissolution of the stratum corneum lipids by the vehicle or the penetration accelerator
B T_{Peak} lowered, decrease of von ΔH	Lowering of the state of order of the lamellar gel structure of the stratum corneum lipids, possibly with additional dissolution of the stratum corneum lipids Selective dissolution of structure promoting cholesterol from the double layers
C Disappearance of the phase transitions	Complete fluidization or dissolution of the lipids

Changes in the DSC curve and possible causes

Position of the peak maxima or phase transition temperatures		
$\Delta T_{Peak} \geq 2.4$ °C	++ / --	very marked increase / depression
$\Delta T_{Peak} \geq 1.2$ °C $\wedge$ < 2,4 °C	+ / -	marked increase / depression
$\Delta T_{Peak} < 1.2$ °C	o	effects within the limits of significance
Changes in the peak area or phase transition enthalpy		
$\Delta H \geq 20\%$	++ / --	very marked increase / decrease
$\Delta H \geq 10\% \wedge < 20\%$	+ / -	marked increase / decrease
$\Delta H < 10\%$	o	effects within the limits of significance

Table 3. Practical limits of significance for changes in DSC features

Influence of the vehicle

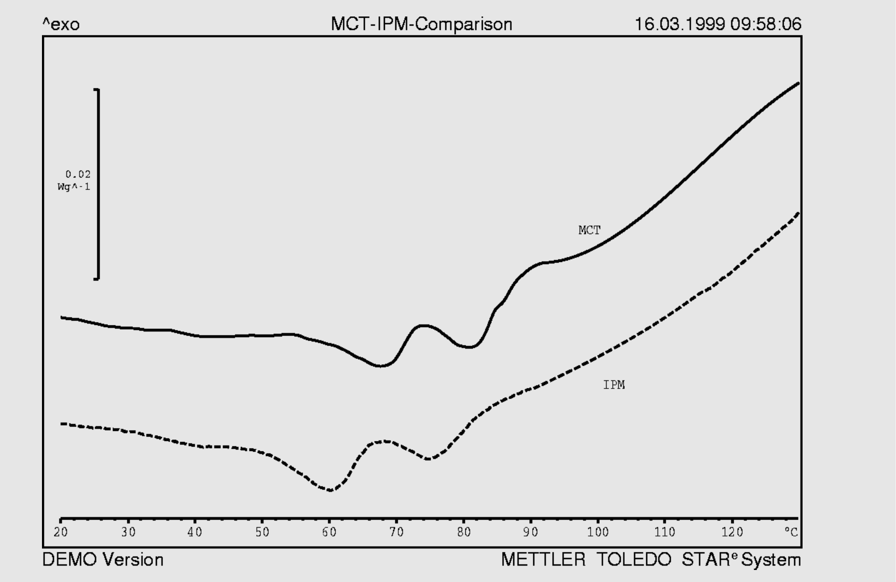

Fig. 2. Comparison of the DSC curves of HSC after treatment with neutral oil (MCT) or isopropyl myristate (IPM), in each case the first heating run. Decrease of T1, T2 and ΔH through IPM pretreatment (see Table 2, B).

Effect of oleic acid as penetration accelerator

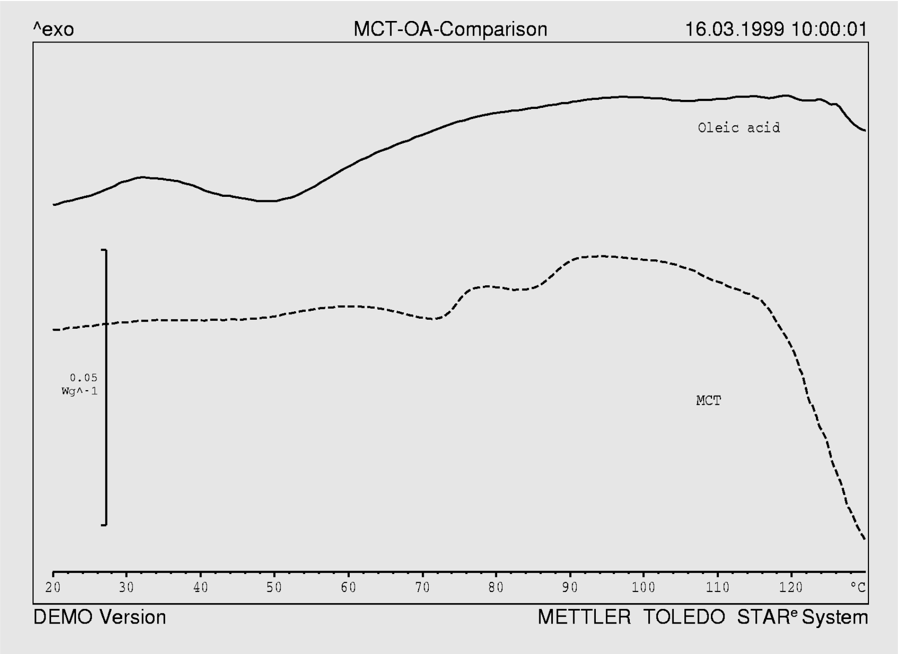

Fig. 3. Comparison of the DSC curves of HSC after pretreatment with neutral oil (MCT) or oleic acid, in each case the first heating run. The phase transitions have practicaly disappeared on account of the pretreatment with oleic acid (see Table 2, B or C).

Propylene glycol

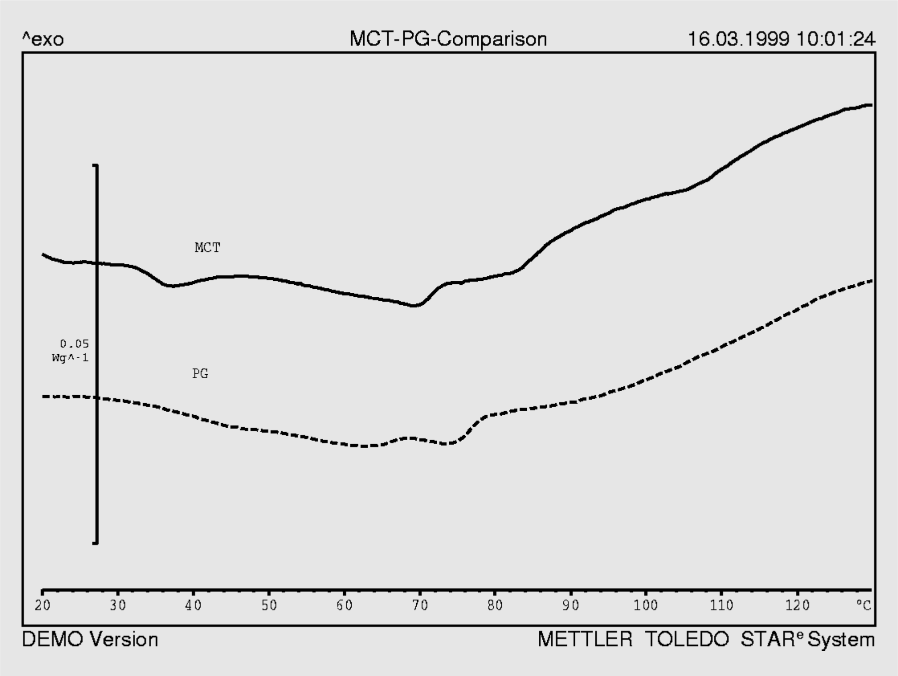

Fig. 4. Comparison of the DSC curves of HSC after pretreatment with neutral oil (MCT) or propylene glycol (PG), in each case the first heating run. Decrease of T1, T2 and ΔH through PG pretreatment (see Table 2, B).

Conclusions

DSC measurement of isolated human stratum corneum is an effective method to detect specific interactions of vehicles or added penetration accelerators with components of HSC and to investigate the mechanisms involved. The comparison of the effectiveness of different substances as penetration accelerators is possible [4].

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Tips

Influence of the crucible on the results of thermogravimetric analysis

With the aid of thermogravimetric analysis (TGA), the thermal decomposition of a sample in an inert atmosphere, or a chemical reaction in the presence of a reactive gas can be investigated. Whilst an inert gas has only an indirect influence on the decomposition reaction, the use of a reactive gas has a direct effect on the reaction process because of the contact between the sample and the gas. This interaction can be influenced by the position of the sample in the TGA furnace, by the nature of the surface and the size of the sample as well as by the type of crucible. For example, the gas exchange should be better in a shallow crucible rather than in a tall crucible.

In order to satisfy the many requirements in thermal analysis, we offer a large range of different crucibles [1]. For TGA measurements, crucibles made of alumina are frequently used (see Table 1). The user can select the optimum crucible for his own specific purposes from this range.

Volume in µl	Base area in mm²	Height in mm	Order number
900	113	10.0	51119960
150	50	4.5	24124
70	28	4.5	24123
30	28	2.5	51140843

Table 1. Alumina crucibles used

The effect of the crucible on the measurement curve will be demonstrated using the thermogravimetric analysis of an elastomer as an example. The measuring module was a TGA/STDA851^e. Samples with masses of 4.0 ±0.2 mg were placed in the center of each crucible and heated up to 900 °C at 30 k/min with a purge gas flow rate of 50 ml/min. At 600 °C the purge gas was switched over from nitrogen to air. Typical curves are shown in Figure 1.

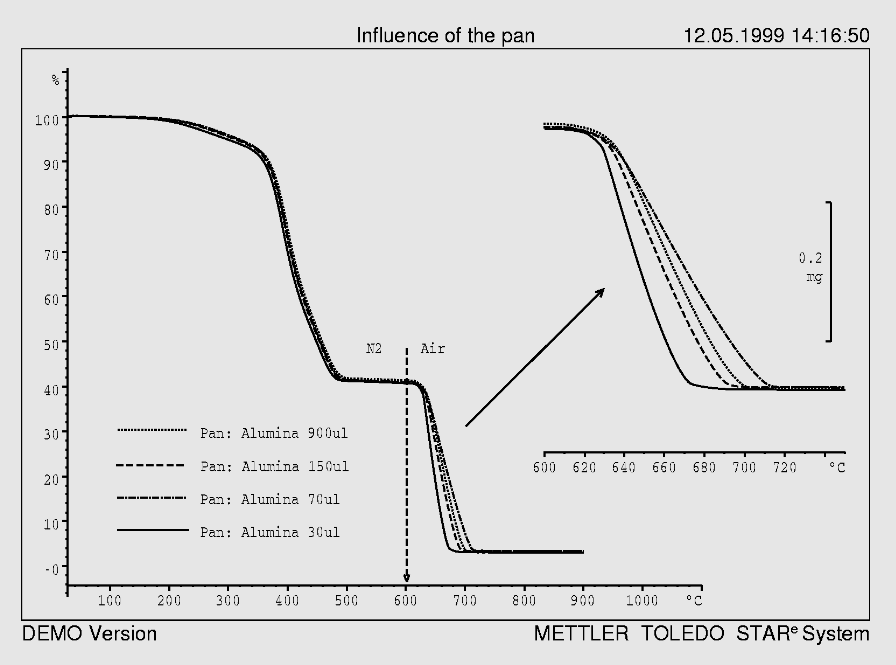

Fig. 1. TGA curve of the thermal degradation of an elastomer, measured in different crucibles (heating rate : 30 K/min, gas flow: 50 ml/min; switch over from nitrogen to air at 600 °C.

The thermal degradation of the sample takes place in three steps in the temperature range 200 °C to 500 °C. The sample weight has at this point been reduced to 43% of the initial sample weight. The remaining components are essentially soot and other solid residues[2]. Switching over the gas to air enables the carbon to be oxidized.

The measurement curves show that thermal decomposition in an inert atmosphere does not primarily depend on the type of crucible used. The removal of the gaseous products liberated from the surface of the sample is in any case possible. Things are quite different when a reactive atmosphere is used. In this case a good gas exchange at the surface of the sample must be guaranteed. This gas exchange process depends on the geometry of the crucible. With reduced gas exchange the measurement curve is broadened. It can be clearly seen in Figure 1 that the degradation reaction is slowest in the 70 µl crucibles. In this case the sample is in a crucible with relatively high walls and small base area. Less broadening is obtained when the base area is increased, as is the case with the150 µl and 900 µl crucibles. If one makes sure that gas exchange is practically unhindered, then optimum results can be obtained. This is the case with the shallow 30 µl crucibles.

Conclusions

The geometry of the crucible has an influence on TGA curves. This effect should be taken into account when using reactive gases and can be reduced by using shallow crucibles (30 µl crucibles). This type of crucible also minimizes the broadening of the measurement curve. An improvement of the temperature and the time resolution of the TGA curve is thereby achieved.

These considerations and effects are especially important when kinetic evaluations are made on the basis of such measurement curves.

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