USER COM

Information for users of
METTLER TOLEDO thermal analysis systems

June 1997

Dear customer

Thermal analysis, today an established and dependable analysis method, has seen a few changes in recent years. The requirements regarding the results (accuracy and traceability) have increased enormously.
On the other hand, costs are being tightly squeezed in this field the world over.
Mettler-Toledo recognized both trends at an early stage. With the **STAR**^{e} system the two requirements can easily be met.
Innumerable robots have been working dependably around the clock since the launch in 1993 and help save costs.

Contents

Crucibles in thermal analysis

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TA TIP

General remarks

Crucibles are used as sample containers in thermoanalytical measurements. The crucible has a great influence on the quality of the results. Selection of the crucible, especially with DSC instruments, influences important system properties such as signal time constant and calorimetric sensitivity. A few considerations before the measurement frequently help save a great deal of time later in the interpretation of the curve.
The following points are important, especially in DSC and SDTA measurements:

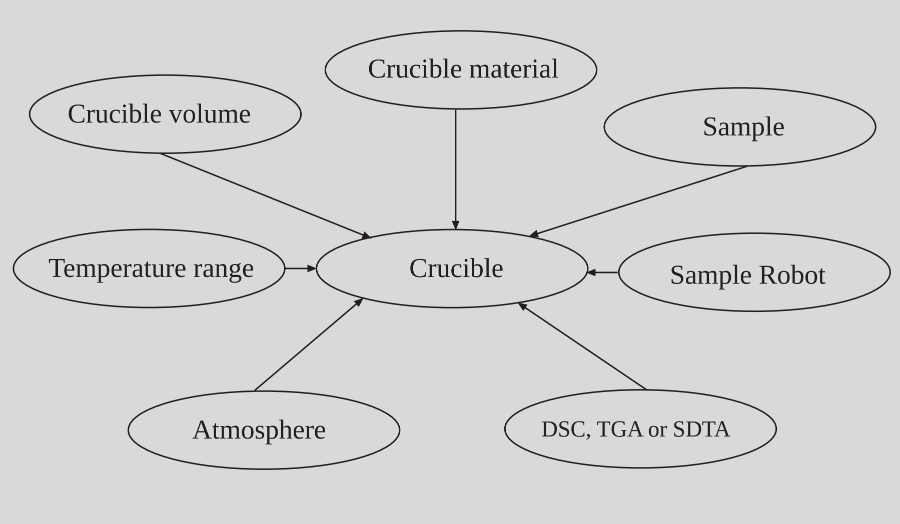


Fig. 1: Factors Influencing the choice of crucible

- Protection of the measuring system against direct contact with the sample -> no contamination of the DSC sensor or the SDTA sample holder.
- In DSC the shape and the heat capacity of the crucible influence the specifications of the DSC cell such as the calorimetric sensitivity and the signal time constant. A short time constant results in tall and narrow peaks and thus a good resolution of effects close together.
- The high heat conductivity of the crucible material and the flat bottom of the crucible enable an optimum heat transfer with minimum temperature

gradients between sample holder and sample.

- Usually the pan material should be inert, i.e. there should be no interaction with the sample in the measured temperature range. Exceptions: copper stability of polyolefins or lubricants measured in a copper pan as well as certain chemical reactions determined in the catalytically active platinum crucible.
- The pan material should not undergo any physical transitions in the temperature range used. Especially important is a sufficently high melting point.
- The crucible also defines the contact of the sample with the cell atmosphere. We distinguish three different types
  - hermetically sealed, pressure resistant pan
  - “self generated atmosphere” where volatile products remain in the pan without causing a considerable pressure increase. The sample is in equilibrium with its volatile products. This is obtained by pressing the lid in the light Al pan. With the standard Al pan you pierce a very small hole in the lid (diameter 20 to 50 µm, check it under the microscope) or you scatter approx. 1 mg Aluminum oxide powder on the rim before sealing. This creates small channels for the diffusion of gases.
  - Free access of furnace atmosphere in the open pan. To protect the cell from creeping or splashing samples a pierced lid is often used. For this purpose the lid is pierced once or even several times with the pin (diameter approx. 1 mm).
- Particularly but not exclusively for TGA measurements using the automatic sample robot, the waiting times on the turntable, might cause certain samples dry out or absorb water or oxygen from the atmosphere. To solve the problem there are two possibilities:
  - The aluminum oxide crucibles can be protected against direct ingress of air by covering them with an aluminum lid. This lid is removed during the measurement.
  - The aluminum pan with its piercable lid is gas tight during waiting. Just before the measurement the sample robot penetrates the lid.
- Hermetically sealed DSC crucibles should be weighed before and after the measurement. If the weight loss remains below approx. 30 µg (surface moisture), the pan remained tight.

Selecting crucibles for DSC measurements

Often you will use the *standard* or *light Al pan*. If a first measurement doesn’t show the expected thermal effects try a second measurement with as much sample as possible or with an expanded temperature range (50 to 100 °C higher). If there is still no effect on the curve try the *tall Al pan* with as much sample as possible.

There are also other reasons for using special crucibles:

- You insist on best peak separation and therefore use the *light Al pan* and /or helium as a purge gas. You can often separate physical transitions occurring very near each other, i.e. two peaks within a few seconds or less as seen, e.g. with liquid crystals. Remark: the resolution is also enhanced by a smaller sample size.
- You suspect chemical reactions of your sample with aluminum and look for a chemically stable crucible: *medium pressure crucible* made of stainless steel, *high pressure crucible* made of stainless steel (gold plated) or *gold pan.*
- You suspect insufficient sealing strength, e.g. when heating an aqueous solution above 130 °C and look for a pressure resistant crucible: *medium pressure crucible* made of stainless steel or *high pressure crucible* made of stainless steel (gold plated)**.**

Selecting crucibles for TGA measurements

Normally, you would employ the 70 µl *aluminum oxide crucible*. But thermogavimetry is another method where you may wish to use special crucibles:

- You place great importance on informative SDTA curves and use the platinum crucible or, below 640 °C, an aluminum crucible. Caution: melting metals readily form an alloy with platinum resulting in a hole in the crucible.
- Since your sample has a very low

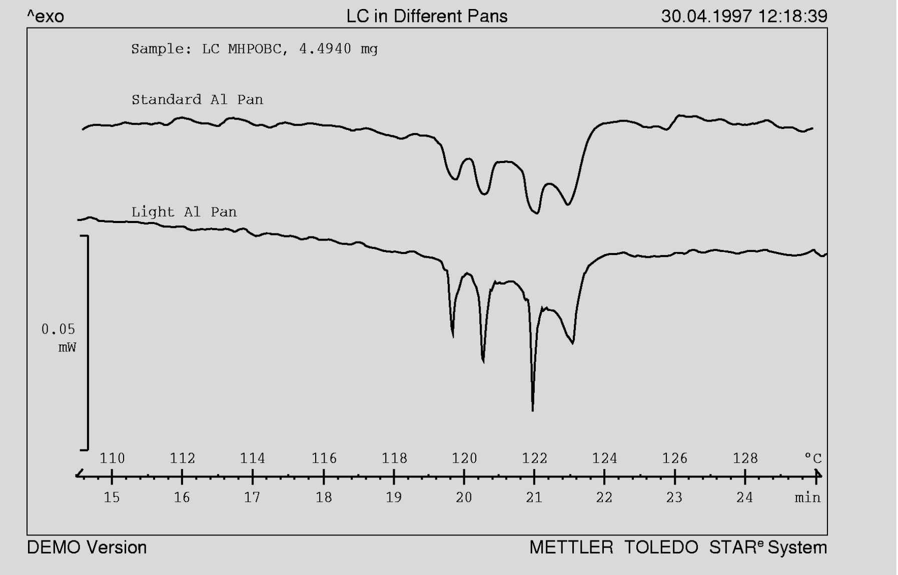


Fig. 2: Measurement of a liquid crystal with 2 K/min in the light Aluminum crucible showing the better peak separation

volatile fraction or is very inhomogeneous, you would like to use as much sample as possible. You can use larger crucibles in the TGA/SDTA851^{e}/LF: 150 µl platinum or aluminum oxide crucible or the 900 µl aluminum oxide crucible.

- You work with the automatic sample robot and wish to avoid adverse changes in your sample during the wait time. In this case, you should use the aluminum pans with piercable lids (40 or 100 µl).

Comments on the individual crucibles

Standard Al pan:
According to the needs you seal this pan hermetically (to suppress endothermal peaks caused by vaporization, evaporation or sublimation of volatile material) or you pierce the lid to obtain a self-generated atmosphere or free access to the surroundings.

Light Aluminum pan:
This pan has the shortest signal time constant especially in conjunction with helium purge gas. It is very suitable for pressing films, disks or powders to the bottom. The tight gap between pan and lid creates a self-generated atmosphere. However, free access to the atmosphere is also possible when the lid has been pierced prior to closing the pan. Closing requires a special tool kit for the crucible sealing press.
Standard aluminium pan versus light aluminium pan Figure 3 shows how the pan mass and the atmosphere used influences the shape of a melting peak. If we define the shape factor to be height divided by width, we get 8.7 for the Al standard pan in air, but 17.3 for the new light Al pan and helium.

Measurement conditions: DSC821^{e}, 5.0 mg azoxydianisole, 20 K/min.

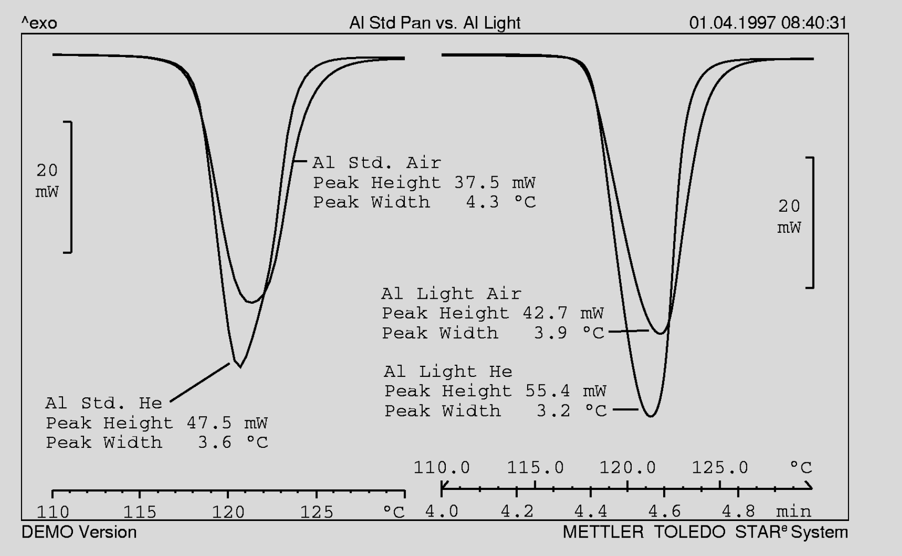


Fig. 3: Comprison of the Light and Standard Aluminium crucible

Polymorphic transitions are more strongly influenced by the crucible mass and the atmosphere than are melting peaks. For such comparisons a new sample must be used for each measurement. (see Application 3016 on Polymorphism).

Measurement conditions: DSC821^{e}, 5.0 mg sulfur, 20 K/min

Aluminum oxide crucibles:
These crucibles are especially suitable for thermogravimetric measurements. They can be reused (after mechanical cleaning and if need be soaking in water and heating to redness) and covered by a pierced lid to prevent the sample splashing.

Copper pan:
This pan is supplied without lid. It is used to determine the oxidative stability in the presence of the catalytically active copper.

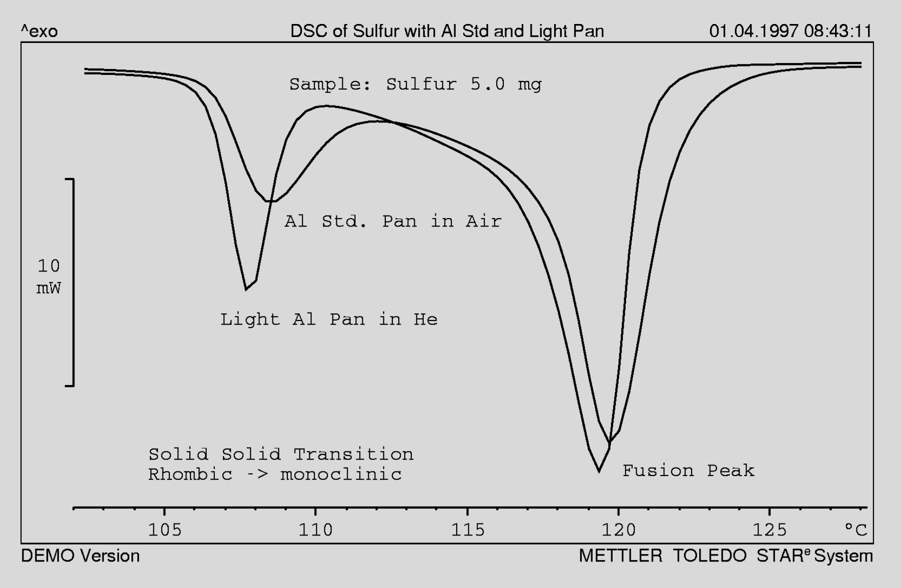


Fig. 4: DSC measurement of sulfur in the Light and Standard Aluminum crucible

Gold pan:
Gold is chemically stable but unfortunately very expensive. After extended storage there is some precipitation on the surface that hinders cold welding. To solve the problem, heat pan and lid to approx. 500 °C prior to use. Caution: melting metal samples can form alloys causing a hole in the pan.

Platinum crucible:
These crucibles are used primarily at temperatures above 640 °C . Caution: melting metals can easily form alloys causing a hole in the pan. They can be resused. After mechanical cleaning, if need be immerse in water (many salts are water soluble) and heat to redness.

Medium pressure crucible made of stainless steel:
Place the O-ring in the lid and weigh the sample into the crucible. Press the lid onto the crucible and seal it in the crucible sealing press (equipped with the special female and male die). The crucible can also be used open or closed without an O-ring (self-generated atmosphere) .

***High pressure crucible made of gold plated steel* for press fit:**
A stopper is pressed into the crucible with a force of around 1 metric ton so that a membrane which serves as both a seal and a bursting disk seals the crucible tightly. A toggle press is used as the sealing tool. This crucible has well proved its worth in the field of safety investigations.

***Reusable pressure crucibles (steel or gold plated steel)*:**
Threaded, these crucibles are easy to seal with the appropriate tool. After the measurement, they can be opened, cleaned and reused around 20 times with a new gold plated copper seal. Should the crucible base exhibit burrs owing to multiple use, these can easily be removed with a polishing cloth.

New ceramic sensor (FRS5) for the DSC82X instruments

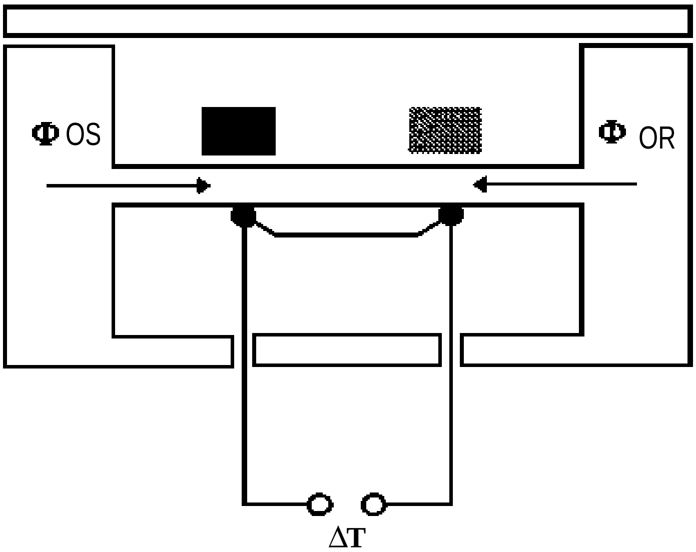


Fig. 5: *Cross section of the DSC cell with the 14 pile Ceramic sensor*
Φ OS: *Heat flux from furnace to sample*
Φ OR: *Heat flux from furnace to reference*
ΔT: *Temperaturdifferenz*

A further step in DSC sensor development at METTLER TOLEDO

When Mettler first launched a DSC instrument on the market in 1971, this was accompanied by the introduction of a new type of sensor. The temperature was measured by not only one sensor but several thermocouples connected in series resulting in an averaging of the temperature and a higher signal gain. The measured temperature difference between sample and reference is converted into a heat flux using a calibratable sensor characteristic curve (heat flux principle).
In order to manufacture such a small sensor with several thermocouples, special manufacturing know-how is required. The thermocouples are vapor deposited on a substrate. This technology has been developed further and improved. The present-day ceramic sensors are manufactured using a patented screen printing process (patent “Multiple temperature sensor”, US Pat. 5,033,866). The latest offspring in this sensor family (glass sensor, metal sensor, 14-thermocouple ceramic sensor) is the full-range sensor 5 (FRS5).

Photo 1: New DSC sensor (FRS5)

Heat flux measurement in the usual DSC instruments

With the DSC sensor, the temperature difference between the sample and the reference sides is measured with a thermocouple under the crucibles (Fig. 5). The measured temperature difference is proportional to the amount of heat evolved or absorbed by the sample. This thermocouple arrangement has one disadvantage. The ideal, thermal symmetry of the measuring cell can be reached only approximately in reality (manufacturing tolerances, furnace cover seating, varying crucible position). Temperature gradients can thus not be completely avoided without an unreasonable amount of work. Owing to the relatively large distance between the sample and the reference sides, troublesome temperature differences arise. These can not be clearly distinguished from the temperature difference due to the sample and lead to signal disturbances.

Heat flux measurement with the new ceramic sensor (FRS5)

With the new ceramic sensor (FRS5), the temperature difference decisive for the heat flux is measured directly on the sample and reference sides (Fig. 6). The measurement signal is formed from the difference between the two temperature differences. Even though temperature gradients still exist, they thus disturb the measurement signal very much less. This appreciably simplifies interpretation of the curve.
As with the existing sensor, the new sensor is manufactured by the screen printing process patented by Mettler-Toledo. On the DSC sensor there are now 28 thermocouples on both the sample and reference sides connected in series and arranged radially around the crucible support. This assures a heat flux acquisition with minimal leaks and generates a relatively large signal for the measuring amplifier. Together with a good amplifier, this leads to a very favorable signal to noise ratio.

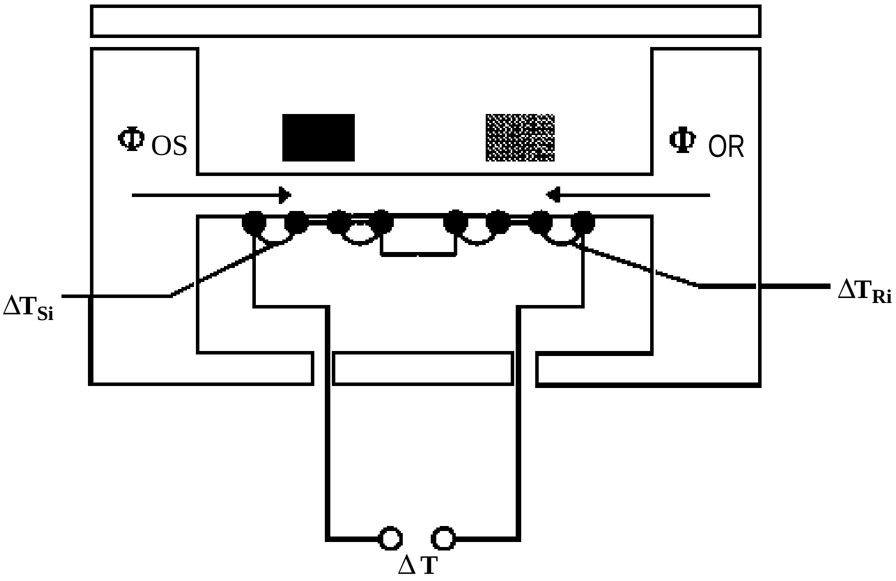


Fig. 6: Cross section of the DSC cell with new 56 pile Ceramic sensor (FRS5)
Φ OS: *Heat flux from furnace to sample*
Φ OR: *Heat flux from furnace to reference*
Δ T: *Temperature difference*
$\Delta T = \sum \Delta T_{Si} - \sum \Delta T_{Ri}$

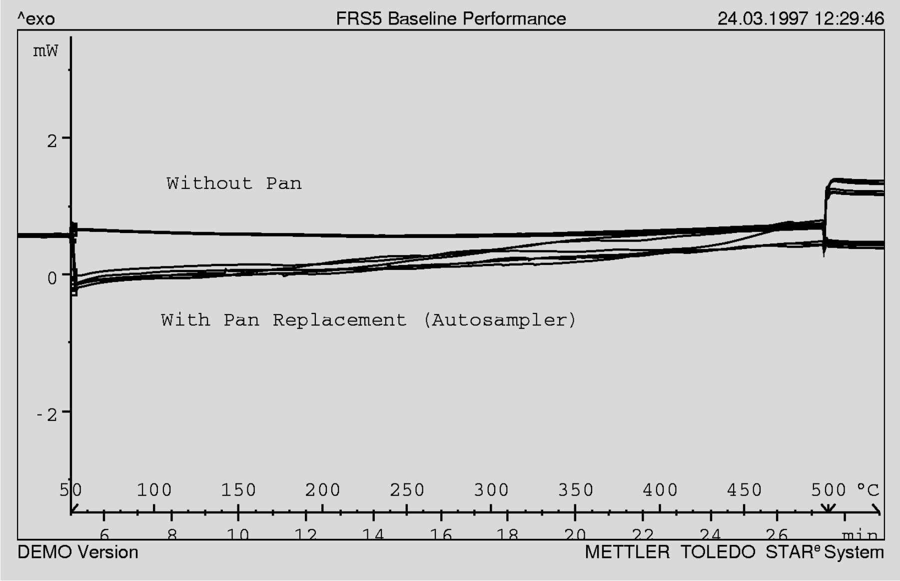


Fig. 7: Baseline reproducibility with and without pan

Features of the new ceramic sensor (FRS5)

- Extremely high chemical resistance as the thermocouples are protected by a hard ceramic coating.
- Temperature range from -150 to 700 °C (full range).
- High sensitivity as 28 thermocouples (Au-Au/Pd) connected in series are positioned beneath each crucible.
- Low drift thanks to new arrangement of the thermocouples.
- Relatively insensitive to sensor installation.
- Improved long-term stability of the baseline and hence greater accuracy of the cp measurement (Fig. 7).
- Low signal time constant of approx. 2.3 s with the light aluminum crucible.
- Interchangeability: All DSC82x instruments can be retrofitted with the new sensor.

STARe SW V5.0 (SOLARIS)

With software version V5.00 we are switching from interactive UNIX to SOLARIS UNIX. This opens up completely new possibilities for you. We are now in a position to increase the screen resolution and support new and modern HW resulting in shorter system response times. SOLARIS also offers a Windows (WABI) environment so that you can use other programs at the same time as the TA program. For instance, during the measurement you can already start to write reports in MS Word. In addition to these possibilities opened up by the new operating system, we have naturally also developed our own **STARe** software further and have implemented the following new features:

Storage of user settings
When a program is started, the values of all settings are automatically set to those when the program was last quit. They are thus specific to each user.

Storage of programs
When SOLARIS is started, all programs (e.g. evaluation window) which you had open before exiting SOLARIS are restarted.

Multiexport/import of files from diskettes
Analogous to the DOS data import, you can now export or import several files at once.

Log axes
With the abscissa and the ordinate, you can select between a linear or a logarithmic representation (suitable primarily for MS and FTIR curves)

Calibration with more than 3 substances
With more than 3 different substances, a 2nd order correction curve is now calculated with all calibration types (a, b and c values are changed).

Glass transition
The glass transistion evaluation has been expanded so that all standards known to us are supported (there is unfortunately no unambiguous international definition of Tg).

Model-free kinetics
The model-free kinetics have been further developed by Dr. S. Vyazovkin. The integral $\int \exp(-E(\alpha)/(R\cdot T))d\alpha$ was previous calculated with the approximation $R\cdot T^2/E(\alpha)\exp(-E(\alpha)/(R\cdot T))$, which strictly speaking applies only when $2R/T/E(\alpha) \ll 1$.
This integral is now calculated completely numerically with a new algorithm (nonlinear isoconversional method) developed by Dr. S. Vyazovkin.

New crucibles

Our crucible range has been expanded and we are now satisfied that we can offer the appropriate crucible for all types of applications. All new crucibles are suitable for automatic operation (without centering pin) with the universal gripper. The new crucibles have been optimized with regard to low mass and good thermal behavior resulting in low signal time constants. They can thus measure extremely small effects.

Crucible	Volume:	Pressure	Material:	Mass:	Time constant:
Light Aluminum crucible	20 µl	-	Aluminum	C: ca. 12 mg L: ca. 8 mg	2.3 s
Reusable High pressure crucible	30 µl	150 bar (15 MPa)	Steel, gold plated Steel M; gold plated copper	C: ca. 300 mg L: ca. 280 mg M: ca. 70 mg	11.0 s 6.0 s
Copper crucible	40 µl	-	Copper	C: ca. 70 mg	2.7 s
Gold crucible	40 µl	2.5 bar (0.25 MPa)	Gold	C: ca. 250 mg L: ca. 130 mg	3.0 s

C : Crucible L: Lid M: Membrane

Our crucible range at a glance

New in our crucible range:

51 119 810	Light aluminum crucible	20 µl	100 Pcs	(Crucible and lid)
51 140 405	High pressure crucible (Steel, gold plated)	30 µl	3 Pcs	(Crucible and lid)
51 140 404	High pressure crucible (Steel)	30 µl	3 Pcs	(Crucible and lid)
51 140 403	Gold seal for high pressure crucible		60 Pcs	
51 140 407	Copper crucible	40 µl	100 Pcs	(Crucible)
27 220	Gold crucible	40 µl	6 Pcs	(Crucible and lid)

The light aluminum crucible and the reusable high pressure crucible need special sealing tools.

51 140 547	Special male and female dies to press the lid into the light aluminum crucible (can be mounted on the standard crucible sealer)
51 119 915	Crucible sealer for the reusable high pressure crucibles with defined torque

The following are still carried in our product range:
For sample robot (all without pin):

00 026 763	Aluminum standard	40 µl	100 Pcs	(Crucible and lid)
51 119 870	Aluminum standard	40 µl	400 Pcs	(Crucible)
51 119 871	Aluminum lid	-	400 Pcs	(Lid)
51 119 872	Aluminum	100 µl	400 Pcs	(Crucible)
51 119 873	Lid for piercing	-	400 Pcs	(Crucible)
00 024 123	Aluminum oxide	70 µl	20 Pcs	(Crucible and lid)
00 024 124	Aluminum oxide	150 µl	20 Pcs	(Crucible and lid)
51 119 460	Aluminum oxide	900 µl	4 Pcs	(Crucible and lid)
51 119 654	Platinum (*)	70 µl	4 Pcs	(Crucible and lid)
00 024 126	Platinum (*)	150 µl	4 Pcs	(Crucible and lid)
00 029 990	Medium pressure crucible	120 µl	25 Pcs	(Crucible and lid)
00 026 731	High pressure crucible (gold-plated steel with gold seal)	50 µl	25 Pcs	(Crucible and lid)

(*): only suitable for automation without platinum lid

For special applications:

00027331	Aluminum standard	40 µl with pin	100 Pcs	(Crucible and lid)
00027811	Aluminum	160 µl with pin	40 Pcs	(Crucible and lid)
00027812	Glass crucible	100 µl	50 Pcs	(Crucible)
00026929	Medium pressure crucible	120 µl with pin	25 Pcs	(Crucible and lid)
00026732	High pressure crucible (gold-plated steel with gold seal)	50 µl with pin	25 Pcs	(Crucible and lid)
00650072	High pressure crucible Nimonic (Steel with gold seal)	270 µl with pin	1 Pcs	(Crucible and lid)
00650066	High pressure crucible Nimonic (Steel with gold seal)	500 µl with pin	1 Pcs	(Crucible and lid)

Thermoplastics handbook

The Thermoplastics handbook, appropriate for the software database, is now available in English (English ME 51 725 002, German ME 51 725 001).

The use of thermal analysis to estimate shelf-life of drugs

Active components of drugs are usually not thermally stable. Even when stored at ambient temperature, drugs undergo various chemical changes that influence their pharmaceutical activity. It is therefore important to know the shelf-life (the time during which a drug preserves its activity) of drugs. Directly evaluating shelf-life requires a drug to be kept in a thermostat at slightly elevated temperatures (30-40 °C) for several months. An analysis of samples taken at intervals permits the composition of a drug to be monitored. Under the assumption that the pharmaceutical activity is an immediate function of the concentration of an active drug component, shelf-life may be estimated as the time to reach some critical concentration. While capable of providing reliable values of shelf-life, direct evaluation is a costly and time-consuming procedure.

Thermal analysis techniques (TGA, DSC) in combination with model-free kineties provide a fast track to estimating the shelf-life of drugs. The general strategy is quite simple. A thermal analysis method is used to monitor the rate of the thermal decomposition of a drug subjected to a linear heating program. A kinetic analysis of the data yields parameters of the temperature dependence of the reaction rate. These kinetic parameters are then used to extrapolate the elevated temperature data to ambient temperatures. This way of estimating shelf-lifes places stringent requirements upon reliability of kinetic parameters. The commonly used procedure for evaluating the kinetic parameters E and A in equation

$$d\alpha/dT = k_o \exp(-E/(RT))\, f(\alpha)/\beta \quad (1)$$

(where α is the extent of conversion, T is the temperature, β is the heating rate, k_o is the preexponential factor, E is the activation energy, R is the gas constant) by force-fitting of experimental data to different reaction models, $f(\alpha)$, does not meet these requirements for two reasons. Firstly, this procedure results in a wide range of values of E and k_0 with $f(\alpha)$. Shelf-life can be determined by the equationtation

$$t_\alpha = g(\alpha)/k_0 \exp(-E/RT) \qquad (2)$$

(where $g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha$,$t(\alpha)$ as the time to reach a given extent of conversion at a given ambient temperature). Substituting differing sets of E, k_0 and $g(\alpha)$ into equation 2 results in ambiguous values of shelf-lifes. Secondly, the procedure of force-fitting of reaction models gives rise to a single value of the activation energy which is assumed to hold throughout the entire interval of conversions. However condensed phase reactions generally show multi-step kinetics comprising several elementary steps with different values of the activation energy. The relative contributions of these reactions to the overall reaction rate vary with the temperature. As a result the effective activation energy always tends to vary with the extent of conversion.

All these problems have been resolved in the software option “Model free kinetics”. The software employs a model-independent way of evaluating the activation energy. This allows one to avoid the ambiguity peculiar to kinetic parameters evaluated by force-fitting of the reaction models. Additionally, the new software yields the activation energy as a function of the extent of conversion. This feature makes it possible to predict complex kinetics taking into account an actual variation of the activation energy throughout the entire interval of conversions. It is also important that the method implemented in the new software enables kinetic predictions to be made without the knowledge of both the reaction model and preexponential factor [1]. Thanks to excluding A and $g(\alpha)$ from a predictive procedure, we have eliminated corresponding errors inherent in these experimentally determined values. Model-free predictions performed on various reaction systems have shown [1,2,3] a high degree of reliability that cannot be accomplished with the methods based on force-fitting of the reaction models [4].

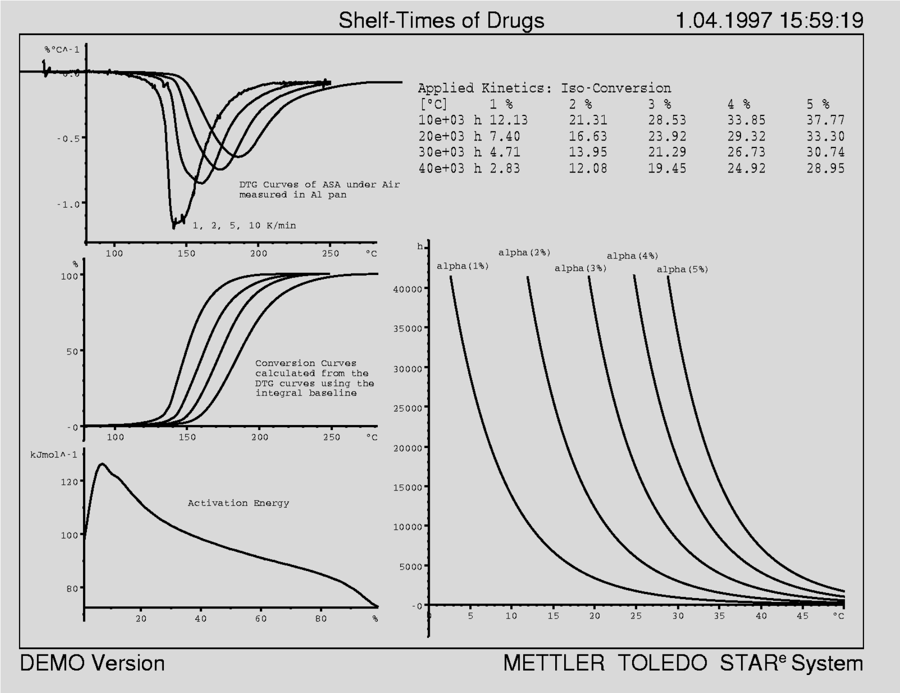
Here, we demonstrate how “Model free kinetics” software can be applied to estimate the shelf-life of drugs. Acetylsalicylic acid is used as an example. Thermal decomposition of acetylsalicylic acid (Merck Darmstadt, article 85) has been studied on a Mettler-Toledo TGA/SDTA851^e instrument.

Conditions:
Instrument: TGA/SDTA851^e
with sample robot
Conditions: Samples of 2...3 mg
Heating rates:1,2,5, and 10 K/min
Atmosphere: Air, 50 cm^3/min

The samples were placed in sealed aluminum pans with a small hole of diameter approx. 50 µm pierced in the lid diameter to suppress sublimation (self generated atmosphere). The TG curves are shown in Figure 8 together with the conversion curves of the first step (T < 250 °C) of decomposition. The model-free kinetic analysis has resulted in the activation energy that varies with the extent of conversion. The occurrence of this dependence unmistakably suggests the thermal decomposition of acetylsalicylic acid is a complex process. In this situation, force-fitting of the reaction models to obtain a single value of the activation energy for the overall process is obviously meaningless.

Conventionally we have chosen shelf-life as the time to reach 1, 2, 3, 4, and 5 % of decomposition. “Model free kinetics” software offers a way of estimating these times in a temperature region of interest. The figure shows the estimated shelf-lifes in the temperature region 20 ... 50 °C which covers the typical interval of ambient temperatures. The estimated times agree with measured shelf-lifes reported in the literature [5, 6].

The present example demonstrates that thermal analysis in combination with “Model free kinetics” software can be an efficient tool for estimating shelf-lifes of drugs. While capable of producing reliable estimates for shelf-lifes of drugs, this approach should not completely replace actual measurements. Its real place is at the stage of preliminary selection of formulations. Because all necessary experiments take only a few hours, this approach can be used to immediately control the effect of an additive on the shelf-life of a formulation. This provides an opportunity to quickly design most stable drug formulations whose long-term tests and detailed studies will most likely be advantageous.



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Applied Kinetics: Iso-Conversion
[°C]      1 %       2 %       3 %       4 %       5 %
10e+03 h 12.13     21.31     28.53     33.85     37.77
20e+03 h 7.40      16.63     23.92     29.32     33.30
30e+03 h 4.71      13.95     21.29     26.73     30.74
40e+03 h 2.83      12.08     19.45     24.92     28.95
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Fig. 8: Estimation of the shelf-time of acetylsalicylic acid

[1] S. Vyazovkin, Int. J. Chem. Kinet., 28 (1996) 95
[2] S. Vyazovkin, N. Sbirrazzuoli, Macromolecules, 29 (1996) 1876
[3] M. S. Kelsey, Am. Lab., January, 1996, p. 13
[4] S. Vyazovkin, W. Linert, Anal. Chem. Acta, 295 (1994) 101
[5] S. R. Byrn, Solid-State Chemistry of Drugs, Academic Press, NY, 1982
[6] D. J. Ager, et al. J. Pharm. Sci.75 (1986) 97

If you are interested please ask for the data sheets of Model Free Kinetics (51 724 784) and Kinetic nth order (51 724 805).

TG-MS coupling

Evaporation or decomposition effects are observed when many materials are heated or conditioned.
These effects can be detected with DTA, DSC or TGA. Unfortunately, these measurement techniques provide no information on which products or fragments are formed, information which would be very useful in many situations.
An additional analysis of these formed gases (also know as Evolved Gas Analysis = EGA) would provide further information on the product under investigation. For this reason, different measurement techniques are frequently coupled with each other online to make use of the information content of both analysis techniques. In the field of thermal analysis, thermogravimetry can be used for such a coupling with mass spectrometry (TG-MS coupling). A special TGA-MS conversion set is thus available for the TGA850 and the TGA/SDTA/851^e which allows coupling with a mass spectrometer in a simple manner.
Such coupling systems are used in many fields, for example in the plastics, pharmaceutical and rubber industries for the detection of either decomposition products, additives or solvents. In the pharmaceutical branch, virtually all products are investigated by thermal analysis for identification purposes or determination of the purity or stability. Control measurements with a coupling of TG and MS can here provide extensive information on the products or the liberated substances in a single measurement. For instance, on the nature and amount of the bound solvent or on an incipient decomposition. The following example (Fig. 9) shows the application of the TG-MS coupling using a pharmaceutical product that has been recrystallized from a mixture of methanol and acetone. The TG curve by itself can show only the time (temperature) and extent of the weight change. It is only with the aid of the superposed experimental curves of the mass spectrometer that an assignment becomes possible. It is apparent that both solvents used in the recrystallization are released in succession at temperatures which lie way beyond the actual boiling point. Both analysis methods together thus result in a complete picture of the ongoing processes which can then be used to optimize the methods used to work up this product.

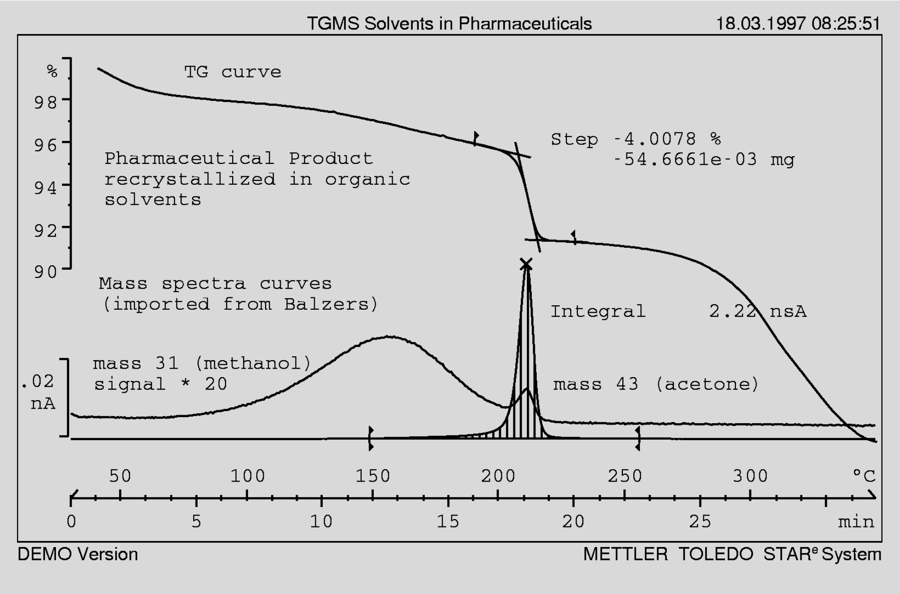


Fig. 9: Superposed TG and MS experimentsal curves of a pharmacuetical product measured with the TGA850 and Balzers ThermoStar. The MS experimental data were imported into the **STAR**^{e} *software as an ASCII file.*

Calcium sulfate measurement

We are pleased to be able to show you a completely new high temperature TGA/SDTA curve. Measurements were performed in the temperature range 1000 to 1600 °C (Fig. 10).
Sample preparation: The anhydrite was prepared from the dihydrate (Fluka 21 245) by heating to 500 °C in a furnace for 10 min.

Experimental conditions:

Instrument: TGA/SDTA851^e (with large furnace)

Sample mass: 41.02 mg

Sample crucible: 70 µl platinum crucible heating rate: 20 K/min

Purge gas: nitrogen

Purge rate: 60 ml/min

Above 1200 °C the SDTA curve exhibits an endothermic peak arising from the solid-solid transition of anhydrite II to anhydrite I.
At higher temperatures, anhydrite I decomposes in 2 steps losing SO_2 and O_2 leaving CaO as residue. The DTG curve shows the 2 individual peaks.
Calcium sulfate occurs naturally in sedimentary rocks in the form of gypsum, calcium sulfate dihydrate.
On heating to 500 °C, it splits off water of crystallization to form anhydrite.

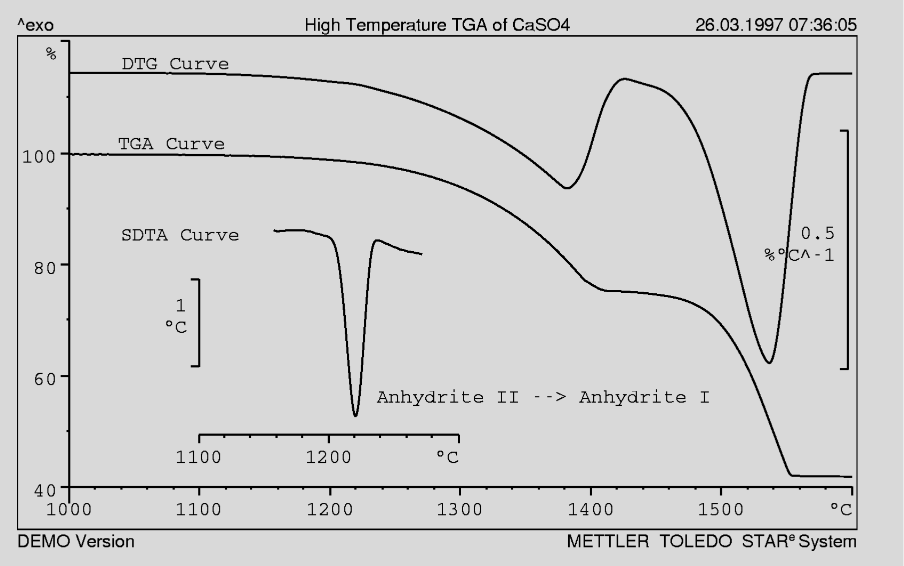


Fig. 10: Calcium sulfate between 1000 and 1600 °C

Determination of the vinyl acetate content by TGA

W. Weber, Huber & Suhner AG, 8330 Pfäffikon/ZH

Principle

Vinyl acetate, VAc, decomposes between 200 °C and 400 °C with loss of acetic acid (Fig. 11). This degradation step can be used to calculate the VAc content in copolymers (EVA types) provided the sample shows no additional weight loss in this temperature range (e.g. water loss from Al(OH)$_3$).

The sample is heated continuously to 850 °C. Adsorbed moisture is removed up to 200 °C . Loss of acetic acid occurs between 200 and 380 °C and thermal destruction of the residual polymers between 390 and 500 °C . From 600 to 850 °C any carbon residues or carbon black are combusted in oxygen. Fillers are found at 850 °C in the form of oxidic residues.

With pure EVA copolymers without fillers, the temperature range up to 600 °C should suffice in most cases.

Apparatus

TG50 with TC15 and the Mettler-Toledo **STAR^e** system

Experimental parameters

Initial weight:	20 to 25 mg
Heating rate:	30 °C/min
Start temperature:	35 °C
End temperature:	850 °C
Gas switching :	at 600 °C from nitrogen to oxygen (200 ml/min)

Evaluation

The mass loss is calculated between 200 °C and 384 °C (DTG minimum at a heating rate of 30 °C/min). This evaluation is done with the horizontal step in the evaluation window. As the step corresponds to the loss of acetic acid, it must be multiplied by a factor of 1.43 for vinyl acetate (Fig. 12).

The method has been checked using 5 commercially available polyvinyl acetate copolymers.

Table

Designation	Producer	VAc content [%] Producers' data	Measured Step height [%]
Lupolen V 2910 K	BASF	8 ± 2	6.88
Elvax 670	DuPont	12± 1	8.66
Escorene UL 00220	Exxon	20± 1	15.16
Escorene UL 00226	Exxon	26± 2	19.63
Evatane 3345	Atochem	33 ± 2	23.86

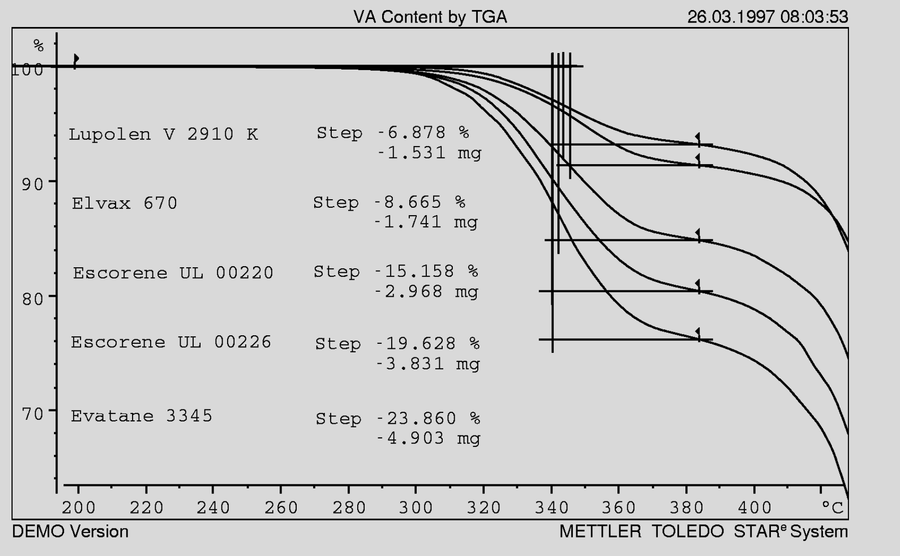


Fig. 11: TGA curves of the investigated copolymers

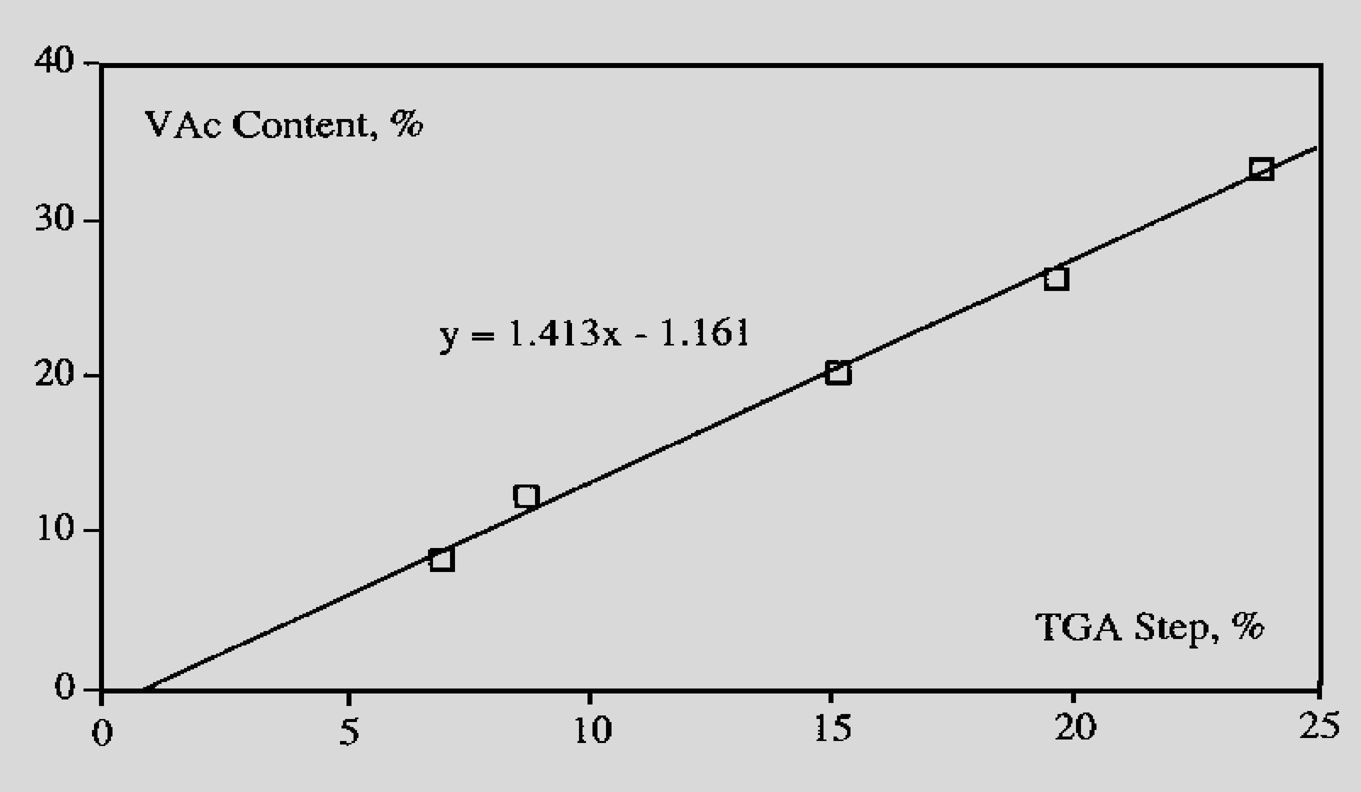


Fig. 12: VAc content and TGA step height with linear regression (the graph does not pass through zero as a small weight loss is also found in the temperature range 200 to 384 °C with polymers free from VAc)

Vinyl acetate content [%] = 1.41 x step height [%] - 1.16 %

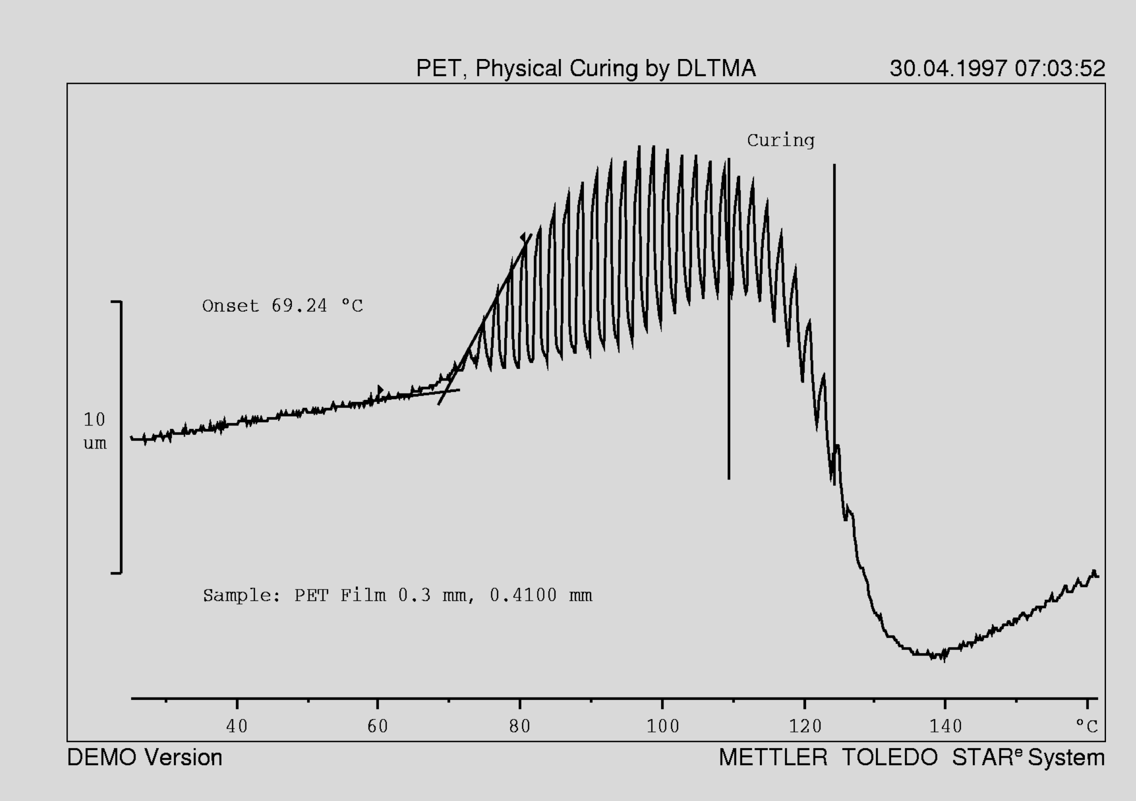
The conversion factor of 1.413 found is slightly less than the stoichiometric factor of 1.43. The reason lies in the weight loss of the PE fraction; this is also why an ordinate intercept of -1.61 % is found.

PET, Physical Curing by Dynamic Load TMA

Sample	Disk of polyethylene terephthalate (Mettler-Toledo tutorial kit)

Conditions

Measuring cell:	TMA40 with 3 mm ball-point probe
Pan:	The sample is placed on a fused silica disk of 6 mm diameter and 0.5 thickness
Sample preparation:	No preparation needed
TMA measurement:	Heating from 25 to 150 °C at 10 K/min
Load:	Changing every 0.01 from 0.19 N, Periode 12 s
Atmosphere:	Static air



Interpretation

With the small mean force of 0.10 N no indentation is visible up to and during the glass transition at 70 °C. On the contrary, the sample becomes slightly thicker owing to stress relief of the previously oriented film. Above T_g the sample responds as a soft elastic to the periodic force change. The maximum amplitude is reached at 95 °C. On further heating the sample undergoes plastic deformation of approx. 15 µm. At the same time physical hardening or curing by crystallization begins as indicated by the decreasing amplitude. At 140 °C the definitive crystallinity is achieved, the sample is hard again. Unlike chemical reactions, physical curing takes place in a very short time and is reversible by melting the crystallites.

Evaluation

The onset of the amplitude increase corresponds to the glass transition temperature of 69.2 °C. The expansivities as well as Young's modulus may not be calculated since the 3 mm ballpoint derectly touches the sample (penetration mode with increasing contact area).

Conclusion

By means of the dynamic load TMA the unusual thermomechanical properties of PET are easy to discover. Glass transition and cold crystallization can certainly be investigated by DSC as well, but DSC curves do not contain any mechanical information.

Exhibitions/conferences

Nordic Polymer Days	June 16 - 18, 1997	Lund, Sweden
Jornadas Mediterraneas de Calorimetria y Analysis Thermico	June 24 - 27, 1997	Palma de Mallorca, Spain
Polymer Processing Society Meeting	August 19 - 21, 1997	Gothenborg, Sweden
NATAS97	September 7 - 9, 1997	McLean Virginia, USA
GEFTA Jahrestagung	September 24 - 26, 1997	Berlin
3rd Symposium / Workshops on Pharmacy and Thermal Analysis	October 12 - 15, 1997	Ascona, Switzerland
Einführungskurs zu kinetischen Untersuchungen mit thermischen Analysenverfahren	November 3/4, 1997	Beilngries, Germany
Fachseminar Thermische Analyse an Kunststoffen	November 25,1997	Frankfurt, Germany
ICTAC 2000	August 14 - 18, 2000	Copenhagen, Denmark

TA customer courses and seminars (CH):

For further information, please contact METTLER TOLEDO, Analytical
Tel. ++41 1 806 72 65 (Helga Judex)
Fax ++41 1 806 72 40

Kundenseminar in Thermischer Analyse	November 4 - 6, 1997	Greifensee, Switzerland
Customer Seminar in Thermal Analysis	November 25 - 17, 1997	Greifensee, Switzerland

TA Kundenkurse und Seminare (Deutschland)

Für weitere Informationen wenden Sie sich bitte an Mettler Toledo Giessen
Tel. 641 507 431 (Suzanne Pouchie)

LabTalk Kundenworkshop DSC	4/5 November 1997	Giessen
LabTalk Kundenworkshop TGA	6/7 November 1997	Giessen

TA information days and training courses (USA):

Please contact your local instrument specialist or Jon Foreman
Tel. 1 800 METTLER (63 88 537) 88 21 or Fax 1 609 448 47 77

TA information days and seminars (Scandinavia):

Information Seminar on **STAR**^{e}	September 25, 1997	Stockholm, Sweden
Information Seminar on **STAR**^{e}	September 30, 1997	Helsinki, Finland
User Course **STAR**^{e}	October 1 - 2, 1997	Helsinki, Finland

Books
Thermal Characterization of Polymeric Materials (2nd edition) Edited by Edith A. Turi, Academic Press

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Internet: http://www.mt.com

Editorial office
METTLER TOLEDO GmbH, Analytical
Sonnenbergstrasse 74
CH-8603 Schwerzenbach, Switzerland
Tel. ++41 1 806 73 87; Fax. ++41 1 806 72 60
E-Mail: joerimau@mtanapo1.mt.com

Dr. S. Vyzovkin, W. Weber, Dr. J. deBuhr, Thomas Hütter, U. Jörimann, J. Widmann, Dr B. Perrenot
Layout and Production: Promotion & Documentation Schwerzenbach G. Unterwegner
ME–51709711