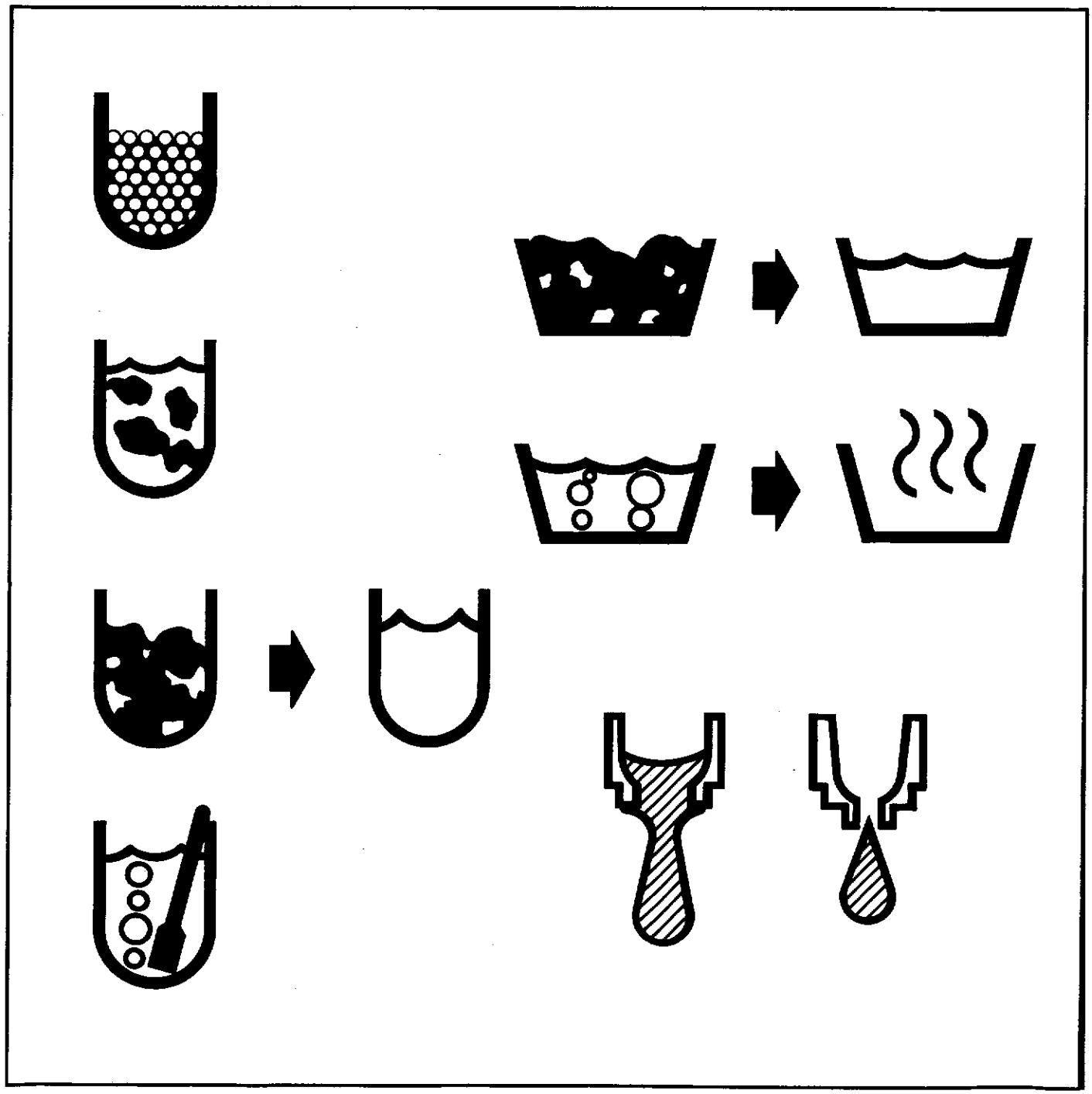
FP800 Thermosystem



METTLER

TABLE OF CONTENTS

1. INTRODUCTION

The Mettler FP800 Termal Analysis System is composed of a control instrument and five measuring cells for measurement and determination of the most varied thermal values:

FP80: Test parameters are entered over the keyboard of the FP80 Central Processor control instrument using the dialog procedure. Analysis results appear in the alphanumeric display and can be printed out by a connected printer. In addition, it is possible to record analog information (heat flow, luminosity or transparency as a function of temperature) with a chart recorder. All information can be transferred to a computer over a standard RS232 data interface; this allows further processing of data.

FP81: With the FP81 Cell, melting points and melting ranges are determined in capillary tubes. This measuring cell is also used for determining boiling points and cloud points.

FP82: The FP82 Hot Stage is used to observe the thermal behavior of a sample under the microscope. In addition, luminosity in the observation field is determined by a photomonitor and recorded.

FP83: This measuring cell is used to determine the dropping point and softening point of fats, resins and other procucts according to various national and international industrial standards.

FP84: On this hot stage, a DSC measuring sensor is mounted where the slide is located on the standard hot stage (FP82). While the sample, which is placed in a transparent crucible, is being observed, heat flow to the sample (endotherm) or from the sample (exotherm) can be measured and recorded.

FP85: With the FP85 TA Measuring Cell, samples are placed in a small aluminum crucible. Here, too, the heat flow due to physical or chemical changes of the sample can be measured and recorded.

2.2. Switching on the instrument

Before turning on the instrument for the first time, read appendix D (page 97).

Before turning on the power switch, the kind of determination wished should be selected (explanation of the symbols can be found at the beginning of each measuring cell description). When the instrument is switched on, all segments light up briefly in the display. The cooling fan for the measuring cell can also be heard.

In the FP81 and FP82 Measuring Cells, an automatic calibration of the detection system takes place at this point. The following instruction appears:

	REMOVE CAPILLARIES	(FP81, except boiling points)
or		
	LIGHT INTENSITY 1	(FP82)

The exact meaning of these of these two instructions can be found in the particular measuring cell description (pages 10, 32). After this automatic calibration, the test conditions can be defined:

[RUN/STOP]	T - - - - C / 1.0 C/MIN

The dashes after the letter T (start temperature) mean that no starting temperature has been defined yet. The scan rate is always at 1 °C/min. when the instrument is switched on, and the end temperature corresponds to the particular maximum or minimum temperature of the connected measuring cell.

2.3. Entering the start temperature and heating or cooling rate

The sequence in which start temperature and heating/cooling rate are entered is unimportant. These two parameters can be modified at any time. Defining the end temperature is necessary in only a few cases (page 6).

In the following example, the starting temperature should be 120 °C. By pressing the numerical keys [1] [2] [0] [0] one after, the following appears in the display:

[1] [2] [0] [0]	INPUT 120.0

Here the position of the decimal point is fixed. It is always located between the next-to-last and last digits.

An incorrect entry can be cleared by pressing [CE]. If the entry is complete, the figure 120.0 can be defined as the starting temperature.

[START TEMP.]	T 120.0 C / 1.0 C/MIN

The processor FP80 will now control the temperature of the measuring cell to the indicated start temperature.

Any change in the heating/cooling rate can be made in the same way. A minus sign in front of rate (cooling) must be entered after the actual number.

Note: Any entered test parameters that are too high or too low are automatically adjusted to the limiting values of the measuring cells (appendix A).

2.6. Measurement

With the next press of the [RUN/STOP] key, the instrument asks for the sample identification number, if it is configured (appendix D, page 98):

[RUN/STOP]	IDENTIFICATION

This sample identification number may have up to four digits, but no decimal point. The printer now prints out the heading and the temperature program can be started by pressing the [RUN/STOP] key.

```
SAMPLE NO.          1
START TEMP.  120.0 C
RATE         1.0 C/MIN
END TEMP.    150.0 C

IDENTIFICATION  4711
```

The display is somewhat different for each measuring cell. For this reason, the actual determination procedures will be handled in the chapters dealing with each cell.

General remarks on test procedures:
During the run the display shows always the true cell temperature. The temperature program can be interrupted by pressing [RUN/STOP]. The following appears in the display:

[RUN/STOP]	INTERRUPTION 121.6 C

While in this condition, the scan rate and the starting temperature can be requested:

[RATE]	RATE 1.0 C/MIN
[START TEMP.]	START TEMP. 120.0 C

If there are any results available which have not yet been displayed, they can be recalled by pressing the [RESULT] key. The temperature program can be reactivated by again pressing the [RUN/STOP] key.

Usually, the temperature program is automatically stopped if all possible results have been found. After a brief isothermal phase (approx. 10 sec.), the instrument returns to the basic condition, and the measuring cell temperature is returned to the starting temperature. If after pressing the [RUN/STOP] key, the word "READY" appears in the alternating display, the instrument is ready for another determination.
However, if a chart recorder is connected, the temperature program is continued until the end temperature is reached, regardless of any results determined. Only then will the instrument return to the basic condition.

When the instrument is switched off, the determination parameters are lost and sample numbering begins again at 1.

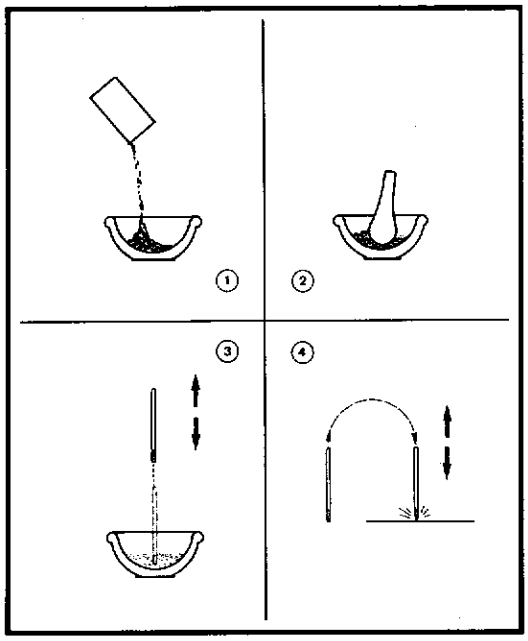
With recorder: When all possible results are available, the temperature program continues with the same scan rate until the end temperature is reached. For the user, this means that if he is working without a printer, he cannot get any results before the end temperature is reached interrupting the program. If he is working with a printer, no further processing of results is possible until the end temperature is reached or the program is interrupted. For this reason, it is advantageous to define the end temperature so that the expected results will appear within a reasonable time period.

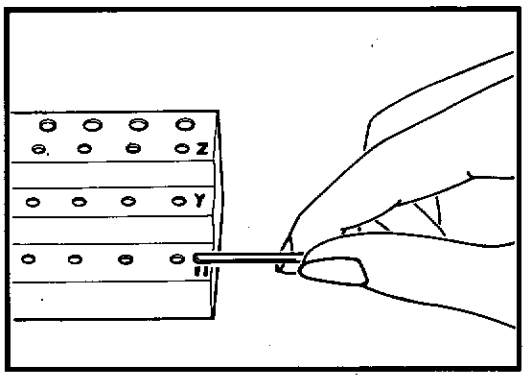
2.10. Connection of a computer

The FP80 Control Instrument has a bidirectional computer connection which operates according to the RS232C standard. An appropriate computer can be connected directly to the control instrument to process the arriving raw data and results, and to carry out any remote controlling of the FP800 System. How this can be done is explained in Appendix B.

3.2. Determination of melting points and melting ranges using the example of benzoic acid

Sample preparation





Finely crush the dry sample in a mortar, (If necessary, predry the crushed sample in a dessicator. The sample capillary tubes are filled 3...6 mm high. To do this, it is best to press the open end of the tube into the sample, and get the sample down to the bottom of the tube by tapping the capillary tube on a hard surface or by lightly tamping the sample with the tamping wire. The fill level can be checked using the marker line on the sample stand (front right). For precision measurements, the optimum fill level of 4 mm should be maintained! Note: If at all possible, use capillary tubes from Mettler. For Order Numbers, see page 91. If other capillary tubes are used, their diameter (1.3...1.5 mm) should be checked by using the hole gauge which is included along with the instrument accessories.
For the following determination, three equal samples should be prepared.

For determination below room temperature, the tube should be filled with sample in the liquid form. This can be done using the disposable syringe or by heating the capillary tube and dipping its opening into the liquid. When cooled, the liquid is drawn into the tube and can be forced to the bottom by shaking it. The substance is then quick chilled in a cold bath (e.g. liquid nitrogen, acetone/dry ice, etc.) so that the crystals formed are as small as possible.

Test procedure

The selector switch on the connector of the FP81 cell must be set on for melting point determination and on for melting range determination. If the selection is changed, confirm with [RESET]. The FP80 will then ask again for a calibration (page 10).

Pure benzoic acid has a melting point of 122.35 °C. With a scan rate of 1 °C/min, the starting temperature selected must be about 3 °C lower. Accordingly, a starting temperature of 119.0 °C should be entered. The scan rate is 1 °C/min. The last time [RUN/STOP] was pressed, the instrument was put in the ready condition.

[RUN/STOP] T 119.0 C / 1.0 C/MIN ↔ T READY / 1.0 C/MIN

On the other hand, the values in thermodynamic determination are corrected in a way that makes the melting temperatures identical to the corresponding sample temperatures, i.e., a pure substance now has a melting range of virtually zero. In addition, the results are theoretically independent of the heating rate. In reality, the unreliability of the determination increases as the heating rate increases.

Obviously the two methods provide slightly different results. In order to distinguish the two types of results, the Celsius unit appears as C' in the pharmacopoeia method; in the thermodynamic method, it appears simply as C without the dash.

Remarks on melting point and melting range determination

Selection of the starting temperature: The starting temperature must be at least 3 °C (6 °F) above ambient temperature. If the approximate melting temperature of the sample is known, the starting temperature is selected, so that the heating takes about 3 min.

	Heating rate		start temperature		
	°C/min	°F/min	°C	°F	
Reference values:	0.2	0.4	1	1.8	lower than expected
	1	1.8	3	5	melting temperature
	2	3.6	5	9	
	3	5.4	8	14	
	10	18	30	54	

Accuracy of the results: The deviation of the measured melting temperature depends on the reating rate. Generally, it is valid to say that precision measurements are carried out at 0.2 °C/min, routine measurements at 1 °C/min., and orientational measurements at 10 °C/min.

Standard deviation and mean value: Basically, these two values are calculated only for melting point and cloud point determination. Standard deviations with values of more than 9.9 are not displayed, nor a standard deviation from only two individual results. Two results, however, do provide a useful mean value.

Standard deviation is calculated according to the following formula:

$$s = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{N - 1}}$$

x_i = Measured values
$\bar{x}$ = Mean value of N values
N = Number of values

However, melting point determinations of polymorphic substances can be difficult. By a special method of sample preparation, i.e. by crystallization from the melt, one or the other modification can occur by chance. If the melting points of these modifications are very close to each other, determination reproducibility seems very poor. If a single modification is needed in order to eliminate this uncertainty recristallisation in an appropriate solvent can help.

3.4. Determination of cloud point using the example of a surfactant (tenside) *)

Sample preparation

Depending on its solubility, the surfactant is diluted with butyldiglycol solution, water or salt solution. For the surfactant in this example (Genapol 0-150, Hoechst), 1 g of substance is diluted with 100 ml of 10% salt solution. It is transferred into three capillary tubes with a disposable syringe (needle lenght: 80 mm) (fill height: 15...18 mm). If problems with remaining air bubbles arise, file off the diagonal tip of the needle.

Test procedure

The selector switch on the FP81 Measuring Cell connector must be set to  . If this was not done before the instrument was switched on, the [RESET] key must be pressed after switching to . The instrument will then ask for a recalibration (page 10).

A starting temperature of approx. 5 °C below the expected cloud point of 72 °C is chosen. The scan rate is 1 °C/min. The last press of [RUN/STOP] puts the instrument in the ready condition:

T 68.0C / 1.0 C/MIN	↔	T READY / 1.0 C/MIN

Then the capillary tubes are inserted into the X, Y and Z measuring slots. The temperature program can now be started. With the determination of cloud points, the instrument cannot sense whether a measuring slot is occupied or not. For this reason, three pairs of dashes always appear in the display:

[RUN/STOP] | TEMP. 68.1 C -- -- --

As soon as the individual samples cloud, each display changes from -- to *X, *Y or *Z and the printer will successively print out the results. When all results are available, the following question appears in the display:

MEAN ?

This question can be answered either by pressing [RESET] (no calculation of mean value), or by pressing [RESULT]. A press of the [RESULT] key causes the printer to immediately print out the mean of the three temperatures, X, Y and Z along with the corresponding standard deviation:

[RESULT] | MEAN 72.5 C + - .62

*) Surfactants are surface active agents (soaps, wetting agents)

The cloud point of aqueous solutions can be measured practically only in the range between room temperature and boiling point, and therefore cannot be determined with low ethoxylated products, which are always cloudy when diluted. They can neither be determined with very highly ethoxylated products for which the cloud point does not occur below the boiling point. For this reason, a "better" solvent than water is used for the low ethoxylated products, while for the highly ethoxylated products, a "worse" solvent is used. For the former, it is a 25 % solution of butyldiglycol; for the latter, a 10 % salt solution (NaCl).

In practice, the following test solutions are used, among others [3]:

a) for low ethoxylated products:
   5 g of test substance in 25 ml butyldiglycol solution (25 %)

b) for clear soluble products in water:
   1 g of test substance dissolved in 100 ml distilled water

c) for highly ethoxylated products:
   1 g of test substance dissolved in 100 ml aqueous salt (NaCl) solution (10 %)

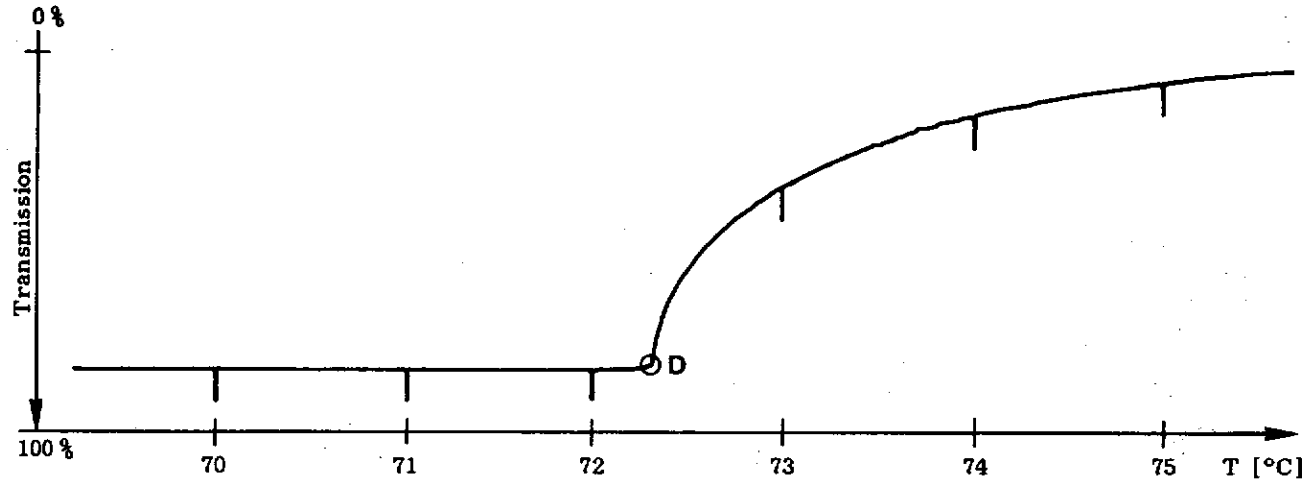
According to the conventional method [3], 25 to 30 ml of the test solution is heated over a bunsen burner in a large beaker (30 x 200 mm) and stirred carefully with a thermometer which is graduated in tenths of a degree. This is done until the content is evenly cloudy. The flame is then removed and the content is allowed to cool while stirring is continued. This is done until the solution suddenly becomes clear again. The temperature read from the thermometer is the cloud point. The method described above is not identical to the standards [4]. But the results can easily be correlated with standard results.

Literature:

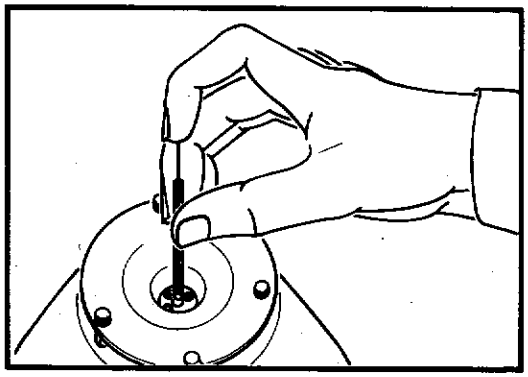
[3] Hoechst Dye Works: Prüfvorschrift für nichtionogene Tenside, z.B. Merkblatt Hoe 2662 TH/S

[4] German Standards: Prüfung von Tensiden, DIN 53917 (1981)

The same measuring principle is used in cloud point determination, however the surfactant solution is clear at the beginning of the procedure and becomes less and less transparent as temperature increases. The cloud point, defined as the beginning of clouding, corresponds to Point D in the following curve.



Points A, B, C (last page) and D are determined automatically by the instrument.



The sample tube, with the inserted capillary tube, is inserted straight down into the center opening and pushed down carefully all the way until it stops. Determination can then be started.

[RUN/STOP] WAITING 60 S

Depending on the starting temperature, a waiting time of one or two minutes is suggested to give the sample time to reach equilibrium with the starting temperature.
Starting temperature < 100 °C, → 1 min.; starting temperature > 100 °C, → 2 min.
After this waiting period is over, or after forcing start by pressing the [RUN/STOP] key, the temperature program begins to run:

TEMP. 72.1 C

As soon as the boiling point temperature is reached, the following is displayed:

BOILING TEMP. 78.2.C

This result corresponds to the boiling point at ambient atmospheric pressure (e.g. 968 mbar).
The request for the boiling point at standard pressure appears in the display:

BOILING PT. ?

This question can be answered either by pressing [RESET] (no conversion) or by pressing [RESULT]. Conversion to standard pressure of 1013 mbar (760 Torr) is then made automatically. The following appears in the display:

[RESULT] PRESSURE 0 MBAR

If the question about the pressure is answered with 0, the display changes from "mbar" to "Torr" (Torr is the same as the old unit "mm Hg"). If zero is entered again, "mbar" appears again. In this way, the ambient pressure can be entered in either of the commonly used units. After entry of the pressure, the instrument requests the designation of the sample type. Ethanol belongs to sample type 8 (page 23).

[RESULT] or
[RUN/STOP] [8] SAMPLE TYPE 8

The instrument calculates boiling point at standard pressure using pressure and sample type:

[RESULT] or
[RUN/STOP] BOILING PT. 78.8 C

Table of material classifications (for correction of boiling points to standard pressure)

Correction of Boiling Points to Standard Pressure

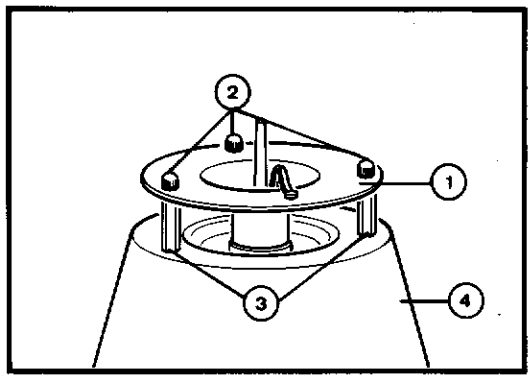
Compound	Type
Acetaldehyde	3
Acetic acid	4
Acetic anhydride	6
Acetone	3
Acetophenone	4
Amines	3
n-Amyl alcohol	8
Anthraquinone	1
Benzaldehyde	2
Benzonitrile	2
Benzophenone	2
Benzyl alcohol	5
Butylethylene	1
Butyric acid	7
Carbon suboxide	2
Carbon sulfoselenide	2
m.p. Chloroanilines	3
Chlorinated derivatives	same type as though Cl were H
o.m.p. Cresols	4
Cyangogen	4
Cyangogen chloride	3
Dibenzyl ketone	2
Dimethyl amine	4
Dimethyl oxalate	4
Dimethyl silicane	2
Esters	3
Ethanol	8
Ethers	2
Ethylamine	4
Ethylene glycol	7
Ethylene oxide	1
Formic acid	3
Glycol diacetate	4
Halogen derivatives	same type as though halogen were hydrogen
Heptylic acid	7
Hydrocarbons	2
Hydrogen cyanide	3

Compound	Type
Isoamyl alcohol	7
Isobutyl alcohol	8
Isobutyric acid	6
Isocaproic acid	7
Methanol	7
Methyl amine	5
Methyl benzoate	3
Methyl ether	3
Methyl ethyl ether	3
Methyl ethyl ketone	2
Methyl fluoride	3
Methyl formate	4
Methyl salicylate	2
Methyl silicane	1
α, β Naphthols	3
Nitrobenzene	3
Nitromethane	3
o.m.p. Nitrotoluenes	2
o.m.p. Nitrotoluidines	2
Phenanthrene	1
Phenol	5
Phosgene	2
Phthalic anhydride	2
Propionic acid	5
n-Propyl alcohol	8
Quinoline	2
Sulfides	2
Tetranitromethane	3
Trichloroethylene	1
Valeric acid	7
Water	6

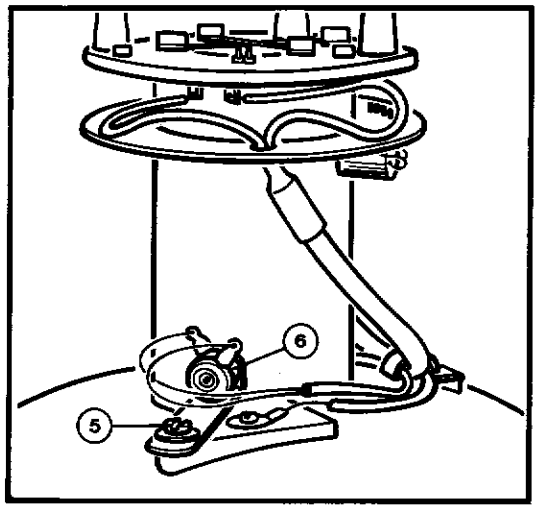
3.11. Maintenance

With normal use, the FP81 requires no major maintenance, even over long periods. Maintenance by the user is limited to replacement of burned-out bulbs and to cleaning the furnace interior.

Replacing a burned out bulb



- Switch off the control instrument.
- Disconnect the plug on the control instrument.
- Remove the funnel (1) (remove the three knurled nuts (2).
- Unscrew the three hexagonal supports (3) and remove the furnace jacket (4).
- Remove screw (5) from the bulb socket (6).
- Remove the bulb socket (6) from the furnace housing.



- Replace the burned-out bulb.
- Insert the bulb socket (6) all the way back into the furnace housing and fasten it with the screw.
- Adjust the lamp (see below).
- Place furnace jacket (4) back on. Screw in hexagonal supports (3).
- Place funnel (1) on furnace and fasten with the knurled nuts (2).
- Connect furnace to the control instrument.
- Order replacement bulb.

Adjusting the lamp bulb in the FP81

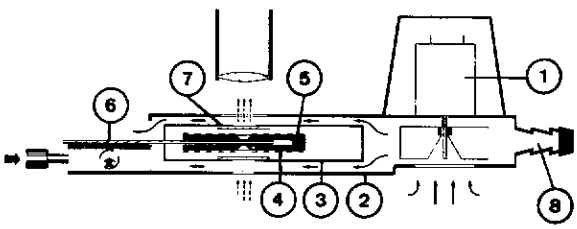
If a bulb has been replaced in the FP81, or if X, Y and Z values always appear in the display when the instrument is switched on, the lamp must be readjusted. However, this must not be done when the lamp is cold. It is best to have the measuring cell with the instrument on for at least 20 minutes beforehand. After the power has been switched off, the measuring cell housing can be removed by losening the screws. Then, a filled capillary tube is inserted into one of the three measuring slots, the instrument is switched on, the instruction "Remove capillaries" is acknowledged by pressing [RUN/STOP], and the capillary tube is removed. By moving the lamp mount around slightly, the displayed measuring value of all three slots must lie within 1500 and 3900. This must also be the case with the housing placed back on the instrument.

4. THE FP82 HOT STAGE AND FP84 TA MICROSCOPY CELL

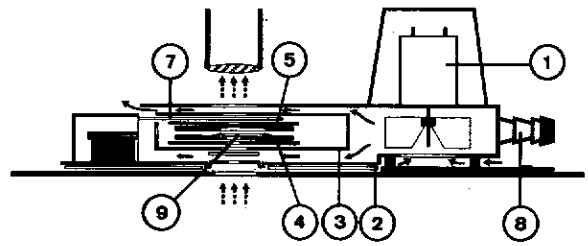
Both hot stages are very similar as far as appearance and operation are concerned. The most important difference is as follows:

FP82 As with the normal microscopic technique, the sample is placed between a slide and a cover glass and the sample can be observed during the temperature program. In addition, use of the photomonitor permits quantitative determination and recording of the light intensity of the field of view. The field of application for the FP82 is called thermo-optical analysis, or simply TOA.

FP84 Here, the sample is placed in a transparent sapphire crucible or is sandwiched between two sapphire disks. Simultaneously with visual observation of the sample (TOA), the heat flow to or from the sample is determined and recorded. This calorimetric measurement is based on the principle of heat flow DSC (Differential Scanning Calorimetry). Accordingly, this simultaneous process is called TOA-DSC.



FP82



FP84

Sectional view of the hot stages

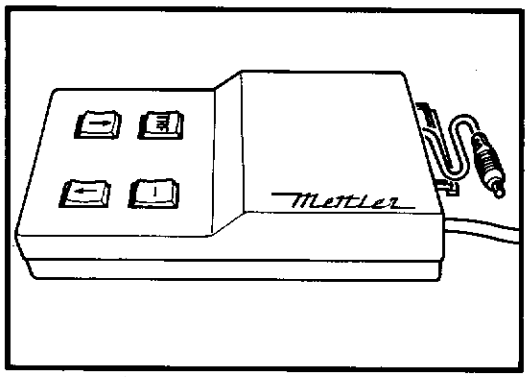
1 Fan
2 Outer casing
3 Inner casing
4 Metal plate with heating wires and Pt100 temperature resistance
5 Metal plate with heating wires
6 Slide
7 Heat protection filter
8 Cooling connector
9 DSC-Sensor

In both the FP82 and FP84 Hot Stages, the principle of two-sided heating of the sample is applied. The slide, or the sapphire crucible with the substance, is located in a flat, rectangular sample chamber which is formed by the two metal plates of the furnace heater body. The arrangement of the heating elements assures homogeneous heat distribution. Temperature is measured by a platinum resistance thermometer which is imbedded in the lower plate near the round observation opening. The furnace formed by the two heating plates is built into a double-walled housing. A mirror finish on the inside housing walls assures that heat will be reflected towards the center of the cell. A fan blows air between the inner and outer housings and the observation opening is covered by a heat protection filter. These measures assure a temperature difference of up to 300 °C between the cell and the outside of the instrument and assure that delicate microscope parts are protected. The top of the hot stage can be flipped up together with the upper heating plate so that the sample chamber is freely accessible.

For cooling, a device composed of a compressed nitrogen bottle, flow meter and a cooling coil immersed in liquid nitrogen can be used.

4.2. The hand set

In addition to the standard operating functions controlled by the FP80 control instrument (page 4), the hot stages can be remotely controlled with the hand set while the user is observing through the microscope.



Function of the keys:

[-] The temperature program is stopped (isothermally)

[↓] The temperature drops at the rate set, regardless of whether plus or minus has been set for the scan rate. This key is active in both the isothermal and dynamic modes.

[↑] The temperature climbs at the rate set, regardless of wheter plus or minus has been set for the scan rate. This key is active in both the isothermal and dynamic modes.

[TRF] The transfer key allows the user to print out the temperature of an observed event on the printer or to store the information in the memory of the control instrument. When this is done, the event is assigned a sequential number from 1...99. In addition, the particular event temperature appears in the display, e.g.:

[TRF] EVENT 01 116.7 C

The event counter is reset when a new experiment is begun or by pressing the [RESET] key. If no printer is connected, the last three events are stored in memory. These can be displayed by pressing the [RESULT] key.

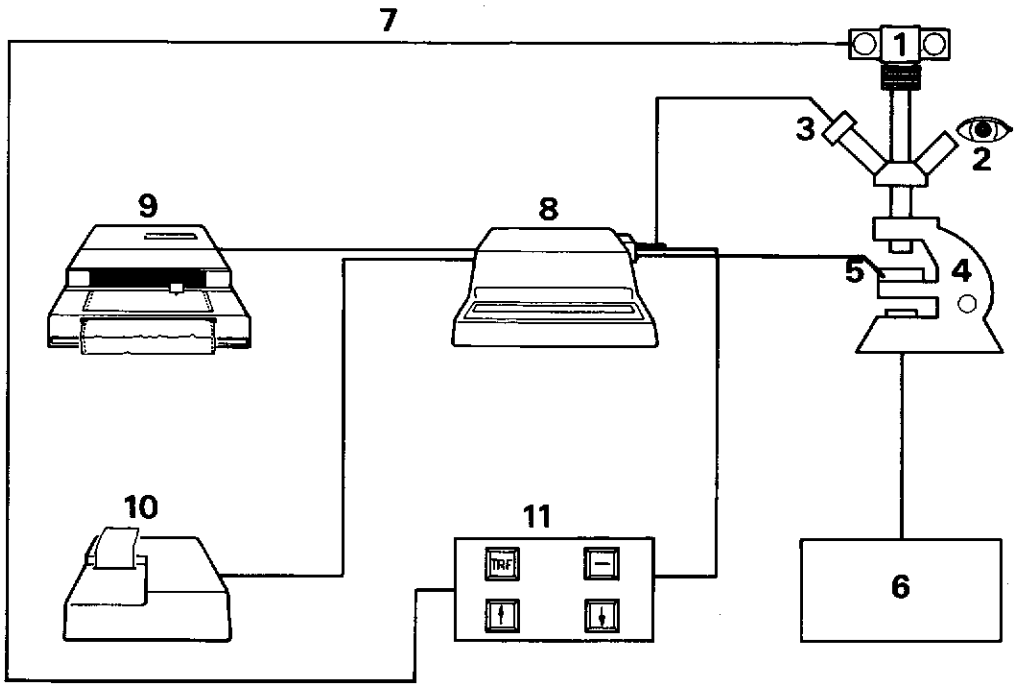
If a chart recorder is connected, a mark is made automatically every time the [TRF] key is pressed.

A mark is also set if events are photographed. To do this, the connection cable located in the small compartment in the manual control panel must be connected to the camera using a commercially available extension cable. This connector is plugged into the flash socket of the camera. Pressing the shutter button of the camera now achieves the same function as a press of the [TRF] key.

The displayed event temperatures correspond to the cell temperature. The sample temperature can be calculated with the aid of τ_{lag} (page 64). This calculation is not needed with the FP82 which has a very small lag.

Installation and measuring principle

The illustration below shows a complete measuring station setup for thermo-optical analysis with camera, photomonitor and recording instrument.



1 Camera
2 Eye piece
3 Photomonitor
4 Microscope
5 FP82 Hot Stage
6 Light source and stabilizer
7 Connection cable to flash contact
8 FP80 Control Instrument
9 Recorder (GA17)
10 Printer (GA40)
11 Hand set

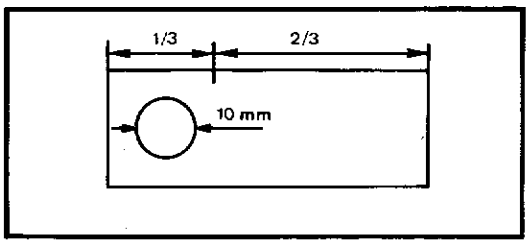
If used together with a chart recorder and a binocular microscope, the photomonitor permits simultaneous observation and automatic recording of the optical changes. If a monocular microscope is used, only measurement or observation is possible at one time.

The photomonitor can be used in most commercially available microscopes, as long as the diameter of the ocular or binocular is 23 mm. For the larger diameter of 30 mm, the ME-17728 Adapter must be used. To take maximum advantage of the entire field of view, it is recommended that 6 x objectives be used. Stronger objectives can also be used, as long as free working space is larger than or equal to 7 mm. If, when using a binocular microscope, the substance is not being observed through the free ocular, it should be removed and the opening covered with a cap to prevent light scatter.

4.4. Microscopic determination of a melting point with the FP82 Hot Stage using the example of phenacetin (acetophenetidine)

Sample preparation

Clean, dust-free slides (max. dimensions: 75 x 25 x 1 mm) and cover glasses (max. size: 20 x 20 x 0.1 mm) should be used for sample preparation. The samples can be studied either in a premelted state or in their crystalline state (also powdered). The sample should be placed in the last third of the slide (see sketch) so that after the slide is inserted into the hot stage, the sample comes into the field of view. The spread over this area should be about 10 mm in diameter, i.e., it should be possible to select a suitable section with only slight movement of the slide. Pre-melted samples are obtained by melting on a Kofler plate or in the hot stage itself, i.e., the sample is heated on the slide without the cover glass. The sample, which is present as a single drop, is spread out by capillary action between two glass plates. This is achieved when the cover glass is quickly placed on the sample. Depending on the rate of cooling, large or small crystals will be formed. Procedures without a cover glass should be carried out only if working with samples that have very low vapor pressure, otherwise the sample will condense on the heat protection filter just above it, and will inhibit the view. The size of the crystals to be examined must be adapted to the depth of focus of the optical system used, otherwise only partial observation will be possible.



Test procedure

Before the prepared specimen is inserted into the hot stage, the light intensity must be correlated with recorder sensitivity, both with and without the sample. Without the sample intensity I abs. is, for example, 21. The recorder should be positioned almost at zero, e.g. at 6 scale divisions. After inserting the sample into the hot stage, i.e., into light passage of the microscope, the upper limit of light intensity should be set by adjusting the control transformer of the light source device. In this example, it is an I abs. of 2500. Recorder deflection is then set to 89 scale divisions, as an example. A press of the [RUN/STOP] key calibrates the display and computer output (see page 32) for the following measurement. At this point, neither the light source nor the crossed polarization filters should be changed.

Phenacetin has a melting point of about 134 °C. Accordingly, a starting temperature of 130 °C should be selected. The scan rate is 1 °C/min. Microscopic measurement is carried out with crossed polarization filters and with 40 x magnification.

The last press of the [RUN/STOP] key put the instrument in the ready condition:

[RUN/STOP] T 130.0C / 1.0 C/MIN ↔ T READY / 1.0 C/MIN

Remarks about microscopic determination of the melting point

Recording light intensity with the photomonitor:

In the examination of chemical compounds that also manifest an increase in light intensity during the temperature program, a test run should be carried out first, i.e., the measuring range of the recorder should be selected so that the entire curve will be on the chart.

Hand set:

Influencing the temperature program by pressing the [↑], [↓] and [-] keys on the hand set creates some interesting possibilities:

By pressing a key, the temperature program can be brought to isothermal conditions to observe such things as recrystallization, for example. It is also possible to measure the crystal growth of badly crystallizing substances whereby a switch is made to cooling during the melting process shortly before the clear melting point. This means that crystallization can proceed again from the crystalline remains. If this experiment is carried out at different isothermal temperatures after seed crystal formation has occurred, it is possible to calculate the activation energy of this process from the growth rate.

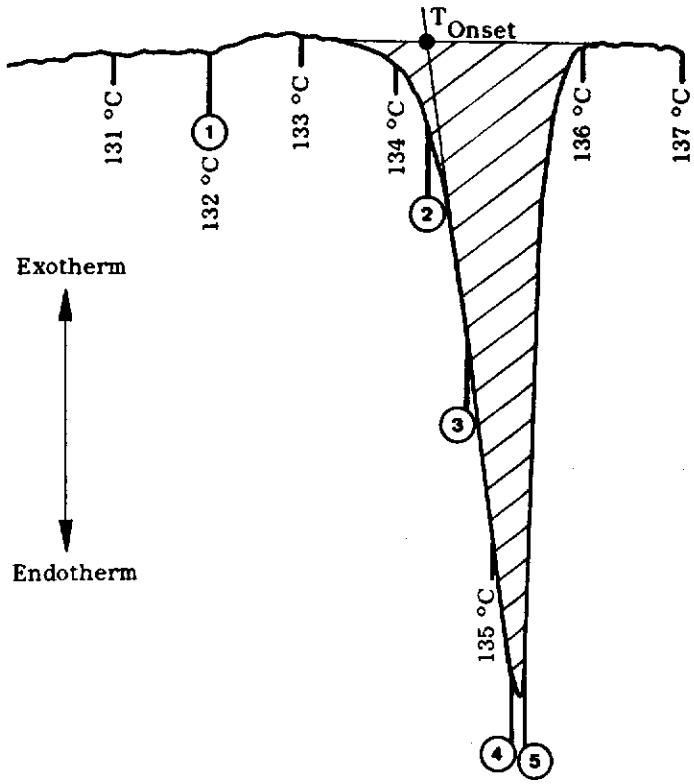
4.5 Determination of melting point and heat of fusion with the FP84 TA Microscopy Cell (TOA-DSC) using the example of phenacetin (acetophenetidine)

A standard chart recorder (e.g. the Mettler GA17) is connected for manual determination of the melting point and heat of fusion. The measuring range is set to 100 mV and the zero point is set on the left. Chart speed is 2 cm/min. Automatic evaluation requires connection of a computer (page 85).

Sample preparation

Approximately 1.6 mg of sample is weighed into a sapphire crucible, covered with a 5 mm sapphire disk and pre-melted on a Kofler plate or in the hot stage itself (melting point < 136 °C). After cooling of the crucible and recrystallization of the substance, the weight of the substance is re-checked carefully, because small losses can occur during pre-melting through sublimation of the sample (in the example, the weighed-in substance is 1.573 mg).

To determine the melting point, the peak tangent is intersected with the dynamic baseline (onset point). The calculation of the sample temperature and the corrected event-temperature is described on page 64. The area under the peak is a measure for the heat of fusion.



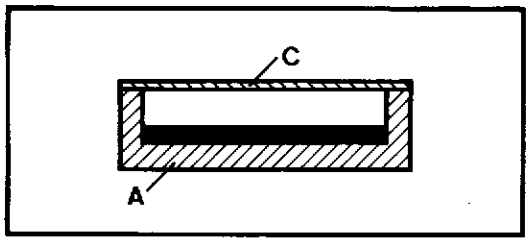

```
SAMPLE NO.          3
START TEMP.  130.0 C
RATE          1.0 C/MIN
END TEMP.    137.0 C

EVENT     01 132.0 C
EVENT     02 134.3 C
EVENT     03 134.8 C
EVENT     04 135.2 C
EVENT     05 135.3 C
```

Photographs of events 1 through 5 can be found on page 42.

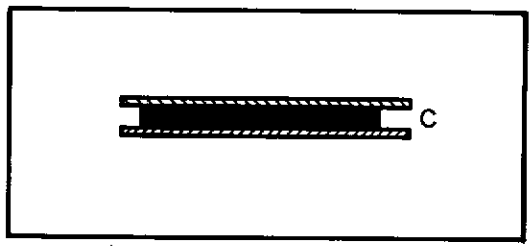
The pre-melted and recrystallized sample indicates a lattice texture at 132 °C (Picture 1 of the photographs on page 42). The bubbles that are formed during crystallization form the crystal junction lines. Picture 2 shows a brightening of the sample at 134.3 °C; the liquid formed during the first melting smoothes out the surface and has partially filled the hollows. In Picture 3, this process is advanced; the color shift of the interference colors can be correlated with reduction of the layer thickness. The formation of bubbles shows that a part of the sample has already passed over into the vapor phase, even if some of the bubbles can be regarded as air pockets. The last crystals are melting in Picture 4 and Picture 5 shows the final homogeneous melt. If the DSC curve plotted at the same time is compared to the microphotographs, the pictures correspond to the various stages of the melting process.

Evaluation of the DSC curve

Evaluation of the curve is carried out in the same manner as described in the FP85 paragraph: Manually (page 64); by computer (page 65).

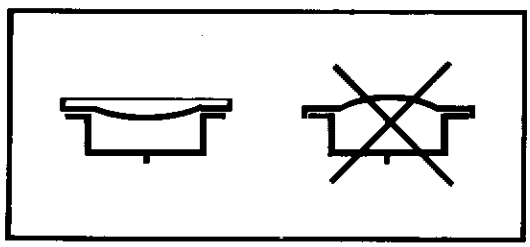


If the small bowl (A) is covered with a thin cover glass (C), the substance in its original form can then be observed under the influence of heat. Because of sublimation on the cover glass (C) during the first heating, the crystals can be observed in their usual state during the second heating, i.e., comparisons between the behavior of the flat sample -- the single crystal -- and the powdered material can be made.



In the adjacent picture, the sample is placed between two large cover glasses. This preparation is possible only for substances with highly viscuous melts, otherwise the measuring sensor could be contaminated if the melting substance spilled out. If there is any subsequent cleaning of the sensor, there is a high risk of damagins the thermopile. This should be avoided.* This method of preparation has proved itself even for very small sample quantities of approx. 0.1 mg or less.

The same crucible configuration as is used for the sample is used as a reference. As an inert reference substance, aluminium oxide can be used. Because of the minimal amount of sample, it is also possible to use an empty reference crucible. For measurement, the crucible material should be very clean, kept free of dust and handled with tweezers.

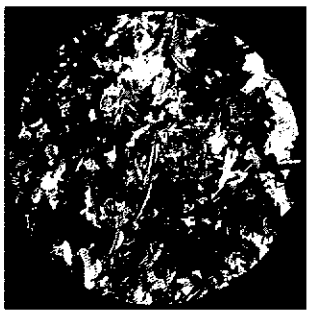


If the hot stage is not needed for sample observation, DSC crucibles made of aluminium can also be used (page 69). Make sure that the cover is turned the other way around when covering the crucible, and that the instrument is also calibrated with AL-crucibles.

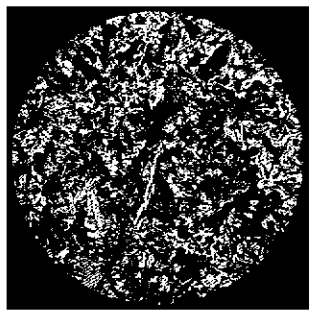
* No guarantie replacement

4.7. Pictures of some TOA-experiments

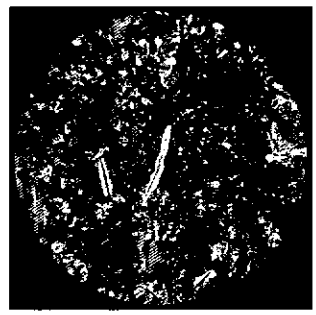
Pictures of events 1 to 12 of experiment on page 30:



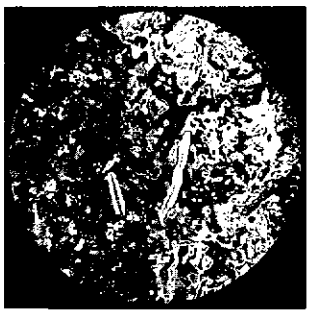
①



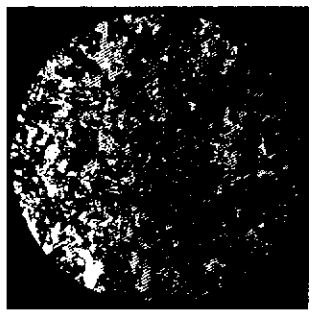
②



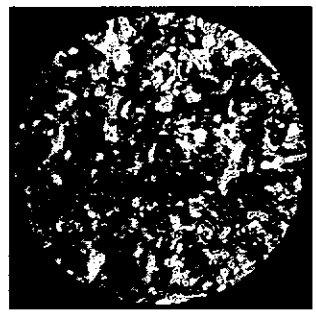
③



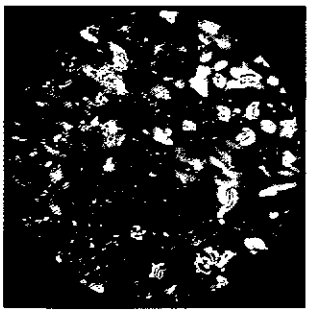
④



⑤

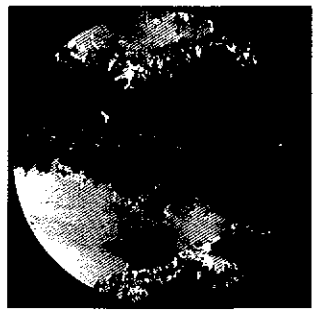


⑥



⑦

⑧



⑨

⑩

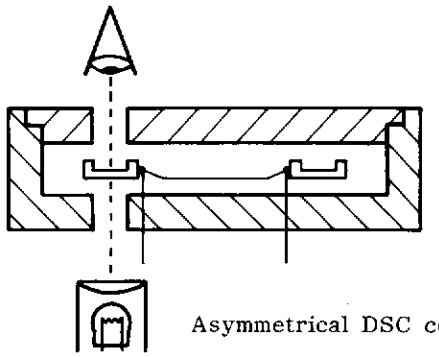
⑪

⑫

4.8: Measuring principle of TOA-DCS

Unlike conventional heat flow DSC, in which the heat flows to the sample and to the reference are virtually identical because of their symmetrical configuration, this cell can be called asymmetrical because of its design and use. With this cell, the heat flows are different during a temperature program; however, the relationship of the two is reproducible.

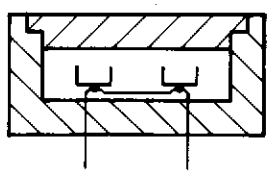
FP84 TOA-DSC



Asymmetrical DSC cell

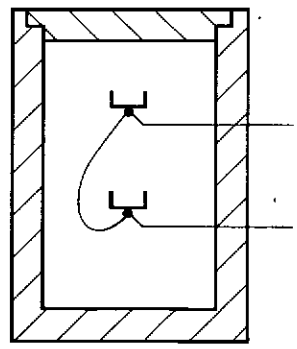
Unlike in the FP85 (page 68), the DSC signal is determined by two vapor-deposited, five fold gold/nickel thermopiles. Otherwise, the same rules and principles apply (for the measuring principle see page 72).

TA3000 DSC



Symmetrical DSC cell

FP85 DSC



Symmetrical DSC cell

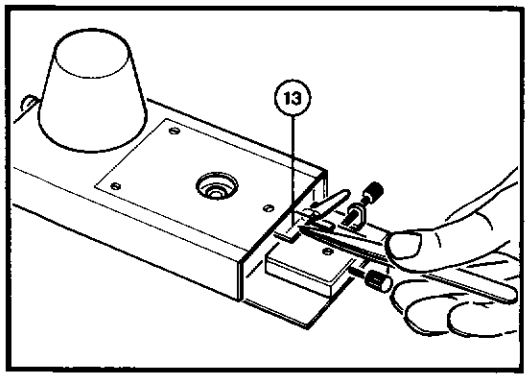
Microphotograhpy

In most cases, commercially available microscopes can be fitted with a camera accessory. It is important that the camera used be equipped with an automatic light meter that can measure extreme light intensities (e.g. Olympus OM2, etc.). In addition, shutter speed should be adjustable from between 1 to 30 seconds. Suitable film is available from various manufacturers. Film with the standard exposure values is not suitable for this type of photography. Instant cameras have the advantage of immediate documentation, and in case of improper exposure, photos can be retaken immediately. When not using instant films, it is recommended that a test film be prepared first. If single lens reflex cameras are used, a check must be made to determine wheter focusing with the eyepiece is the same as with the viewfinder. In monocular microscopes, the sample is observed on the viewfinder of the camera. Exposure time of the photographic material and operation of the camera (film advance, refocusing, shutter release, etc.) influence the time-dependent steps for selection of heating or cooling rate. The cable used with the hand set can be connected to the flash socket of the camera. If this is done, a mark is placed on the curve during measurement at the same time the shutter is released (setting of marker see page 98). If a printer is used, the signal triggers printout of the particular event temperature. For day light films, a commercially available filter for color correction can be attached.

NOTE: Samples with high vapor pressure condense very easily on the heat protection filter, as well as on the lower protective glass. These filters must be cleaned before each test (see page 47), otherwise all values determined will be meaningless.

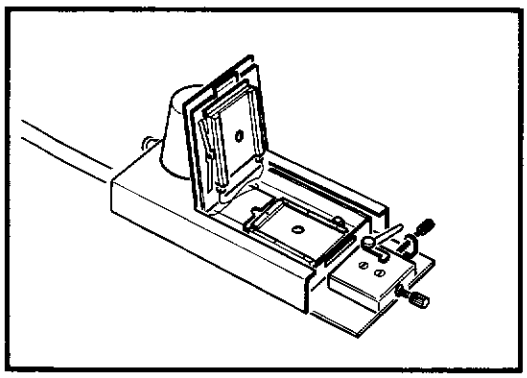
4.11. Maintenance

Cleaning the heat protection filter



- Grip the heat protection filter (13) with tweezers and remove it from the furnace.
- Clean the heat protection filter (13) with a soft cloth; if necessary, a solvent can be used.
- Insert the heat protection filter back into the furnace.

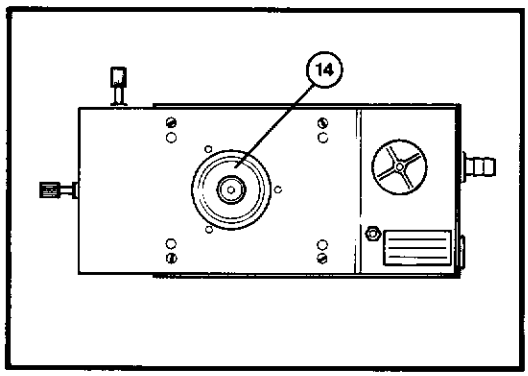
Cleaning the furnace core



- Switch off instrument.
- Open the cover.
- Clean furnace interior with a soft cloth. If necessary, the cloth can be moistened with a solvent.
- Close cover.

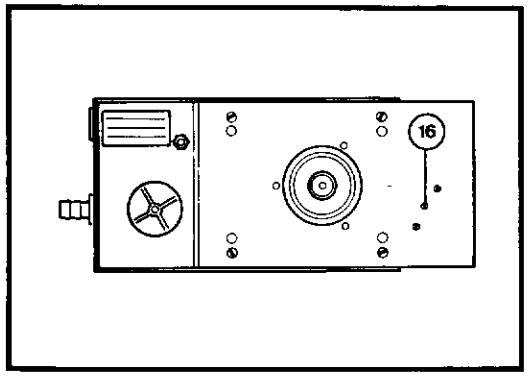
Cleaning the lower protection glass

This step should be carried out only if glass is especially dirty.

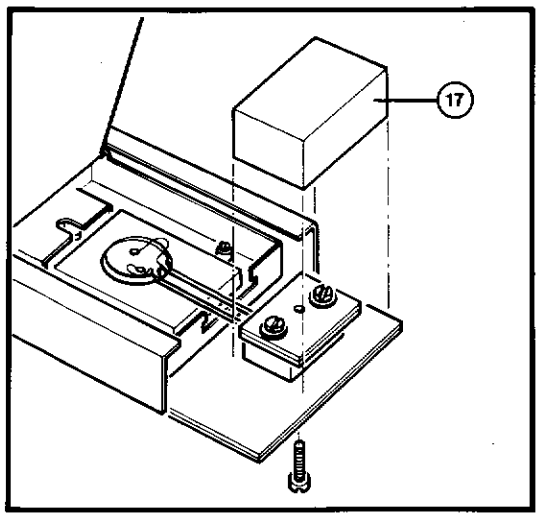


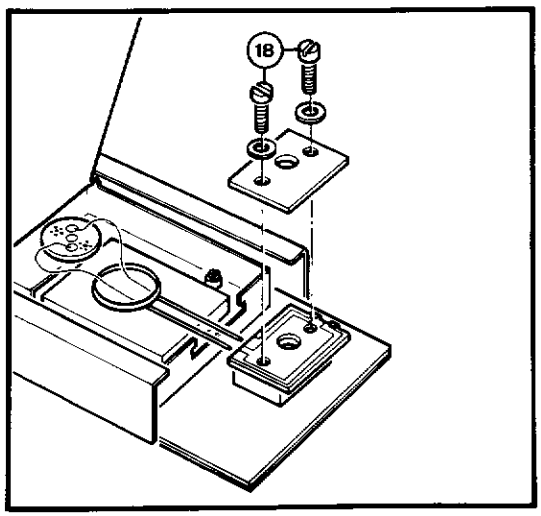
- Swich of instrument
- Turn hot stage over (bottom facing up; Note: first secure FP84 DSC sensor with tape).
- Push out cover (14) from the bottom of hot stage. (use screwdriver to pry up, if necessary).

Replacing the DCS sensor



- Loosen screws (16) and lift off cover (17) (Note: secure the DSC sensor).





- Remove the two screws (18) and remove the upper conductor plate.
- Lift up the furnace housing cover and prevent it from falling back down by securing it with a rubber band or some other appropriate means.
- Depending on whether the sensor is defective or can still be used, the flat ends of the gold wires should be cut off or the roughly square loops on the ends should be bent back so the wires do not jam in the capillaries when they are pulled through.
- Lift out DSC sensor using tweezers and pull the gold wires through the capillaries.

5. THE FP83 DROPPING POINT CELL FOR DETERMINATION OF DROPPING AND SOFTENING POINTS

Depending on the determination to be made the selector switch on the cell connector is set on one of the two symbols and confirmed with [RESET].

Dropping point
Softening point

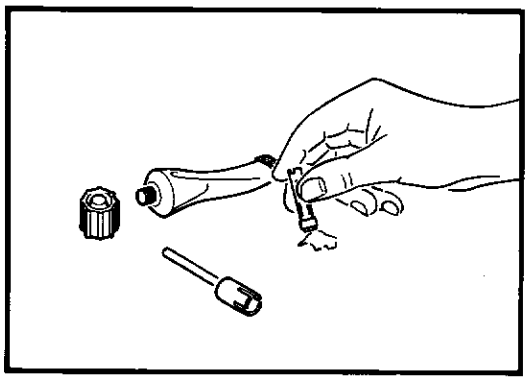
Compatibility with existing standards

The determination of the dropping point and softening point is subject of various national and international standards. When this instrument was developed, great care was taken to maintain compatibility with the two preceeding FP models (Mettler FP3/31 and FP5/53), which in some cases, were integral part of the standards. Consequently, all results obtained from this new instrument are comparable to results obtained from all preceeding models.

5.1. Determination of a dropping point using the example of vaseline

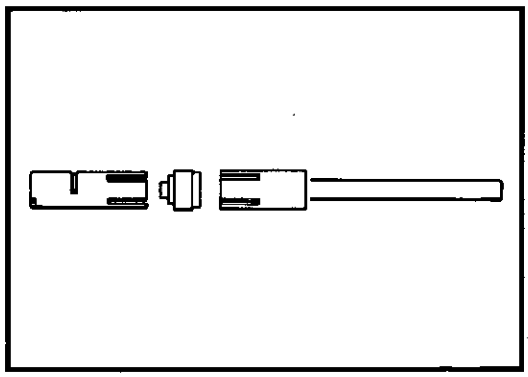
Sample preparation

Note: The ME-18732 sample cup (opening: 2.8 mm) must be used for determination of the dropping point.



- Sample preparation:

  Place the sample on a smooth clean surface (glass plate).
- Press the sample cup into the sample until it begins to squeeze through the opening on the cup. The collector sleeve on top of the sample cup can be used as a holder.
  (The vaseline can also be squeezed directly into the sample cup from the tube.)
- Smooth off the excess from the opening with a spatula.



- According to the pharmacopoeia method (Ubbelohde method), the sample cup can now be used to determine dropping point.
- Assemble the cartridge.

Remarks concerning the dropping point determination

Dropping point determination can also be used for lubrication greases. However, sample preparation according to ASTM, method D 566-64 is a bit different, in that a conical section of sample is removed with a spatula.

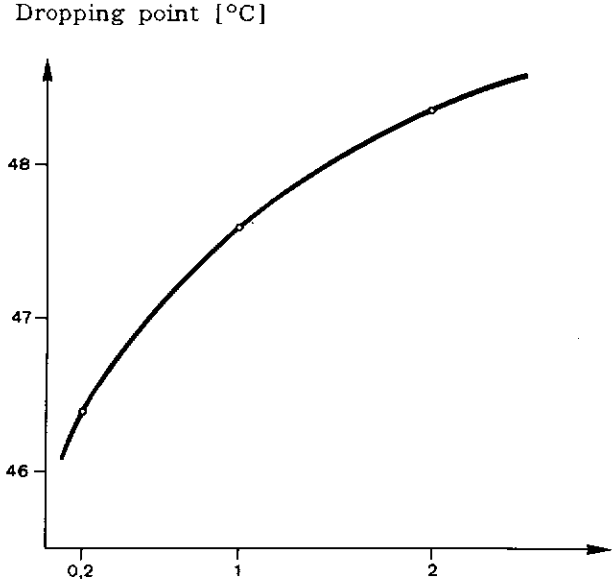
Selection of the starting temperature:

Starting temperature should be at least 10 °C (18 °F) above ambient temperature. If the approximate dropping point of the sample is known, the starting temperature should be chosen lower, according to the following table:

	Heating rate		Start temperature		
	°C/min	°F/min	°C	°F	
Reference values:	0.2	0.4	1	2	below expected
	1	1.8	5	9	dropping point
	2	3.6	10	18	
	3	5.4	15	27	
	10	18	30	48	

Selection of the heating rate:

For preliminary determinations, 10 °C/min should be used. On an average, results are 4...7 °C higher than at 0.2 C/min. The pharmacopoeia, as well as DIN 51801 or ASTM D 566-64, prescribe a heating rate of 1 °C/min. The dropping points measured are 0.5...2 °C higher than those determined with a heating rate of 0.2 °C/min. As a rule, the reproducibility (standard deviation) is better than ± 0.3 °C for vegetable and animals fats. A heating rate of 0.2 °C/min should be used for precision measurements. Usually, reproducibility is better than ± 0.2 °C. This heating rate is not suitable for lubrication greases and fatty polymers.
Since the dropping point is a technical identification value, there is no automatic extrapolation of the result to the zero heating rate. The following curve illustrates the relationship of the dropping point to the heating rate selected.

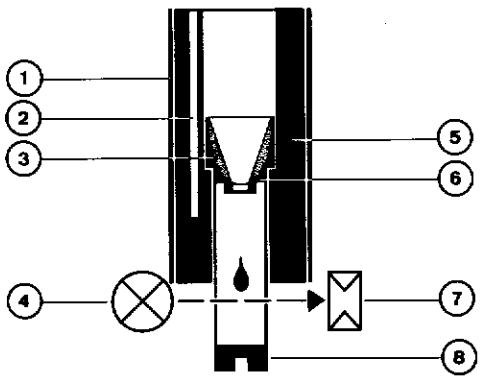


Relationship of the dropping point of vaseline to the rate of temperature increase.

5.3. Measuring principle and application of dropping point and softening point determination

The dropping point or softening point of a sample is that temperature at which the first drop falls or flows out of the opening of a standardized sample cup. In this procedure, results depend very much on how the sample is prepared (pre-melting of the sample or not, manner in which the sample cup is filled) and the heating rate. For this reason, determination is subject to many national and international standards. The determination of this point is an easy and quick thermal method of checking ointments, waxes, edible fats, fatty polymers, pitches, tars and bituminous materials.

In the FP83, the fall of the first drop is recorded photoelectrically and the temperature at which this occurs is displayed in the control instrument:

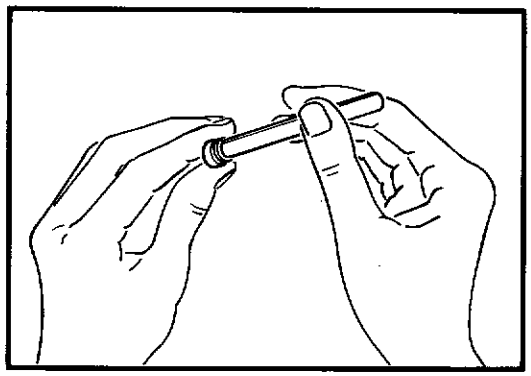


1 Heating element
2 Platinum resistance thermometer (Pt100)
3 Sample
4 Light source
5 Furnace
6 Sample cup
7 Photocell
8 Collector sleeve

5.4. Maintenance

With normal use, the FP83 measuring cell requires very little maintenance. Maintenance is limited to replacement of defective bulbs (see page 25) and cleaning the interior of the cell. No adjustment of the light bulb is required.

5.5. Cleaning



Cleaning the sample cup:

- Use the spatula provided to clean any remaining grease from the sample cup.
- Clean the sample cup with a solvent and dry it with a clean cloth.
- Clean the collector sleeve with the pointed part of the spatula. The viewing slot must be clear and unobstructed.
- Alternatively heat the different parts on a filter paper in an oven to 100 °C (212 °F).

6. THE FP85 TA MEASURING CELL FOR MEASURING HEAT FLOW (DSC)

This instrument measures heat flow from and to a sample. Determination is made either under isothermal conditions or under constant cooling or heating rates. The heat flow is converted into an electrical signal. This signal is proportional to the heat flow. The signal can be plotted on a simple strip chart recorder (e.g. the Mettler GA17) and can then be evaluated manually. It can also be processed automatically if a computer is connected to the system. The instrument itself can automatically determine the melting or boiling range of a sample.

Depending on the determination which is to be made, the selector switch on the cell plug is set on one of the three symbols. The position of the selector switch is recognized by the processor when the FP80 is switched on, or when key [RESET] is pressed.

no numerical results, only recording of curve

melting range

boiling range

} in addition, the curve can be recorded

6.1. Determination of the melting range using the example of benzoic acid

Sample preparation

Approximately 5 mg of pulerverized sample are placed in an aluminum crucible. The crucible is closed with a lid. To do this the crucible is placed in the sealing press, the cover is placed on it, and is pressed by slowly turning the handwheel clockwise, (page 70).

Test procedure

The selector switch on the connector of the measuring cell must be set to  . If this was not done before the instrument was switched on, the [RESET] key must be pressed in order to read the new position.

Benzoic acid has a melting point of approx. 122 °C. A starting temperature of 105 °C should be selected with a heating rate of 5 °C/min. The last press of the [RUN/STOP] key put the instrument in the ready condition:

[RUN/STOP] T 105. C / 5.0 C/MIN ↔ T READY / 5.0 C/MIN

Remarks

The DSC determination is a thermodynamic measurement which yields the sample temperature. A "correction" to pharmacopoeia values was intentionally dispensed with. For this reason, a pure substance will always have a melting range of almost zero. Absolute accuracy is less than with the optical method of the FP81. Calculation of results is based on pulverized substances. Pure metals can therefore show slight deviations from the reference value.

Selection of the starting temperature:

Starting temperature should always be selected so that the expected melting temperature is reached no sooner than 3.5 minutes after the start. Endothermal effects cannot be detected during these first 3.5 minutes.

Heating rate	Start temperature	
1.0 °C/min	3.5 °C	lower than the expected event temperature
2.0 °C/min	7 °C	
5.0 °C/min	18 °C	

Selection of the heating rate:

Unlike with conventional melting point determination, the heating rate selected should not be too low. Values below 1 °C/min. should be avoided. However, the accuracy of the results decreases with increasing heating rates.

If there is to be no conversion to standard pressure, the press of the [RESET] key puts the instrument into a mode in which the instrument is ready for a new measurement. Pressing the [RESULT] key starts the conversion to standardized pressure (as was described on page 21). The standardized result is now printed out or displayed:

STANDARD 75.8...76.2 C

Remarks

Unlike with the FP81 measuring cell, bumping is not recognized with the DSC method.

Selection of the starting temperature:

Starting temperature should always be selected so that the expected boiling temperature is reached no sooner than 3.5 min after the start. Endothermal effects cannot be detected during these first 3.5 minutes.

Heating rate	Start temperature	
1.0 °C/min	7 °C	below expected boiling temperature
2.0 °C/min	14 °C	
5.0 °C/min	36 °C	

6.3. Calorimetric calibration with indium

By melting indium, the quantity of heat in mJ (mcal) represented by a particular peak area can be determined. Indium metal is especially suitable as a standard substance because it is available in a very pure state, crystallizes well and does not oxydize. (The sample can be used over and over again.) Indium melts at 156.6 °C and has a heat (enthalpy) of fusion of 28.5 J/g (6.80 cal/g).
A chart recorder (page 8, 99) is connected to the FP80 control instrument for the calibration. It is advantageous to maintain the following test conditions:

An indium pellet is pressed flat on a hard surface with the end of the tweezers and weighed accurately to ± 0.01 mg. The indium pellet is then placed in an aluminum crucible and sealed with a pierced cover (page 70).
A starting temperature of 140.0 °C and a heating rate of 5.0 °C/min are chosen. An end temperature of 171.0 °C can be used.
A range of 100 mV (zero line to the left) and a chart speed of 60 mm/min are set on the recorder.
The selector switch on the measuring cell must be set to ⎺\/⎺. If this was not done before switching on the instrument, the [RESET] key must be pressed after switching to ⎺\/⎺. The last press of the key puts the instrument in the ready condition:

[RUN/STOP] T 140.0 C / 5.0 C/MIN ↔ T READY / 5.0 C/MIN

After positioning the recorder pen, the test can be started by pressing [RUN/STOP]. The following then appears in the display:

[RUN/STOP] WAITING 180 S

Indium sensitivity E_{In}

E_{In} is used for the determination of the heat flow resp. the calculation of the ordinate scale, and indicates how many mV (on the recorder) correspond to a heat flow of 1 mW.
For the determination of E_{In}, the calibration factor F and the area weight of the chart are needed. For this purpose a rectangle of 100 % chart width and 60 mm length is cut out and weighed. In our example the area measures 100 mV x 60 s = 6000 mVs.

$$E_{In}\ [mV/mW] = \frac{\text{area of the rectangle [mVs]}}{F\ [mJ/mg] \cdot \text{weight of rectangle [mg]}}$$

$$\text{Example: } E_{In} = \frac{6000\ mVs}{0.736\ mJ/mg \cdot 1011\ mg} = 8.06\ \frac{mVs}{mJ} = 8.06\ \frac{mV}{mW}$$

The value of E_{In} which has been determined can be written on the memo-card and used for future determinations of the heat flow.

Remark: E_{In} and F are slightly different for each particular instrument and should be determined approximately once a year. When the recorder paper is changed, the calibration factor F must be redetermined.

6.4. DSC measurements using the example of benzoic acid

The following basic information can be gained from a DSC signal:

- Temperature (e.g. melting temperature), T_s [°C]
- Heat flow (and ordinate scale), $\dot{H}$ [mW]
- Enthalpy change (e.g. enthalpy of fusion), ΔH [mJ, J/g]

For the determination of the heat flow and enthalpy changes the instrument must be calibrated according to chapter 6.3. Furtheron one must take into account that the calorimetric sensitivity is a temperature function which means that the corresponding results must be corrected by E relative (E_{rel}). The values E_{rel} can be taken from the table on page 84 or on the memo-card.

Sample preparation

Approximately 3 mg of powdered benzoic acid are placed in an aluminum crucible and weighed accurately to 0.01 mg. Then the crucible is sealed with the sealing press. To do this, the crucible is placed in the sealing press and the cover is placed on it and sealed by slowly turning the handwheel clockwise. Note: The cover must not be pierced, because benzoic acid sublimes very easely.

Test procedure

Benzoic acid has a melting point of approx. 122 °C. A starting temperature of 105 °C with a heating rate of 5 °C/min should be selected. The end temperature can be 141.0 °C. Recording of the melting curve is done in exactly the same manner as in the previous measurement with indium metal. If the chart speed or the recorder range deviates from the indium calibration, then these factors must be considerated in the following calculation.

Heat quantity (enthalpy change)

The heat of fusion of benzoic acid is determined by cutting out and weighing the melting peak, using the following equation:

$$\Delta H\ [mJ] = \frac{\text{Weight of peak [mg]} \cdot F\ [mJ/mg] \cdot G}{E_{rel}}$$

Example: $\Delta H = \frac{572 \cdot 0.736}{1.075} = 391.6$ mJ

When using the same measuring range and chart speed as for the calibration, G equals 1 and otherwise according to the table below:

chart speed [mm/min]	range [mV] 50	100	200	500
60	0.5	1	2	5
20	1.5	3	6	15
10	3	6	12	30
5	6	12	24	60

$$G = 0.6\ \frac{\text{range [mV]}}{\text{chart speed [mm/min]}}$$

The specific enthalpy change ΔH_{spec} is:

$$\Delta H_{spec}\ [J/g] = \frac{\Delta H\ [mJ]}{\text{sample weight [mg]}}$$

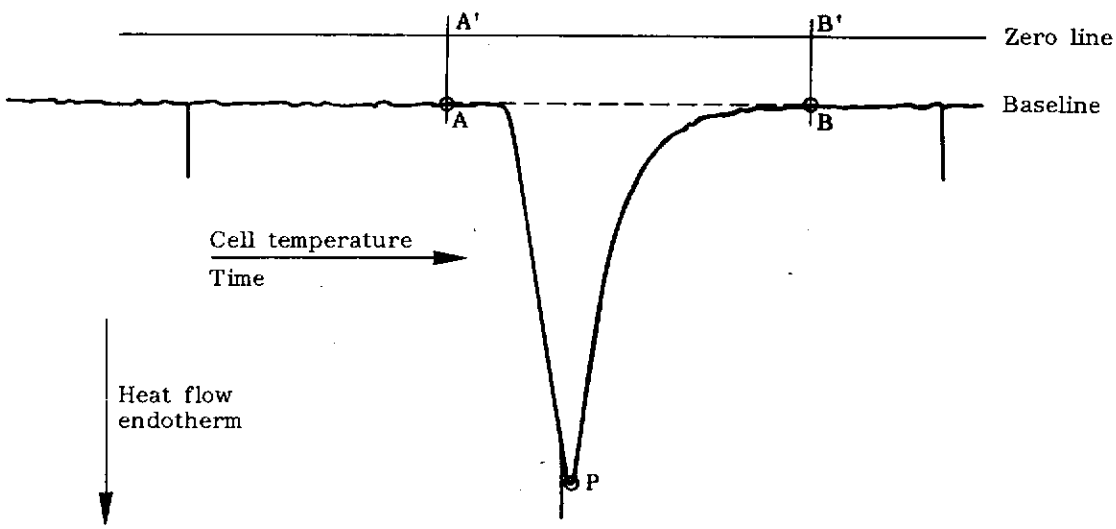
Example: $\Delta H_{spec} = \frac{391.6\ mJ}{2.765\ mg} = 141.6$ J/g

Remarks

If the evaluation is streched over a larger temperature range, either a mean E_{rel} should be used, or the curve should be divided into several sections.
The measuring cell can be placed in a freezer for measurements at or below room temperature.

Computer evaluation of the DSC curve

The FP80 central processor has a standard RS232C computer data interface, to which a compatible computer can be connected directly (page 85). The heat quantity corresponds to the area under the curve. In the following example, it is the area of peak APB. This is determined by simply adding up the DSC signals transferred in approx. 1 second periods. The area of the rectangle ABA'B' represents the sum of two heat quantities. The one results from the asymetry of the cell, and the other is the sensible heat that is required to just heat up the sample (corresponds to specific heat c_p). They are both irrelevant to the calculation of the heat of fusion.



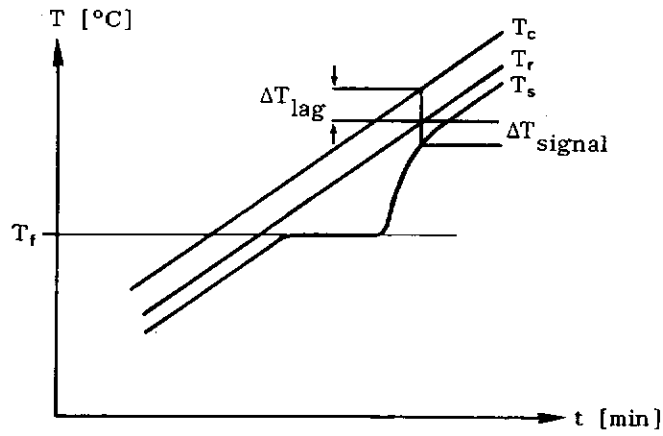
Determination of indium sensitivity E In

E_{In} is an instrument constant, which, once determined, is used in the above equations as a constant. A simple total of the W signals over the baseline AB is sufficient for the determination. Sample preparation is described in the first section on page 62. A heating rate of more than 5 °C/min should not be selected. E_{In} is calculated as follows:

$$E_{In}\ [\text{points/mW}] = \frac{\text{area of the curve [points} \cdot \text{cycles]} \cdot 0{,}9360^{*}\ \text{s/cycles}}{\text{heat of fusion}_{In}\ 28{,}5\ \text{mJ/mg} \cdot \text{mass}_{In}\ [\text{mg}]}$$

Thermometric information

The thermometric information is also available as raw data, whereby the displayed and transferred temperature T_c is the true temperature of the cell. The temperature of the T_r-crucible without the sample (reference crucible) lags slightly behind the cell temperature. The temperature T_s of the sample lags even more due to its heat capacity. T_f is the temperature of the melt, which for pure samples remains constant during the melting.



The following mathematical relations apply:

For the reference temperature T_r:

$$T_r\ [°C] = T_c\ [°C] - \frac{\tau_{lag}\ [s] \cdot \beta\ [°C/min]}{60\ s/min}$$

For the sample temperature T_s:

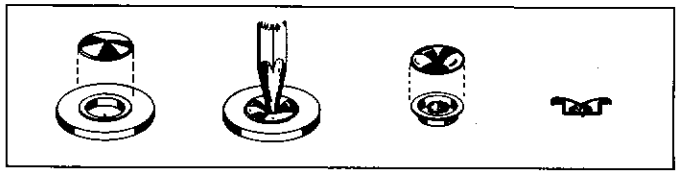
$$T_s\ [°C] = T_r\ [°C] + \frac{(5000\text{-}W)\ [points]}{S\ [points/°C]}$$

* The cycle time for the transfer of signals must be taken into consideration in adding up the W signals:

50 Hz = 0.9360 s

60 Hz = 1.0404 s

Samples with a large volume (e.g. light powders, flakes, fibers) are first packed in a small, grease-free piece of aluminum foil and sealed. Often, it is sufficient to use a deformed crucible cover, which then presses the sample flat against the bottom of the crucible automatically when it is sealed.



To deform the crucible cover, place it on an empty crucible for a mold, and press down on it with a dull pencil point, for example.

Weighing in the sample

It is best to tare out the crucible and the cover on the balance, fill in the sample, seal the crucible and then read off the net weight displayed on the balance. This procedure prevents errors caused by spilling or vaporizing of the sample.

Sealing the crucible

The manner in which the crucible is sealed determines the desired defined contact with the ambient atmosphere:

A crucible cover that has had several holes pierced into it allows free access of the measuring cell atmosphere -- which is important, for example, for dynamic oxidation stability -- while isothermal measurements can also be carried out with a crucible with no cover. In principle, the cover should be perforated before sealing the crucible to prevent deformation of the crucible. (Procedure: turn the cover upside down on a soft surface, for example an eraser, and perforate it five times using a thick needle).

Impeded gas exchange is important, for example in the determination of boiling behavior of liquids, to prevent the sample from evaporating prematurely. For this reason, the crucible cover is placed on a hard surface (e.g. on the crucible box) and perforated once with a sharp needle. If necessary, check the perforation with a microscope; a hole diameter of approx. 20 µm is ideal.

An even more impeded gas exchange is achieved by spreading approx. 1 mg of Al_2O_3 on the lip of the crucible and then sealing the crucible with the sealing press.

A sample is hermetically sealed to prevent any components from vaporizing (e.g. in chemical reactions), to delay undesirable decomposition reactions at higher temperatures (e.g. in purity analyses), and to prevent oxidation reactions. (This procedure eliminates the need to flush the measuring cell with inert gas.)

All crucibles can be hermetically sealed: the standard aluminum and gold crucibles by cold welding with the crucible sealing press. For temperatures above approx. 250 °C the cover must be pierced to avoid deformation of the crucible.

Working with a gas purge

Several objectives can be pursued when working with a gas purge:

- Purging the measuring cell of gaseous or vaporized products. With corrosives, e.g. halogen containing gases, purging saves the measuring cell and cleaning is necessary less often.
- Purging atmospheric oxygen to prevent unwanted oxidation of the sample.
- Introduction of a reactive gas to study chemical reactions on the sample.

After inserting the sample crucible, the measuring cell is purged for 2 to 5 minutes with high flow rate (50...200 ml/min) at the starting temperature. During the test, flow is generally 20 to 50 ml/min. For adjustment of the gas flow, the flow meter with needle valve listed in the accessories is used. For purging with air above room temperature (condensation and icing can occur below room temperature), an aquarium air pump is suitable as a source. Note: a pulsating air current can cause DSC noise. Usually, a hose approx. 2 meters long to the flow meter is sufficient to act as a damper.

Instructions for testing samples with corrosive decomposition products (e.g. PVC)

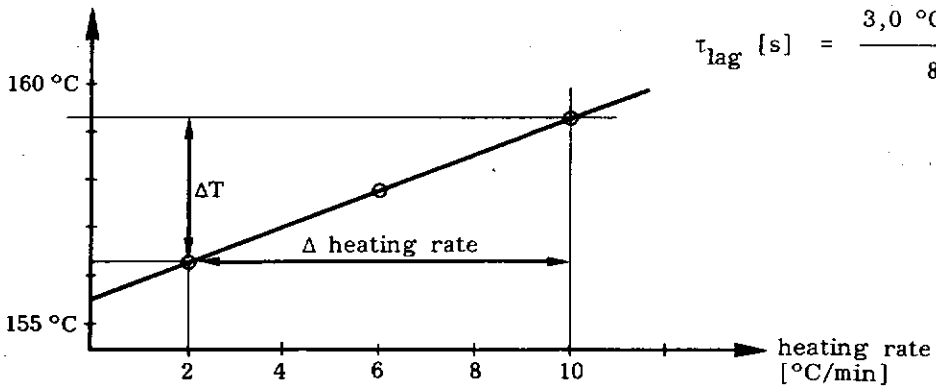
In many cases, complete decomposition proceeds irregularly; however, the beginning of decomposition is reproducible and provides much information:

1st rule: Only determine beginning of decomposition and then cool
2nd rule: Always use a gas purge (50 ml/min.)

Determining the τ lag (TAU Lag)

The time constant of the temperature equalization between furnace body and measuring sensor holding the crucible is determined most easily graphically. For this, the onset point (beginning of melting of a pur substance) at various heating rates is determined (page 63) and the onset temperatures determined are plotted as a function of the heating rate. The slope of the resulting line is proportional to τ_{lag}.

$$\tau_{lag}\ [s] = \frac{\Delta T\ [°C] \cdot 60\ s/min}{\Delta\ \text{heating rate}\ [°C/min]}$$



$$\tau_{lag}\ [s] = \frac{3{,}0\ °C \cdot 60\ s/min}{8\ °C/min} = 22.5\ s$$

The thermal law for heat flow is analogous to Ohm's law. Accordingly, heat flow is proportional to the driving force (temperature gradient) and inversely proportional to thermal resistance R_{th}. Applied to the DSC measuring cell, we get:

$$\dot{H} = \dot{Q}_s - \dot{Q}_r = \frac{T_c - T_s}{R_{th}} - \frac{T_c - T_r}{R_{th}}$$

For reasons of symmetry, the two T_c and the two R_{th} values are identical. Thus,

$$\dot{H} = -\frac{T_s - T_r}{R_{th}} \quad \frac{\Delta T}{R_{th}}$$

To avoid problems with plus and minus signs, an effect will be labeled exothermal (or exo) or endothermal (or endo) and a plus or minus sign left out.

Since the temperature difference is measured with a thermocouple (Chromel-Alumel Model K), the following results under consideration of the thermocouple equation: $\Delta U = \Delta T \cdot S$ resp. $\Delta T = \Delta U/S$ (S = thermometric slope, see Appendix F, page 104).

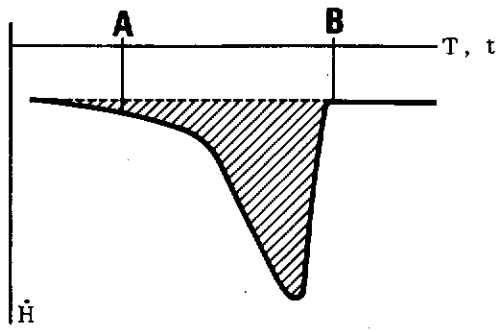
$$\dot{H} = \frac{\Delta U}{R_{th} \cdot S}$$

Since both values in the denominator are a function of the measuring temperature T_c, they are summarized as calorimetric sensitivity E: $E = R_{th} \cdot S$, and are split up into a temperature dependent (relative) component E_{rel} (Table, see page 84) and into a component that is specific for the particular measuring cell E_{In} and independent of temperature:
$E = E_{rel} \cdot E_{In}$. Thus, the heat flow to the sample is written as:

$$\dot{H} = \frac{\Delta U}{E_{In} \cdot E_{rel}}$$

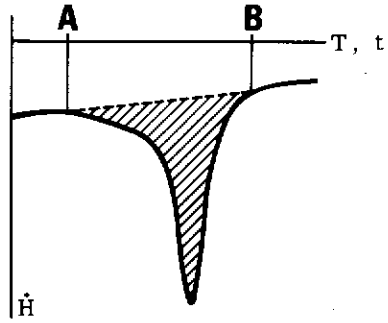
In deriving this equation, no consideration was taken of the fact that in addition to heat resistances, there are also heat capacitors in the path of the heat flow. These heat capacitors act as a damper with a certain time constant, in the same was as an electrical RC element. The τ_{signal} time constant in the FP85 is approx. 13 sec and leads to "smearing" of the DSC signal. By using the following equation, the original heat flow to the sample can be reconstructed ($\dot{U}$ = slope of the signal):

$$\dot{H} = \frac{\Delta U + \tau_{signal} \cdot \dot{U}}{E_{rel} \cdot E_{In}}$$



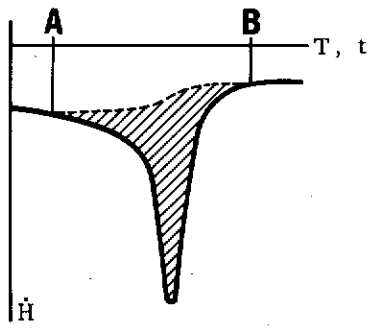
The baseline is equal to the heat flow at the end of baseline B, parallel to the zero line or as extension of the curve after B.

Primary applications: melting plastics.



The baseline connects measuring points of baseline start A and baseline end B.

Primary applications: general peak integration, determination of partial integrals, peak integration with overlapping of several peaks.



What is referred to as the integral baseline is a connection between the measuring points from start of integration to end of integration, which shifts proportionally to the partial integral. In this way, a c_p change of the sample connected with the conversion is taken into consideration. The resulting integral corresponds to the heat of transformation.

Main applications: chemical reaction heats.

6.8. Maintenance

Cleaning the DSC measuring sensor

The measuring sensor should be cleaned only if the baseline gives cause for complaint. The surface of the measuring sensor is cleaned with a cotton swab soaked in alcohol. Most contamination can be removed by heating the sensor to 400 °C and letting it stay at that temperature for approx. 1 hour, whereby it is advantageous to use air or oxygen as a purge gas.
If the contamination cannot be removed using this method, the sensor can be treated carefully with a glass-fiber eraser pencil or with a piece of fine emery cloth (220 grain).

Cleaning the cell cover and furnace lip

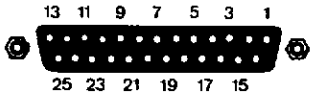
The cell cover must fit snugly on the furnace lip. If the surfaces are dirty, they can be cleaned with alcohol or, if needed, with steel wool or with a glass-fiber eraser pencil.

Computer data interface

Electrical signals: Conforms to the RS232C standard

Data format: Serial, 7-bit ASCII (HEX: 0A, 0D, 20...5F)
2400 baud (timer controlled 1 character / 5 ms)
even/odd parity adjustable (page 97)
FP80 input ignores parity bit
1 stop bit

RS232 connector:



FP80 = Data Terminal Equipment

Pin-No.	Function	Remark
1	protective ground	
7	signal ground	
20	standby out	FP80 switched on
2	data out	Ready-to-receive signal from computer
5	not-busy in	
3	data in	Fixed (FP80 always ready to receive
4	not-busy out	

Recorder output

Output signal: max. ± 15 V, normally ≦ 1 V ≙ 6000 points, ± 10 % (raw signal)
Marking every 10 °C at heating rate of > 3 °C/min or every 1 °C at heating rate of ≦ 3 °C/min

FP81 MBC Cell

Temperature range: room temperature ...300 °C (...572 °F)
with external cooling -20...+300 °C (-4...+572 °F)

Absolute accuracy of the melting point determination (heating rate 0.2 °C/min):

-20...30 °C ± 0.4 °C
30...200 °C ± 0.2 °C
200...300 °C ± 0.4 °C

Absolute accuracy of melting range determination (heating rate 0.2 °C/min):

- Beginning of melt: two-fold tolerance as melting point (typical)
- End of melt (clear point): same tolerance as melting point (typical)

Absolute accuracy of the boling point determination: three-fold tolerance as melting point (Exception: water, because of its high surface tension, the values will be 1...2 °C to high)

Operating capacity: 30 melting points per hour or 10 boiling points per hour

Required sample quantity: 1...3 mg for the caplillary tubes 50...80 µl for the sample tubes

Hand set: Dimensions:	base area 120 x 80 mm, height 31 mm
Lenght of connection cable:	146 cm
Connection synchronization:	
- from camera:	minimum close contact time, 1 msec; potential-free contact with max. 100 Ω contact resistance
- from manual control panel:	Voltage via open contact: 3.75 V, output impedance approx. 1 kΩ; lenght of cable: 32 cm; male connector conforming to DIN. The required extension cable is available in any photography supply store.

FP83 Dropping Point Cell

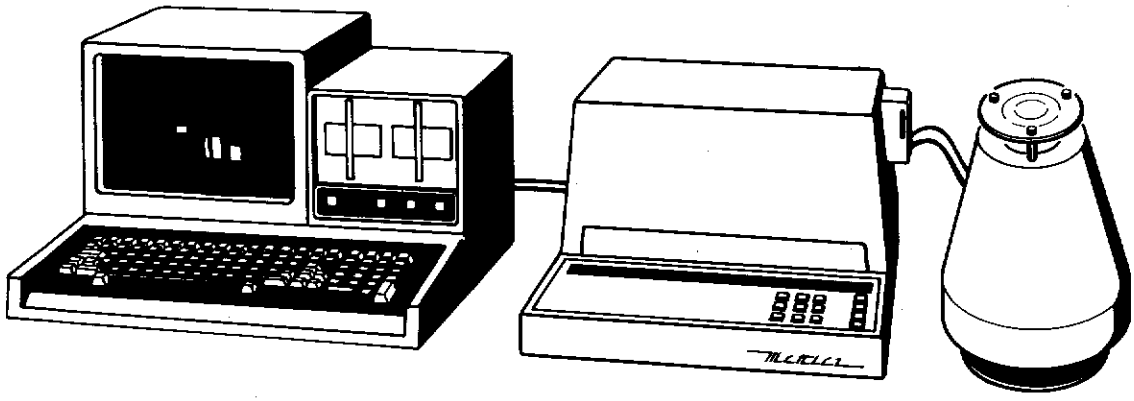
Temperature range: with external cooling	room temperature ...300 °C (...572 °F) -20...+300 °C (-4...+572 °F)
Absolute accuracy of the cell temperature: (heating rate 0.2 °C)	-20...30 °C ± 0.4 °C 30...200 °C ± 0.2 °C 200...300 °C ± 0.4 °C
Reproducibility (standard deviation measured with 3 samples stearic acid, 99.9 %, heating rate 0.2 °C/min	± 0.2 °C
Capacity:	approx. 10 samples/hour
Required sample quantity:	0.4...0.6 g
Cup:	conforming DIN 51801, page 1, ASTM D 566-64 or D2265-78
Cup:	conforming to ASTM D 3104-72 and D 3461-76
Housing, dimensions, connection cable and weight:	same as FP81

FP85 TA Cell

Temperature range: with external cooling:	room temperature ...400 °C (...752 °F) -20...400 °C (-4...752 °F)
Absolute accuracy of the cell temperature (isothermally):	-20...30 °C ± 0.7 °C 30...100 °C ± 0.5 °C 100...200 °C ± 0.7 °C 200...300 °C ± 1.2 °C 300...400 °C ± 1.5 °C
Reproducibility (standard deviation n = 3) Benzoic acid 99.9 % Ethanol 94 %, (Heating rate 1 °C/min):	Melting range: ± 0.4 °C Boiling range: ± 0.4 °C
Cooling rate (typical) - unregulated: - regulated:	from 400 °C to 100 °C in 3.5 min with 10 °C/min to approx. 40 °C at 25 °C room temperature
Tau lag * (typical):	22 s
Tau signal * (typical):	13 s
Calorimetric sensitivity * (typical):	45 points/mW at data output (7.5 mV/mW at recorder output)
Noise * (typical):	at recorder output: 0.5 mV peak to peak on display: 3 points peak to peak (0.07 mW)
Reproducibility of enthalpy measurement * (typical):	1 % (evaluated with personal computer)
Thermometric sensitivity * (typical):	208 points/°C (34,7 mV/°C at recorder output)
DSC measuring sensor:	chrom alumel, Model K
Crucible: - Standard crucible:	aluminium, 40 µl effective capacity; can be sealed tight to 2 bar
- Special crucible:	aluminium 160 µl, 2 bar; gold crucible 40 µl, 2 bar
Purge gas:	Nitrogen, air oxygen, carbondioxide, helium, or mixtures of these gases.
Housing, dimensions, connection cable, and weight:	same as FP81

* (measured with Indium in standard aluminium crucible)

APPENDIX B: Computer connection



The FP80 control instrument has a built-in computer data interface which operates according to the RS232C standard. Regardless of the kind of measuring cell used, a suitable computer can be connected to process incoming raw data and final results. In addition, the control instrument can also be remotely controlled via the same computer. Your Metter representative will be happy to provide you with further information. Mettler has also prepared two programming examples for some personal computers. These examples are intended to give you incentive to develop your own programs and to put you on the right track in writing your own best FP data processing program.

The computer as data receiver

In this operating mode, the computer must always be ready to receive. (Exception: if there is a "busy" signal, active.) The FP80 control instrument and the measuring cells are manually operated as described in these Operating Instructions. Approximately every second, the control instrument transmits the cell temperature (°C) and the measured values of the three measuring positions, X, Y, and Z. Depending on whether or not a printer is connected, the heading, test parameters and results are also transferred. FP800 System error messages are also passed on to the computer immediately. The end of a test, whether finished or terminated with [RESET], is displayed by a special data string: "# (CR) (LF)" (ASCII 23H).

Printer data strings: Maximum of 22 characters, each time

Measurement data strings: Always 22 characters, every 936 msec. (50 Hz) or 1014 msec (60 Hz).
For example, the data string can look like the following:

T1203X□ □-1Y1000Z□ □25(CR)(LF) (□ ≙ Blank)

Table of ASCII character for remote control

'0'...'9'	Numeral keys [0...9]
'A'	[±]
'B'	[CE] (clear entry,)
'C'	[RUN/STOP]
'D'	[RESULT]
'E'	[RATE]
'F'	[START TEMP.]
'G'	[RESET]
'J'	[-] Hand set
'K'	[↑] Hand set
'L'	[↓] Hand set
'M'	[TRF] Hand set
'I'	Request of status in reset condition
'N'	Unblocking of keyboard
'P'	Request of the FP80 display
'Q'	Simulation of power switch-on

All other characters are ignored. All characters except N, P and Q block the FP80 keyboard and the hand set.

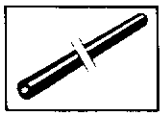
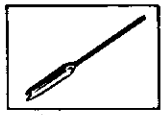
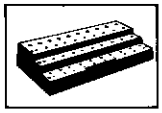
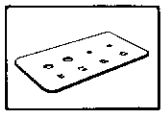
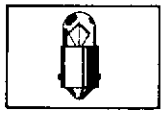
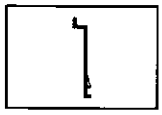
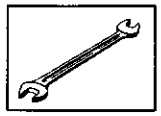
General remarks

- The output of data is made in strings of 2...24 characters in length (exception: display test = 42; definition: string = a character sequence up to and including [CR] [LF]).
- The minimum pause between two data strings is > = 15 msec. (= time for the computer to activate the "busy" signal after receiving a string).
  (The busy signal prevents the output of characters and can be activated at any time. However, it must be taken into consideration that a character that has been started will be completely transferred).
- If the "busy" signal is active for too long a period, data can be lost.
  (The FP80 internal output buffer can hold up to 300 characters.)
  A data loss is indicated by means of a "! [CR] [LF]" data string.
  (The relatively large buffer permits transfer pauses, for example, to allow the computer to put received data into a mass storage (tape/diskette). While a measurement is going on, up to 13 measuring data strings can collect, which corresponds to a transfer pause of approx. 12 s.
- Recommendation: the computer should read out the buffer completely in the reset condition (e.g. after pressing RESET), to obtain a defined start status before a new measurement.
  (Caution: If a computer waits for an input string in a BASIC statement and no string arrives, the computer generally remains blocked. For this reason, it is recommended that a time-out mechanism be used, which forces an interruption of the wait for an input string after 2 seconds.

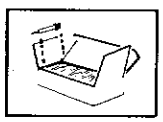
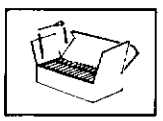
Remarks

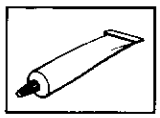
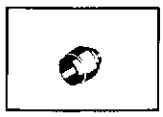
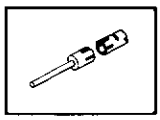
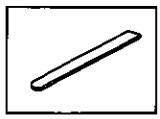
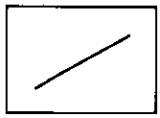
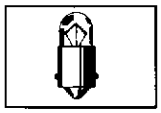
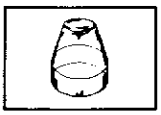
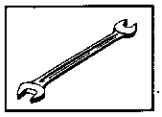
- Remote control of the FP80 is achieved in that the key functions are triggered via a serial data interface. Operating procedure is the same as for manual operation.
- Keys which are inactive in the manual mode, are also inactive under remote control. It is also possible that if functions are triggered too quickly in sequence, they will not be accepted.
  (Recommedation: 1 sec. pause between triggering two function keys.)
- Any remotely controlled press of a key automatically locks the FP80 keyboard so that the FP80 can no longer be influenced manually. The FP80 keyboard must be released by the ASCII character "N".
- If the FP80 display alternates between two texts when a request is made (ready display), it is purely by chance, which of the two texts will be output.

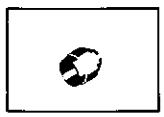
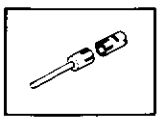
Standard accessories to the FP81

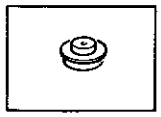
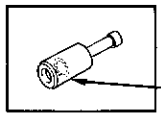
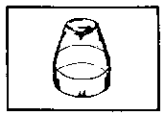
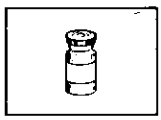
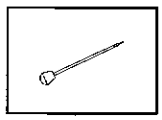
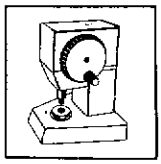
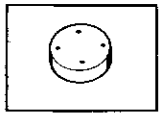
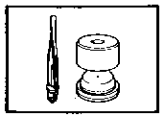
		Order No.	
	1 Test substance (benzoic acid, 99,9 %)	18555	
	2 Set of melting point tubes, each containing 150 pieces, dia. 1.3...1.5 mm including 5 tamping wires	18552	(1 set)
	2 Sets of boiling point tubes, each containg 40 pieces dia. 2.9...3.1 mm	18572	(1 set)
	1 Set of boiling capillaries, each containing 10 pieces	18574	
	1 Sample stand	18399	
	1 Hole gauge	18390	
	1 Set of lamp bulbs, 24 V, 2 W; 3 pieces	18562	
	1 Set of retaining clips, 10 pieces	18567	
	1 Dust cover	18571	
	Open-end hex wrench	73081	

Optional accessories to the FP81

	1 Package of disposable syringes, 1 ml; 100 pieces	71282
	1 Package of syringe needles, 0,8 x 80 mm; 12 pieces	71432

Standard accessories to the FP83	Order No.
 1 Test substance (vaseline)	71436
 3 Sample cups for determination of dropping point; hole dia. 2.8 mm	
 3 Sample cups for determination of softening point; hole dia. 6.35 mm	
 2 Cartriges, assembled (without sample cup)	
 1 Spatula	18719
 1 Rod (for droppening point acc. to ASTM D 566-64)	18720
 1 Set of lamp bulbs, 24 V 2 W; 3 pieces for furnace unit	18562
 1 Dust cover	18571
 1 Open-end hex wrench 5 mm	73081

Optional accessories to the FP83	
 1 Set of sample cups for determination of dropping point; 5 pieces hole dia. 2.8 mm	18732
 1 Set of sample cups for determination of softening point; 7 pieces hole dia. 6.35 mm	18127
 1 Cartrige, assembled (without sample cup)	17725

Standard accessories to the FP85	Order No.
 1 Measuring cell cover	17592
 1 Connector piece for gas connection with O-ring Note: Insert O-ring into the slot of the connection piece hole O-ring	17713 + 70814
 1 Dust cover	18571
 Indium, packed	29749
 1 Test substance (benzoic acid, 99.9 %)	18555
 Needle	29772
 Crucible sealing press	27330
 Set of crucibles	27338
 Crucible holder	28699
 Special DSC tweezers, packed	17682

APPENDIX D: Setting up the instrument and configuring the instrument

Power supply voltage

Before switching the instrument on, check the voltage setting on the rear of the instrument to make sure it corresponds to the local power-line voltage. If this is not the case, the instrument plug can be opened with a screwdriver (with the power-line cable disconnected) and the voltage set to agree with local conditions. The little cylinder is taken out and placed back so that the number which appears in window corresponds to your voltage.

Power fuse

The power fuse is located in the lower part of this same plug. The fuse rating is 1 A Slow-blowing for 220 and 240 V, and 1.6 A slow-blowing for 100 and 120 V.

Configuration

Before the power cable is plugged in, the operating mode of the instrument must bé configured. For this, the small square cover on the rear of the FP80 must be removed and the 8-position switch must be set properly using a small screwdriver or tweezers.

Remarks about the individual switch positions:

LANGUAGES	CODE		
ENGLISH	B	B	B
FRANÇAIS	B	A	B
DEUTSCH	B	B	A
ITALIANO	A	B	B
ESPAÑOL	B	A	A

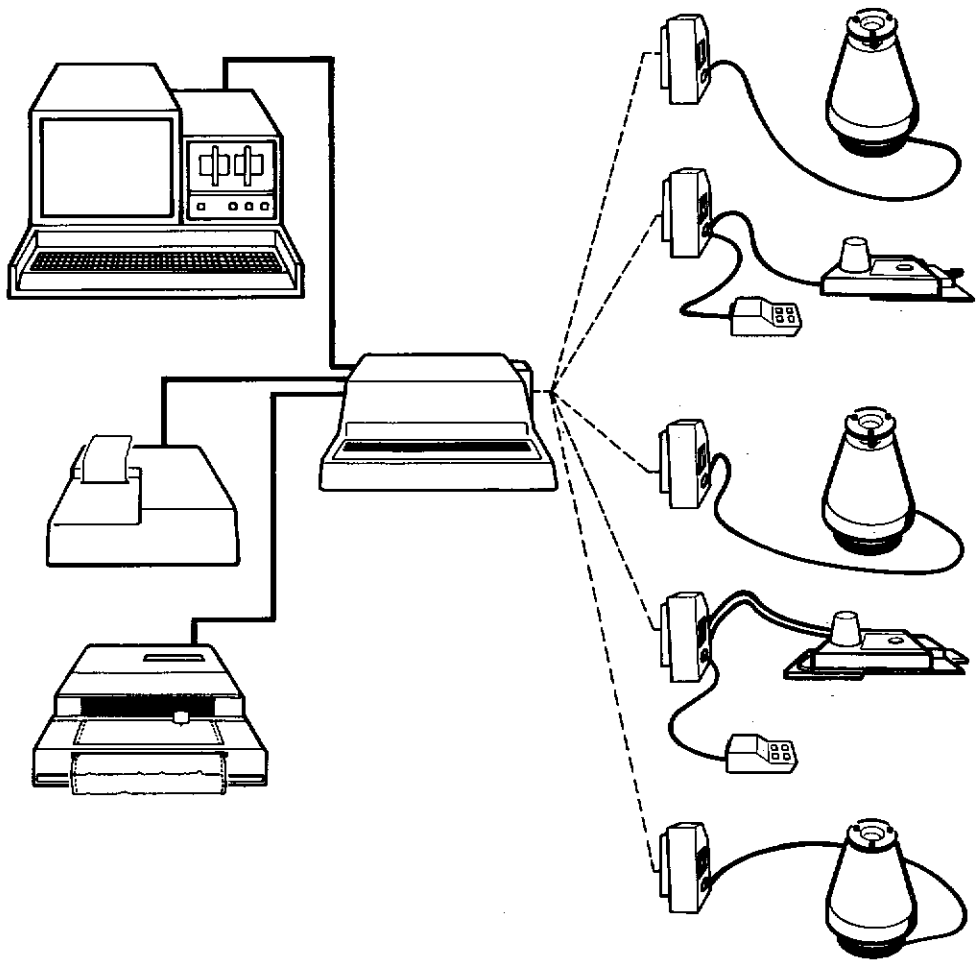
PARITY	FP	PRINTER	MARKER	LANGUAGES			TEMP.UNIT	IDENT
even	PHARMA	YES	YES	A	A	A	°C	YES
odd	THERMO	NO	NO	B	B	B	°F	NO
	1	2	3	4	5	6	7	8

Choice of parity:

Only active with computer interface. Must correspond to parity set on computer. FP80 ignores this parity bit on the receiving channel.

System cabling

Cabling is different for the different measuring cells. In every case, minimum cabling means connection of the measuring cell itself and plugging in the power cable. The maximum possible cabling is the example of the FP82 with printer, chart recorder, computer, hand set, camera and photomonitor, illustrated on page 31.



Warning messages

Such messages show in several ways:

```
X EEE    Y 3041    Z 0067
  ↑                   ↑
wrong               wrong
```

This warning message occurs only in connection with the FP81. The individual values are absolute values of the A/D Converter in points. With a properly adjusted lamp, they should lie between 1400 and 4000.

Values around zero indicate "no light". This can mean there is an improperly inserted retaining clip, a sample has been forgotten, a dirty measuring position or a defective lamp. If the values do not hover around zero and the measuring cell is otherwise okay, the lamp must be adjusted (see page 25).

```
BUMPING
```

The substance in the cell tends toward retarded ebullition (bumping). The resulting boiling temperature is probably too high.

the display is flashing:

```
TEMP 245.6 C
```

The actual temperature measured deviates from the nominal temperature by more than ΔT:

|Heating rate| [°C/min]	In range condition ΔT [°C]
< 0.3	0.25
0.3...2.0	|Heating rate|
> 2	1.0

Malfunctions

In addition to the error messages and warning messages described, there are several conditions that cannot be identified by the microprocessor. In spite of this, they can be recongnized by the user and corrected.

FP83

No results	- Furnace bulb defective (check by looking into the measuring channel) - Light opening in the collector sleeve clogged - Cartridge no inserted all the way to stop - Furnace not sitting on an even surface - Light shaft very dirty

FP84 and FP85

Poor baseline	- Furnace cover not on properly - Surface of measuring sensor very dirty

Factor by which the unit is multiplied	prefix	abbreviation of prefix
10^{-18}	Atto	a
10^{-15}	Femto	f
10^{-12}	Pico	p
10^{-9}	Nano	n
10^{-6}	Micro	µ
10^{-3}	Milli	m
10^{-2}	Centi	c
10^{-1}	Deci	d
10^{1}	Deka	da
10^{2}	Hecto	h
10^{3}	Kilo	k
10^{6}	Mega	M
10^{9}	Giga	G
10^{12}	Tera	T
10^{15}	Peta	P
10^{18}	Exa	E

Table 4

Important physical properties and their units

Temperature T

We attribute the sensation of hotness and coldness to the effect of the temperature T. The temperature, as the intensive parameter of heat, is a state variable and is independent of mass and material composition.

The basic unit for temperature

The Kelvin K is defined by the triple point of water of 273.16 K. The °C is today considered as a unit derived from the Kelvin: T in °C = T in Kelvin -273.15. Differences in temperatures in Kelvin have exactly the same values as in °C, i.e., ΔT = 15 Kelvin = 15°C.

In the FP800 the temperature is measured with a platinum resistence thermometer (Pt100). The resistance of platinum has a well known relation to the temperature and can therefore be used for its measurement.

On the other hand, temperature differences are better measured with thermocouples as their electrical signal is directly proportional to the difference in temperature between the hot and cold junctions: $\Delta U = S \cdot \Delta T$. S, the so-called slope or sensitivity of the thermocouple, is expressed in microvolts per Kelvin. The sensitivity of the gold/nickel thermocouple (FP84) for example is about 20 microvolt per Kelvin (Chromel/Alumel (FP85): 40 µV/K).

For example the change of enthalpy during isothermal fusion of a substance, is known as the enthalpy of fusion or heat of fusion ΔH_f). A process in which the enthalpy of the body of interest increases is called endothermal as heat is drawn from the surroundings. The engineer and also the ICTA (International Confederation for Thermal Analysis) assign a negative sign to such endothermal changes ("heat loss"). From the point of view of the body (scientific stand-point) the endothermal change naturally has a positive sign as the enthalpy increases in this process. Obviously it is opposite in exothermic processes where heat is given up to the surroundings. In order to avoid confusion with the conflicting sign conventions, it is advantageous to use the expressions exothermal or endothermal, abbreviated to exo or endo respectively, instead of the sign:
For example: ΔH endo = 335 J/g.

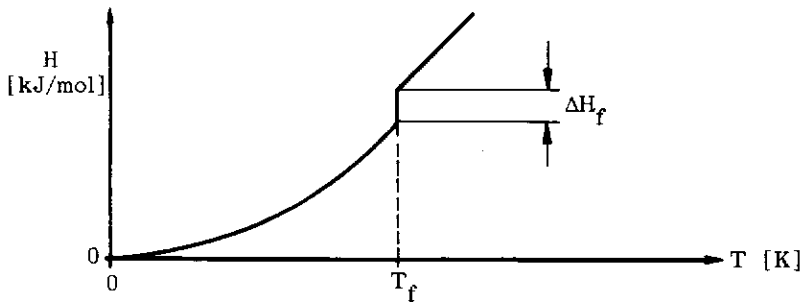


Fig. 1 The enthalpy as a function of temperature (Heating, melting)

Heat capacity, specific heat

The heat capacity, C_p, defines how much energy is required to heat a body by 1 Kelvin. The subscript p indicates constant pressure = isobaric condition.
As the absorbed energy is stored as enthalpy, the heat capacity is also a measure of how much the enthalpy of a body increases when it is heated through 1 Kelvin: $C_p = \Delta H/\Delta T$. The unit for the heat capacity is Joule/Kelvin.
The specific heat, c_p, defines how much energy is needed to heat 1 gram or 1 mole of a substance by 1 K (and by which amount the enthalpy increases): $c_p = \Delta H / \Delta T \cdot m$. The units are consequently 1 Joule/g·K or 1 Joule/mol·K. m = mass of sample.

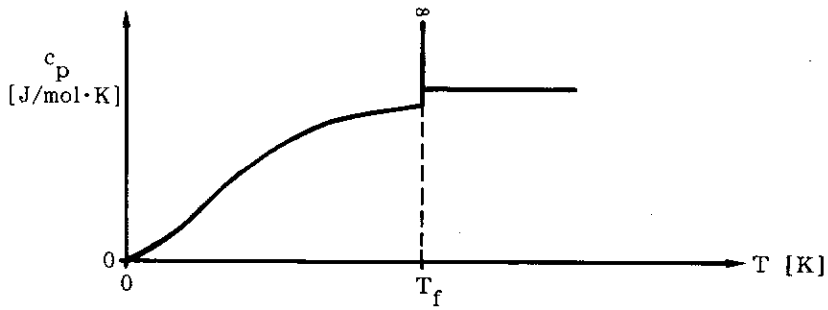


Fig. 2 The specific heat as a function of temperature.

Obviously the c_p temperature function is the first derivative of the enthalpy temperature function. Conversely, the enthalpy is equal to the integral of the specific heat over the temperature.

Physical changes as for example change in the state of aggregation give often rise to very sharp thermal effects. The physical changes are divided into transitions of different order. First order transitions include transitions that cause a sudden change of the state properties:

- Fusion and recrystallization.
- Evaporation and condensation.
- Polymorphic changes (solid-solid transitions).

There are two kinds of solid-solid transitions:

- Enantiotropic transitions may be carried out unlimited times in both directions (e.g. α-β-transition of Quartz at increasing and β-α-transition at decreasing temperature).
- Monotropic transitions only occure in one direction, namely from the metastable to the stable state. The metastable phase can be obtained by crystallization from melt or solution according to Ostwald's step rule (e.g. cocoa butter).

Second order include:

- Glass transitions of amorphous substances
- Electrical and magnetic Curie transitions
- Lambda transitions

Apart from thermal effects the following properties are of interest in thermal analysis:

DSC: Specific heat c_p as a function of temperature.
Enthalpy H as a function of temperature.

TMA: Linear Expansion coefficient α as a function of temperature.

The following table is a summary of typical thermoanalytical curves as an aid for interpretation.

[1] No effect

[2] In DSC pan with small hole

[3] Substances contaminating the measuring cell and air moisture may condensate on crucible and sensor.

[4] Can be repeated several times if wished

[5] Dilatometry without load

[6] TMA with application of compression stress (penetration measurement)

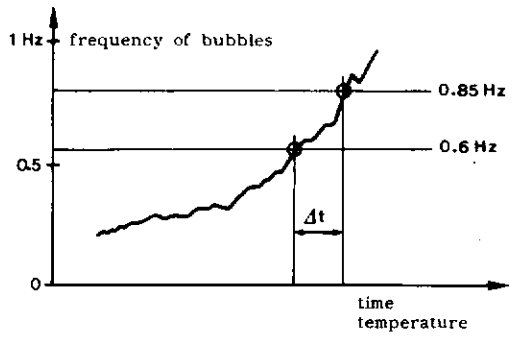
[7] Only magnetic Curie transitions and with magnetic field applied in downward direction (calibration magnet)

[8] Only with infusible materials

[9] Only in hermetically selaed pan (no volume work of evolved condensation products)

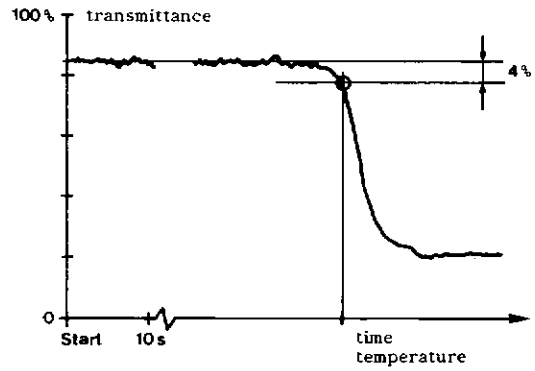
[10] No TMA with liquid samples

Boiling point



The boiling point is recognized at a bubble frequency of 0.6 Hz. It has to remain for at least 3 s at or above 0.6 Hz.
In case the time interval Δt between 0.6 and 0.85 Hz is shorter than 2 seconds, "bumping" is displayed (retardation of ebullition).

Cloud point

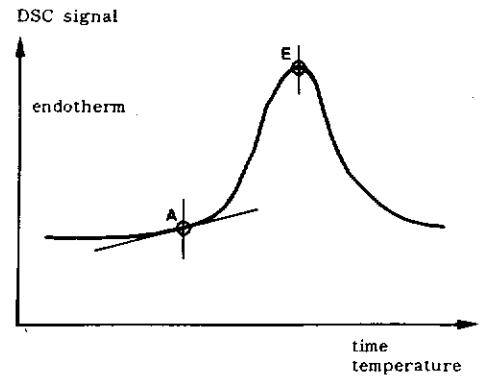


The cloud point is found at T_0 - 4 %. The transmittance has to be equal to or less than T_0 - 4 % for at least 12 s.

FP85 Measuring cell

The computed results on the print out are sample temperatures (manual determination from the recorder chart requires corrections according to the memocard or this operating instructions).

Melting range (A to E) and boiling range (A to E)



Point A is recognized at that point of the curve where the slope (digital points/s) exceeds a limit L:

$L = \beta / 2.05$

The slope has to be greater than or equal to L for at least 6 s.

The end E is found at the beginning of the signal decrease after the peak maximum. The signal has to be below the peak maximum for at least 10 s.