labsys

TG, TG-DTA
TG-DSC Version

USER MANUAL

SETARAM
GROUPE KEP INSTRUMENTATION • REGULATION

1

C/LABTGA

LABSYS™

TG, DTA, DSC, TG-DTA AND TG-DSC VERSION

COMMISSIONING
UTILISATIONS

SETARAM

GROUPE KEP INSTRUMENTATION • REGULATION

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1. REVISIONS TABLE

C	21/06/99	TRANSITION FROM CS 32 TO CS 332	C/LABTGA	C. PARAZZA	K. DAVAT	JL. DAUDON
REV	DATE	PURPOSE REV.	BOOKLET REF	REQUIRED BY	DONE BY	APPROVED BY

INSTRUCTIONS TO THE USER

Operating the instrument requires scientific and technical skill providing for compliance with all the laws of chemistry and physics.

The specifications and applications of our products are always likely to be modified. SETARAM will respond to any foreseeable damage directly linked to faults in its instruments, within the limits of the obligatory provisions in the law applying to the victim's action.

SETARAM is in no way liable for the damage resulting from experiments carried out with its instruments. Non-compliance with the advice and instructions contained in the commissioning or operating booklets will always be grounds for excluding liability, in particular, in case of instrument's alterations expressly not approved by SETARAM.

Before commissioning the instrument carefully read the instructions and fully comply with every point. Commissioning of various instruments require strict compliance with the directions and warnings contained in the various booklets.

To use peripheral instruments together with our apparatus (like for instance, computer, thermostated bath, pump), report to specific users manuals, delivered with each peripheral in order to guarantee a good working order as well as a good safety level of those equipments for our applications.

The instrument does not have a locking system preventing the access to the transducer whereas it could be able to stay at a high temperature. It is necessary to check this temperature thanks to the window ***Direct Programming*** (report to the ***Sefsoft booklet***) before opening the instrument.

Safety recommendations:

Carry the instrument with carefulness.

Think that vibrations or a shock may cause damages inside the instrument.

Read carefully safety labels.

Do not switch on the instrument in case it is damaged.

Before getting the instrument repaired, unplug it.

Do not switch on an instrument on which feed cable is damaged.

Once the instrument has been correctly installed, the customer will ensure that those operating it have the technical and scientific skills. He will make sure that

the products worked upon, as well as the experimenting conditions, are not likely to cause damage resulting from non-compliance with the laws of physics and chemistry. The customer will also ensure, under his public liability, that the instrument and its connections are not accessible to any operating or maintenance staff unaware of the operating instructions.

Any use not corresponding exactly with the instrument's general specifications will require initial contact being made with SETARAM.

The instruction leaflet enumerates other recommendations, indicated through a triangle with an exclamation mark in. Read and follow carefully those recommendations ! If you DO NOT, it could generate serious consequences as a breakdown, material damages as well as hurting people badly and even kill them.

Indicate an area which temperature is high.

Indicate an electric danger.

CHAPTER 1 - COMMISSIONING

1. Presentation

To satisfy the various requirements of laboratories using the techniques of thermal analysis and to fit in with their budgets SETARAM has developed a new range of equipment designated *labsys*™.

The *labsys*™ instruments are designed for ease of operation while offering robustness and high performance. They are appropiate for work in laboratories carrying out research and quality control, in universities and schools, providing that the instructions given at the beginning of this booklet are followed.

This operations booklet deals with the DTA and DSC plate-type versions.

The new instruments in the *labsys*™ line are distinguished by the following features :

- a structure integrating the controller and designed to take the TG balance module that may be associated to the DTA and DSC transducers.
- a metal-resistor furnace
- a multi-task software package piloting one or more modules
- a single series-cable linking the structure to the computer

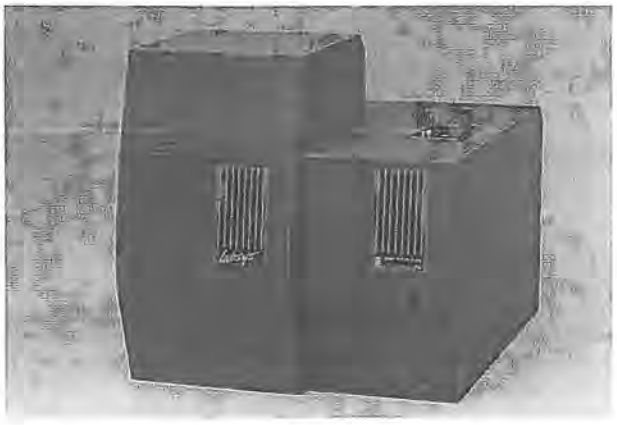


Figure 1: Labsys™ TG

2. Material

Labsys™ TG version is equipped with:

1. Various pipes for water connection and gas connections.
2. A series cable
3. A supply cable
4. An accessory box
5. The software
6. A box for the rods

⚠ When a *labsys*™ instrument has been ordered, the various parts of the instrument are carefully checked and tested before dispatch. Check that the delivered equipment is the one you ordered.

⚠ Upon receipt of the equipment, carefully check the various parts. Should any be damaged, make the customary claim against the transport operator.

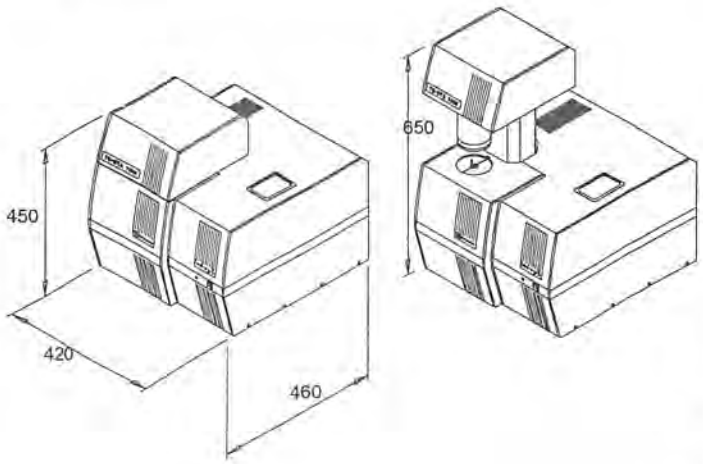
2.1. Location

The *Labsys*™ instrument is best installed on a stable table, in the style of laboratory bench. Flooring-type bases should be avoided, as well as closeness to machines causing vibration.

The instrument must be sheltered from draughts, and, if possible from the sun's rays.

Adjust the instrument's front legs so as to get the assembly horizontal.

2.2. Dimensions and weight



Weight : 44Kgs DTA/DSC version

46 kg TGDTA/TG version

⚠ The unit should be carried by two persons and held at the bottom of the structure.

Figure 2: Dimensions of the instrument

2.3. Cooling water

Water circulates permanently in the instrument's furnace during both the test and cooling. A rate of about 2 litres per minute is required for the instrument to operate properly. A special 8 x 1.25 mm-diameter Polyurethane pipe is supplied for this purpose.

2.4. Electrical circuit

The instrument is to be used at 230 Volts.

⚠ If any other voltage is required, a transformer to be fitted between the instrument and the mains power point is to be added.

⚠ Do plug the instrument ONLY in a ground connection.

2.5. Gas circuit

The metal -resistor furnace has been packaged in an inert gas (Ex-Factory) and does not require any other precautions.

Its operating requirements indicate that a sweeping gas may be used, either to protect the sample from oxidation, or to study a reaction. Such an operation requires a gas bottle, of high purity and fitted with a pressure relief valve and gauge (pressure ≈ 1.5 bar). Diameter 4 unions will be linked on the instrument's rear panel (refer to *Chapter 2 - 5 Connections on the rear panel* for the **tightening instructions**).

Use a rotameter or a gas flowmeter to measure the gas flow at the analysis chamber's outlet.

3. Water and gas connections

3.1. Cooling water circuit

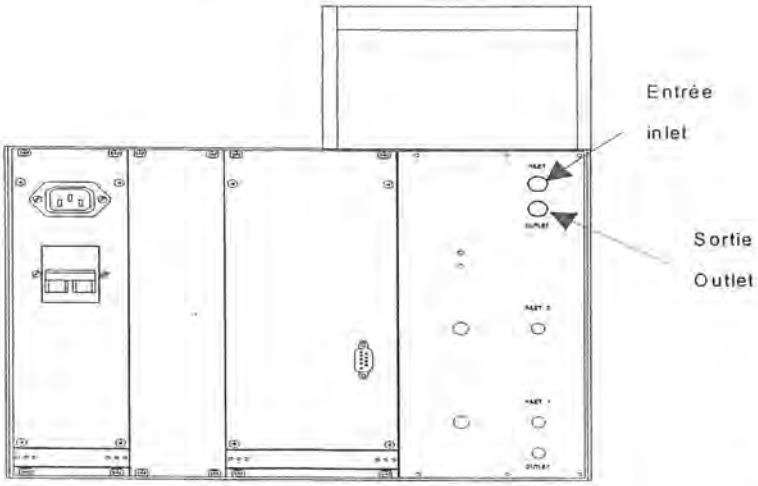


Figure 3: Water connections

1. Use a tube to connect the water tap to the ***inlet*** (on the instrument's rear panel).
2. Use a tube to link the ***outlet*** to the water exhaust fitting (on the instrument's rear panel).

⚠ Fully tighten the unions around the tap and the inlet and outlet on the instrument's rear panel so as to prevent any leaks.

⚠ Do not spray water on the instrument.

⚠ Make sure to have clean water so as to prevent the cooling circuit from getting blocked. Should the water used contain impurities (as found in plant water) a water purifier is recommended.

WARNING Check that the water circulates before running an experiment. If the instrument is heated up with no circulation the power is switched off by a thermic contactor located on the furnace when the enveloppe of the furnace reach 100°C.

3.2. Sweeping gas circuit

The sweeping gas circuit aims at:

1. Preventing the sample from oxidizing by using neutral gas (such as Argon or Helium...)

2. Protect the sensor DSC800 and DSC1200 from the oxidising when the temperature exceed 500°C.

3. Choosing and working with a specific atmosphere so as to obtain a reaction from the sample.

The sweeping gas circuit has a switching piloted by the software. No particular command means that gas 1 is circulating. To switch on gas 2: the electrovalve 1 must be activated via the ***Direct programming*** or in each sequence in ***Acquisition*** (refer to the corresponding software booklet).

Inlet 1 and ***inlet 2*** are both linked to an electrovalve 3/2. An adjustable restriction on each inlet allows to select a rate. Two different types of gas can be switched (neutral and active) or the same gas with different rates (rapid purging for instance to renew the atmosphere before performing an experiment).

Refer to Chapter 2 - 5 - Gas connections on the rear panel in the ***Practical work/Maintenance*** booklet for **tightening the connections**.

Remark The two restrictions are adjusted similarly at SETARAM. The rates are of about 1.5 to 2 Nl/h for a 1.5-bar pressure. They can be re-adjusted so at to obtain 2 different rates. In that case, a rotameter or a flow meter will be used at the outlet of the analysis chamber.

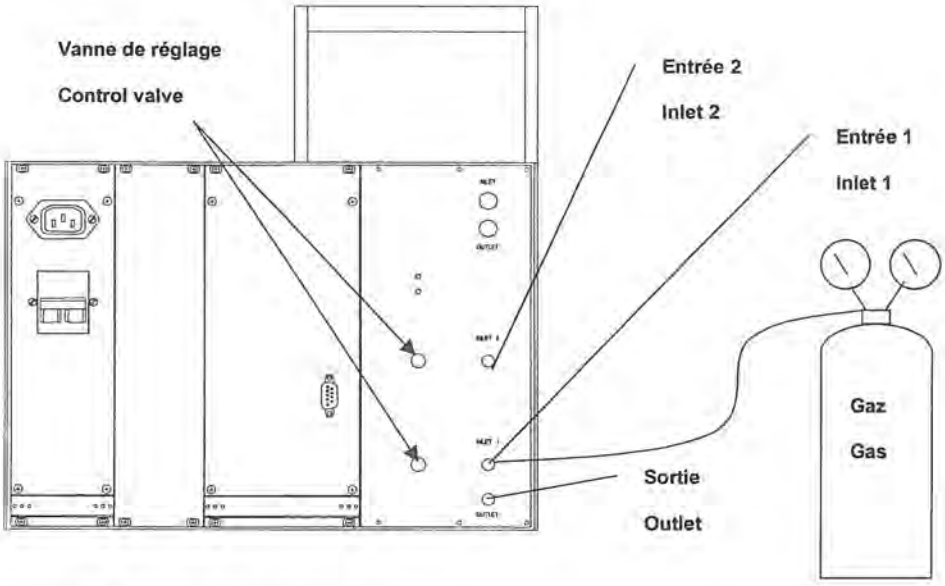


Figure 4: Gas connections

1. Use the pipe supplied to connect the first gas pressure gauge's outlet to the ***Gas/inlet 1***.
2. Use the pipe supplied to connect the other gas pressure gauge's outlet to the ***Gas/inlet 2***.
3. If the gases given off or the sweeping gas are toxic the ***Gas outlet*** (on the instrument's rear panel must be connected to an exhaust system.

WARNING Fully tighten the connectors around the pressure gauge and the inlet and outlet to prevent any leaks and the bottle to get empty rapidly.

To check for fluid-tightness:

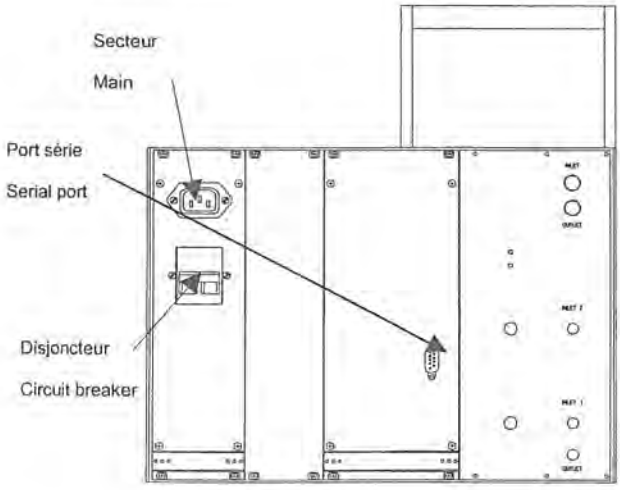
1. Close the sample chamber by bringing the furnace down.
2. Open the gas supply bottle and reduce the pressure to about 1.5 bar. A rate of about 1 to 2 l/h is recommended when performing the experiments.
3. Open the valve on the pressure-relief valve
4. Use soapy water or any other means of detecting leaks to test the various connections.

WARNING The gas used or released by the sample after a reaction must be chemically compatible with the various elements of the gas circuit (refer to the *Chapter 1 – 6.2-* in this booklet).

⚠ If a gas released by a sample is susceptible to be combustible or toxic, ***Outlet***, in the rear face of the instrument, must be linked to a dispositif insuring the safety of persons or goods.

4. Electrical and computer connections

4.1. Electrical connections



A single supply cable on the rear panel is to be connected to the mains 230 V 6A with a ground connection.

Figure 5: Electrical connections

Refer to the ***Maintenance*** chapter in the ***Practical Work/Maintenance*** booklet for any modification on cards.

4.2. Computer connections

Remark As the computer models undergo frequent changes, instructions for connecting the computer itself are subject to modifications. Information about connections for a COMPAQ computer are given in the present chapter.

The instrument and more precisely the CS32 controller, is linked to the computer via an RS232-series cable, containing 9-pin connectors at both ends.

Connections are as shown on the figure hereafter:

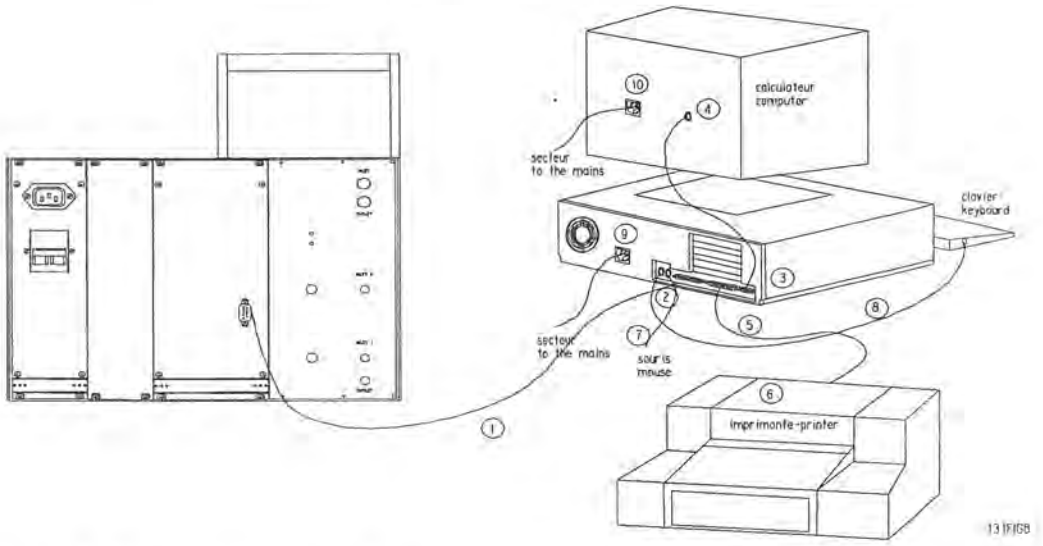


Figure 6: Computer connections

- series-cable between (1) (serial port controller) and (2) (computer)
- screen cable between (3) (central unit) and (4) (screen)
- printer/plotter cable between (5) (central unit) and (6) (printer/plotter)
- connection cable for the mouse on (7)
- connection cable for the keyboard on (8)
- connection to the mains for the central unit on (9)
- connection to the mains for the screen on (10)

Remark If the connector on the computer's series cable contains more than 9 pins, an adaptor -which is not supplied- is required.

5. Commissioning

Switch on the instrument with the circuit-breaker on the rear panel

The green led on the front must be on.

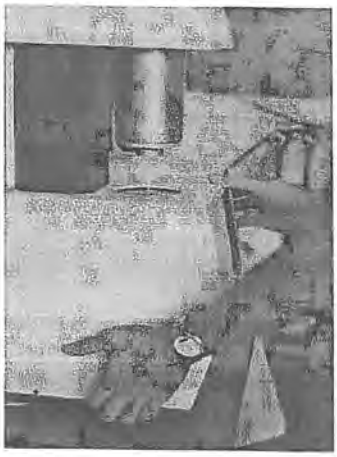
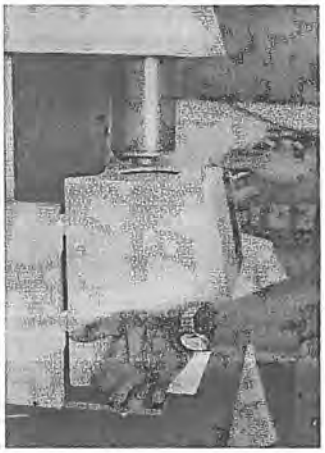
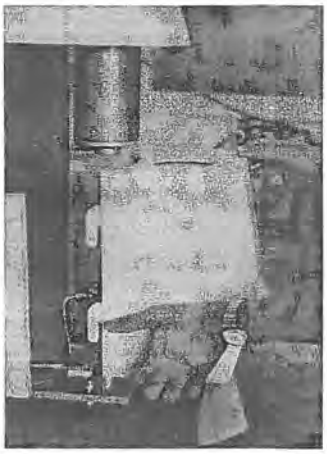
Before positioning the rod move the furnace upward using the switch located on the instrument's front panel.

To position the TG, DTA or DSC rod remove the protective cover.

5.1.1. Removing the protective cover

Follow the instructions:

1. Put your left hand under the bodywork and your right hand on top to the right of the cover.
2. Pull off vertically so as to remove the cover from its catches.
3. Pull off horizontally.
4. Take it down carefully.

5.2. *Labsys*™ TG-DTA/DSC version

5.2.1. Positioning the rod

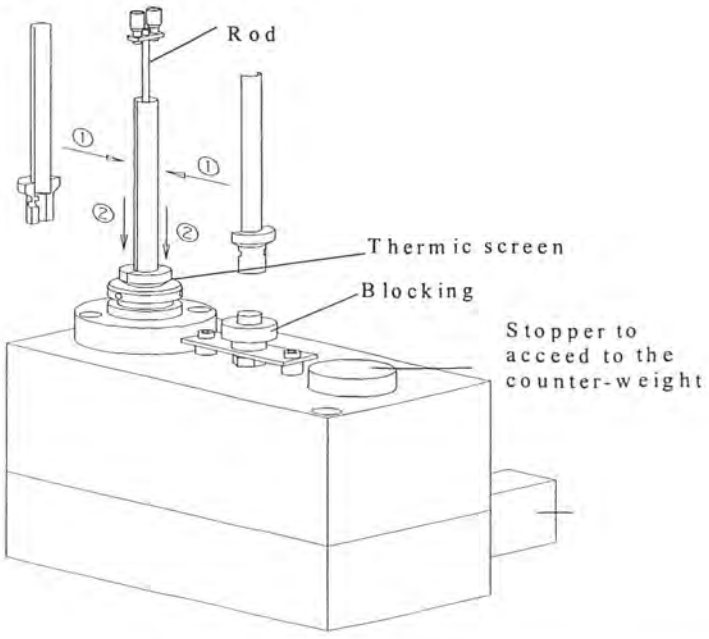


Figure 7: Balance

WARNING **Before positioning the rod check that the balance module is blocked using the wheel located on the upper part of the metal block (the module is blocked for the delivery).**

Introduce the male connector into the female base.

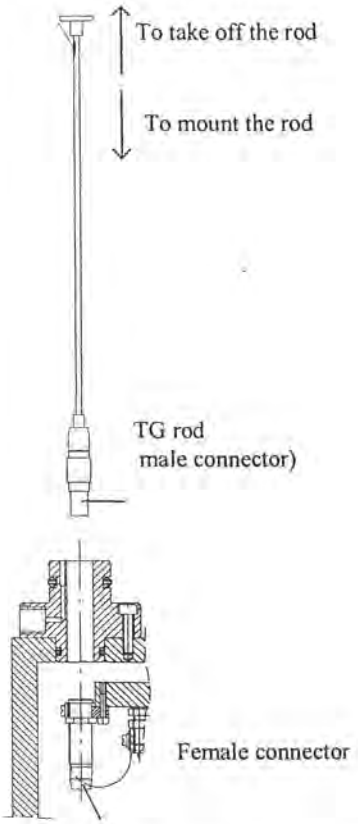


Figure 8: Mounting and taking off the rod

WARNING The centering lug marked with a red dot on the connector must be positioned to the front of the instrument.

WARNING Make sure that the connector is pushed fully home.

WARNING **Block the balance before mounting and before taking off the rod.**

5.2.2. Releasing and compensating the balance

Once the rod is positioned, place one or two crucibles (depending on the version).

Release the balance : unscrew the knurled screw to the stop so as to release the weighing mechanism.

For balance compensation, remove the stopper on the upper part of the balance that is hiding the far end of the beam with a counterweight and a plate for additionnal masses.

Adjust the compensation piece with a snug on the plate at the far end of the beam.

Slip the metal washers supplied with the instrument onto the rod of the compensation piece until a compensation of around 50 µg. Use the software's direct programming (refer to the ***Setsoft*** base software booklet).

WARNING The balance compensation must be done when replacing the rod.

WARNING Mechanical compensation is generally better than electronic compensation even if less easy to perform.

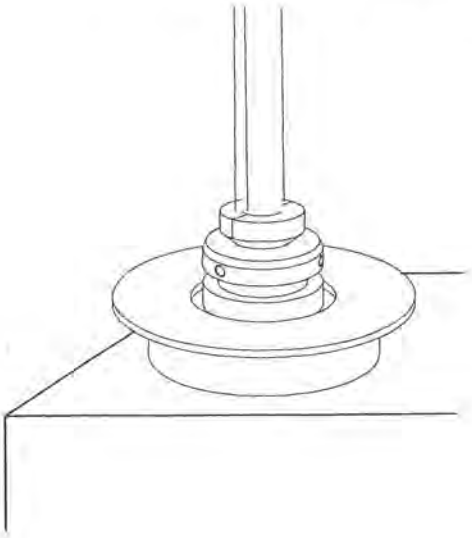
WARNING For your information the coefficient of thermal drift of the magnets used on the balance module only is equal to 0.02 % per °C. Based on a magnet/coil system, it induces a thermal drift that is directly as a function of the re-compensation power. Indeed, any magnet has a coefficient of induction related to ambient temperature. Therefore, the materials used for our instruments have been selected for their low coefficients of temperature.

WARNING The mass measurement is no longer reliable if the balance is blocked. Check the releasing of the balance before putting into operation.

5.2.3. Centering the rod

The rod is automatically centered at the connector's level and cannot be modified. However, a mirror is fitted between the base and the furnace. The centering can be checked via the mirror. It is particularly useful:

- after several heats as a possible distortion can be detected and the rod must be replaced,
- when the instrument is moved to another place and its verticality is no longer ensured (refer to 1.- 2.1.).



Centering is done as follows :

1. Bring the furnace down by operating the switch on the instrument's front panel so that the top of the DTA or DSC rod (i.e. the detector, in the strict sense) is introduced into the furnace entrance.
2. Use the mirror to check that the rod is centered in the furnace.
3. If the centering is not correct, stop the balance and check if the connector of the cane is driven in the balance's connector.

Figure 9: Centering the rod

5.2.4. Sweeping gas pipe

The sweeping gas pipe is made of two half-shells. The two metal parts are inserted on both sides of the rod in the balance upper part.

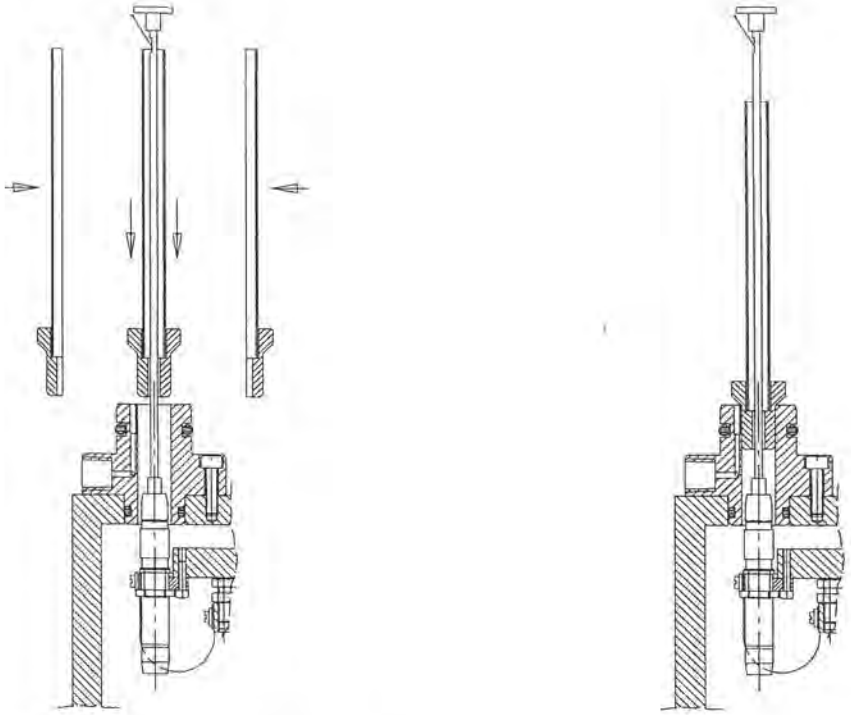


Figure 10: Sweeping gas pipe

WARNING The sweeping gas pipe **must be taken off** when changing the rod.

Gas circulation starts downwards and goes upwards. Gas enters via the sweeping gas pipe and goes out via the left side of the balance upper part.

WARNING In case of condensable vapours it is recommended to check the the bottom of the tubes are clean and clean them up if necessary.

5.3. *Labsys*™ DTA/DSC version

5.3.1. Positioning the rod

Introduce the male connector into the female base.

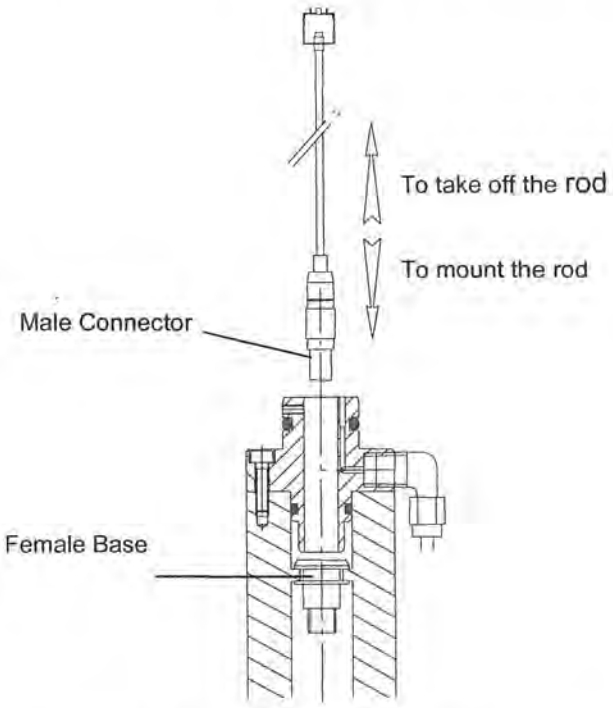


Figure 11: Mounting and taking off the rod

WARNING The centering lug marked with a red dot on the connector must be positioned to the front of the instrument.

WARNING Make sure that the connector is pushed fully home.

5.3.2. Centering the rod

The centering lug mentioned above does not guarantee perfect centering in the furnace.

To correct this centering the base is fitted with 3 side-mounted screws which act upon the rod's positioning.To do this use the mirror fitted between the base and the furnace.

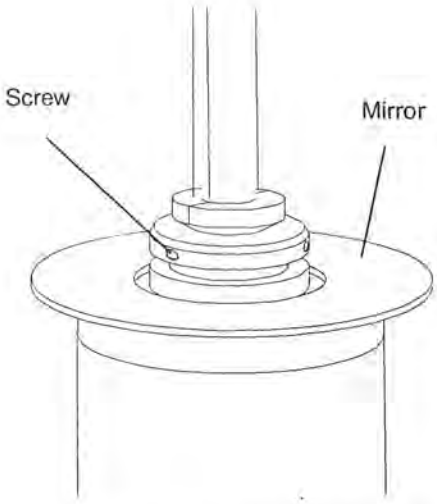


Figure 12: Centering the rod

Centering is done as follows:

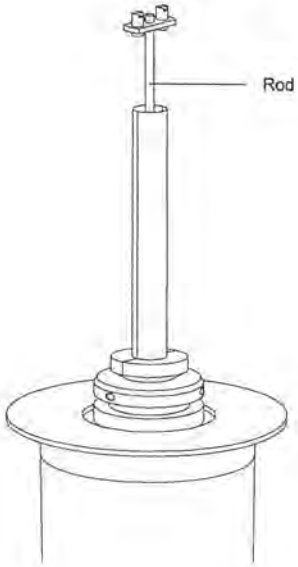
1. Bring the furnace down by operating the switch situated on the instrument's front panel so that the top of the DTA or DSC rod (i.e. the detector, in the strict sense) is introduced into the furnace entrance.
2. Adjust the 3 screws (one after the other) so as to produce geometric centering on the plate (detector) in the furnace entrance.

Remark When centering is done for a set rod, this stays valid for all experiments and must not be modified.

WARNING **Never close the furnace without having put the 3 centring screws for fear of damaging the joint's reach.**

5.3.3. Sweeping gas pipe

The sweeping gas pipe is composed of 2 half-shells. To remove it pull it upward and take the half shells apart.



WARNING Remove the sweeping gas pipe when changing the rod

Figure 13: Mounting the sweeping pipe

5.4. Preparations for using

- Switch on the computer and the printer (see corresponding manual).
- Put the crucibles on the rod. The "measure" crucible is at the front, while the "reference" crucible is at the rear.
- Bring the furnace down by operating the switch
- Start with ***Collection*** on the ***Setsoft*** . On the ***Display*** menu, choose ***Direct programming***. In this window, temperature, Tg signal (TG-DTA/DSC version) and Heatflow signal are shown. We can fix a regulation temperature, and commute a sweeping gas.

The *labsys*™ can start carrying out experiments. Refer to the ***Utilisation*** and ***Setsoft*** booklets.

6. Technical characteristics

6.1 *labsys*™

• Monophase electric network	230 V + - 10 % 50/60 HZ
• Total power consumed	1100 W
• Safety equipment	Programmable safety temperature through a software Thermocontactor of safety on the furnace
• Gas pressure	3 bar maximum
• Water pressure	3 bar maximum
• Working ambient temperature	From 5°C to 40°C
• Relative humidity	Maxi. 80% at temperatures up to 31°C , decreasing to 50% at 40°C.
• Dimension: WxHxD	
Instrument closed	420 x 450 x 460
Instrument open	420 x 650 x 460
• Weight	44 kgs or 46 kgs
• Working temperature's range	Ambiant to 1600°C (Maxi.) 1400°C (Nominal) Those values will be entered in relation to the rod, crucibles or sweeping gas used. Consequently, it is imperative to refer to the instructions leaflet.
• Programmation speed	From 0.001 to 50°C/minute.
• Sample's maximum volume According to the sensor used.	Alumina crucible : 20, 100 and 400 ml Platinium crucible : 20, 100 and 400 ml Aluminium crucible : 160 ml

6.2 Materials in contact with the gas

• Tubing	Polyurethane
• Connector	Brass
• Analyse chamber	Alumina, Dural
• Sensor (according to the type)	Alumina, Chromel, Constantan, Platinium, Platinel, Alumel
• Balance	Dural, inox, platine
• Crucible	Aluminium, Platinium, Alumina

6.3 Conforming to standards

• Safety:	EN 61010-1 EN 61010-1/A2
• Electromagnetic compatibility:	EN 50081-1
• Electromagnetic immunity:	EN 50082-1

Annex Polyurethane chemical compatibility table

Substance	Family	Compatibility
Acetone	Ketones	Not recommended
Acetonitrile	Nitriles	Weak
Aluminium Salts	Aluminium Compunds	Good
Barium Salts	Barium Compounds	Good
Benzyl Alcohol	Hydroxyl Compounds	Weak
Boric Acid	Inorganic Acids	Good
Butanol	Hydroxyl Compounds	Good
Calcium Chlorite	Calcium Compounds	Good
Carbon Disulfide	Sulfur Compounds	Weak
Cupric Chloride	Copper Compounds	Good

Cyclohexanone	Ketones	Not recommended
Dichloromethane	Halogen Compounds	Not recommended
Diethylamine	Aliphatic Amines	Weak
Diethylformamide	Aliphatic Amines	Not recommended
Ethyl Acetate	Carboxylic Esters	Weak
Formaldehyde	Aliphatic Aldehydes	Good
Gasoline	Aromatic Hydrocarbons	Good
Gycol Ether	Ethers	Good
Hexane	Aliphatic Hydrocarbons	Good
Hydrochloric Acid (37%)	Inorganic Acids	Not recommended
Hydrogen Peroxide (30%)	Peroxides	Weak
Hydroflouric Acid (48%)	Inorganic Acids	Not recommended
Jet Fuel (JP-5)	Aliphatic Hydrocarbons	Good
Kerosene	Hydrocarbons	Good
Methanol	Aliphatic Hydroxylic Compounds	Good
Methyl Ethyl Ketone	Aliphatic Ketones	Not recommended
Mineral Oil	Aliphatic and Alicyclic Hydrocarbons	Good
Naphtha	Hydrocarbons	Good
Nitrobenzene	Nitro Compounds	Not recommended
Phenol	Aromatic Hydroxylic Compounds	Not recommended
Propylene Glycol	Hydroxylic Compounds	Good
Sodium Hydroxide (50%)	Inorganic Bases	Good
Sulfuric Acid (98%)	Inorganic Acids	Not recommended
Sulfuric Acid (50%)	Inorganic Acids	Not recommended
Tetrachloroethylene	Halogen Compounds(Vinyl Halides)	Good
Tetrahydrofuran	Alicyclic Ethers	Not recommended
Toluene	Aromatic Hydrocarbons	Weak
1,1,1-Trichloroethane	Aliphatic Halogen Compounds	Weak
Trichloroethylene	Halogen Compounds(Vinyl Hallides)	Weak
Triethylamine	Aliphatic Amines	Good
Turpentine	Hydrocarbons	Good
Water	Misc.	Good

 Those indications are provided as information and are not necessarily reliable for all the conditions for use.

In any case, we are responsible for this table as safety or guarantee terms towards our instrument.

CHAPTER 2 - UTILISATIONS

1. TG Version

This rod is only used with *labsys*™ TG version

1.1. Presentation of the labsys™ balance

The *labsys*™ electronic microbalance is a beam balance which articulates about a torsion strip held under pressure between two spring blades. The beam operates in one position throughout the following procedure:

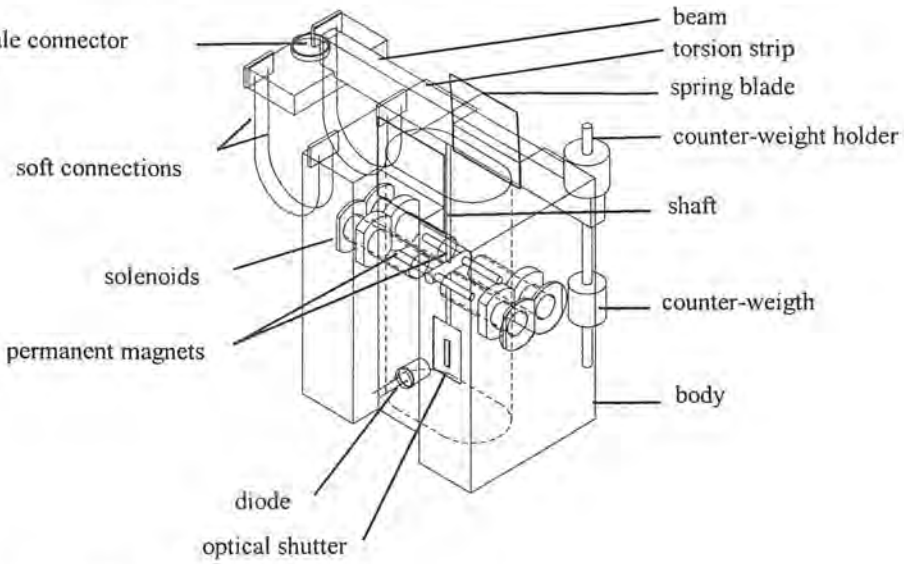


Figure 14: Balance

An optical shutter, which forms one part with the beam, partially blanks out the pencil of light given off by a source which lights up two fixed phototransistors.

The bracket for this shutter is fitted with two, high-stability magnets, whose ends are sunk into four fixed solenoids.

A high-gain amplifier receives the signal from the phototransistors. The output current from this amplifier flows into a double pair of solenoids, there producing a force on the two magnets. This force holds the beam balanced.

There is a proportional ratio between the intensity of the current and the force of electromagnetic balancing. This provides a connection between the measurement of variations in current and that of variations in mass.

A potential difference proportional to the balancing current is amplified and can be put to digital application in the CS 32 controller.

A female base designed to take the male connector of the TG, ATD or DSC rods is fixed at one of the beam's ends. DTA or DSC signals and temperature to the CS 32 controller are transfered via flexible metal threads.

A mobile cylindrical counterweight on a screw rod is hung on the lower part at the other end. This counterweight can be adjusted on the rod so as to adjust the center of gravity of the balance.

A plate, designed to take the washers used to compensate the balance, is fixed on the upper part of the beam.

The balance module is mounted in a tight metal wall.

WARNING The center of gravity of the balance is adjusted at SETARAM for any type of rod required.

WARNING Moving the counterweight would lead to a loss of adjustment of the balance.

1.2. TG rod description

The TG rod consists of :

- A ceramic plate supporting a thermocouple housing for the crucible.
- A 10%-Platinum-Platinum rhodium thermocouple.
- A ceramic shaft supporting the plate and the thermocouple.
- A red mark on the shaft indicating the appropriate position in the female base.
- The shaft is a bifilar rod for the connections of the measure thermocouple.

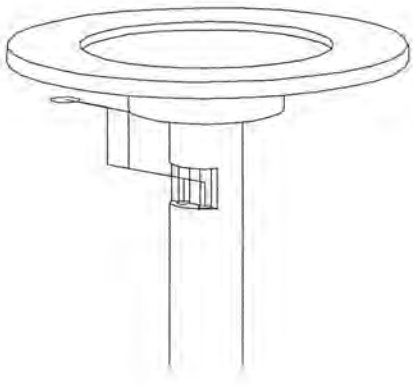


Figure 15: TG rod

Remark The same rod is used over the whole range of temperature, that is to say from 20°C up to 1600°C.

1.3. Selecting the crucible

Various types of crucible are available for the TG rod:

- Alumina (400 mm^3 and 100 mm^3)
- Platinum (400 mm^3 and 100 mm^3)
- Aluminium 100 mm^3

Selecting the crucible depends on the sample to be analyzed. As a general rule :

- If the sample is a metal or contains elements of metal choose the alumina crucible
- If the sample is a mineral or organic choose the platinum crucible

---

WARNING The various recommendations given above cannot cover all the instrument's applications.

WARNING Before analyzing a new product there should be information available about the dangers of how it may corrode the crucible during heating and damage the thermocouple with vapours from the transformation.

WARNING This is a vital choice as it determines the outcome of the experiment. Making the wrong choice can lead to damaging the crucible, and thereby to damaging the TG rod.

WARNING When using a crucible not recommended by **SETARAM**, make sure that it adapted to the TG rod used and the selected temperature.

Remark Refer to the Chapter *Spare parts* in the ***Practical work/Maintenance*** booklet for information related to the references of the crucibles.

1.4. Preparing the experiment

Once the crucible is selected (see previous section) and the necessary precautions are taken, the experiment requires various operations:

1. Weighing a sample
2. Arranging crucibles on the rod
3. Selecting the sweeping gas
4. Entering the experiment conditions
5. Open the water circuit.
6. Recording signals

1.4.1. Weighing a sample

The sample can be a liquid or a solid (powder, granule, film...). In both cases, the sample represents the product to be analyzed and must be carefully used.

Weigh the sample in the crucible, using a balance providing an accuracy of 0.01 mg. The mass depends on the type of analysis to be carried out and on the variation of the expected mass:

- significant variation in mass: the initial mass is about 100 milligrams.
- slight variation in mass: increase the sample mass. In practice, the balance can take 100 grammes and has a range of compensation of +/- 2 grammes.
- if a gas-solid reaction is studied, use a thin layer of sample so as to have a good contact with the gas.

⚠ If the sample is explosive, weigh only a few milligrams of sample.

1.4.2. Placing crucibles

- Bring the furnace down by operating the switch to reach the rod.
- Place the crucible with the sample in the front side of the rod.
- In the rear side, place a crucible that is the same type.
  The crucible could be:
  - empty, in case of a low mass sample or a high thermal effect measurement.
  - filled with an equal mass of alumina (previously calcinated) if the sample mass is important or the thermal effect to measure is low.

The ***reference*** crucible mainly compensates the thermic effect due to the specific heat of the sample.

In practice, the ***reference*** crucible remains empty when the low volume aluminium crucible is used. When the medium volume crucible is used, it may be useful to fill it with alumina.

If a liquid is analysed in a tight crucible it is recommended to use distilled water as a reference but the instructions for use given in the chapter refering to crucibles must be taken into account.

- Check that the balance is in its working area: the sensor must be perfectly vertical.
- Bring the furnace down.
- If necessary, mechanically equilibrate the balance in order to be in the most sensitive range.
  - 2 measure ranges: +/-200mg et +/- 2000mg
  - A range can be chosen and checked in the software window ***Direct programming***, the value ***Untared Mass*** only, is taken into account for the choice of the range.
  - Initial and final values must be between –200 and +200 mg. It means that the **expected** mass loss or mass gain must be taken into account.

1.4.3. Selecting the sweeping gas

The *labsys*™ offers various possibilities:

- Use an inert sweeping gas (argon, nitrogen, helium): the sweeping gas is used to prevent the sample from oxidizing (with opened crucible)

Remark Helium is the best inert gas for use and results.

WARNING If a reactive gas is to be used in the balance, make sure that the various parts of the instrument, and more particularly the balance module and the thermocouple, will not corrode.

- Use an active sweeping gas (oxygen, hydrogen): the sweeping gas is used to investigate the sample/sweeping gas reaction with an opened crucible.

⚠ Before investigating a reaction between a sample and a reactive gas, make sure that the transducer is not likely to corrode or or be damaged due to a violent reaction.

- Use an inert gas and then a reactive gas: in some investigations (determination of induction time for oil for instance), first, the sample must be protected under inert gas, and then the inert gas is replaced by an oxidizing gas (air, oxygen) in order to oxidize the sample.

WARNING Use gases having a close density (argon and oxygen for instance). Indeed, the flow of both gases must be adjusted so as when changing the gas, the Heat flow signal is not disturbed. Use the device for automatic commutation of gases as this operation is performed via the computer.

1.4.4. Entering experimental conditions

This part of the experiment is also detailed in the software booklet which provides information related to the test to be carried out from the computer.

In this paragraph, additional instructions on the experiment itself are given:

- Scanning and sequencing
- PID actions
- Safety temperature
- Control of the eletrovalve

1.4.4.1. PID actions

The regulation of the *labsys*™'s furnace is done via a type K thermocouple. PID coefficients for regulation must be entered in the computer so as to regulate the furnace.

PID values are expressed in:

- °C for P (Proportional)
- Seconds for I (Integral)
- Seconds for D (Derivative).

P	180
I	500
D	20

These values apply to the whole temperature range of the furnace.

1.4.4.2. Safety temperature

Entering a safety temperature is vital for protecting the transducer, the sample and the crucible, depending on the experiments to be carried out.

In general, the following values are to be recommended:

- If the work is performed over the whole temperature range set the value for the safety temperature at the maximum operating temperature plus 20°C.
- If protection is required for the sample under analysis so as to prevent decomposition, oxidation, etc or for a crucible as a function of its temperature capacity, set the value at the safety temperature chosen.

Temperature scanning automatically stops at the selected temperature should there be a problem or previous errors.

1.4.4.3. Control valve

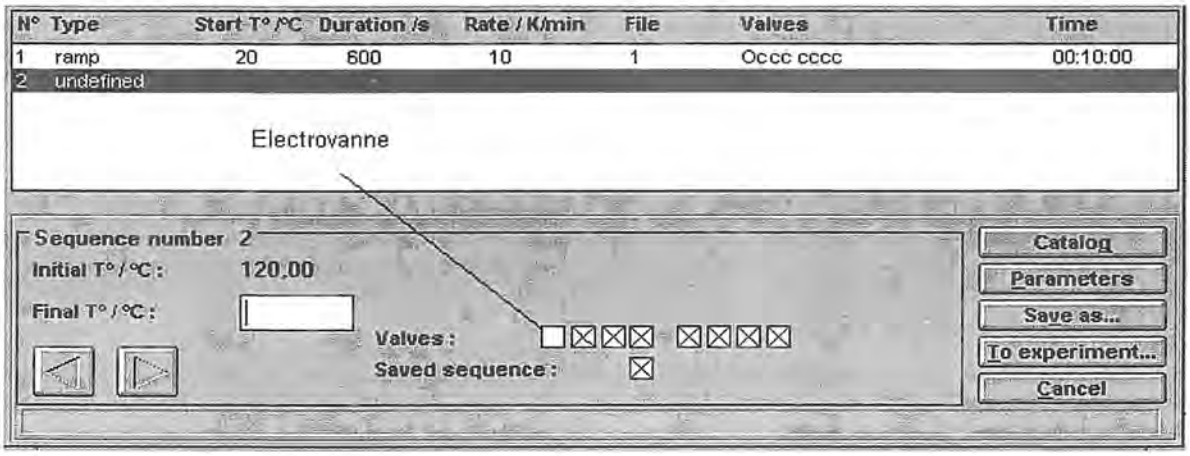


Figure 16: Control electrovalve

1.4.4.4. Scanning and sequencing

Before starting the experiment a sample scanning cycle needs to be prepared. To do this the software offers a sequence-gathering table which carries out heating and cooling operations, as well as periods of constant temperature.

In practice there are two types of sequence:

1. For a scanning sequence, supply the initial and the final temperature, as well as the scanning rate during this sequence.
2. For an isothermal sequence, supply the level temperature (°C) and the length of the level (second).

WARNING	The maximum scanning rate for temperature is 50°C/mn.

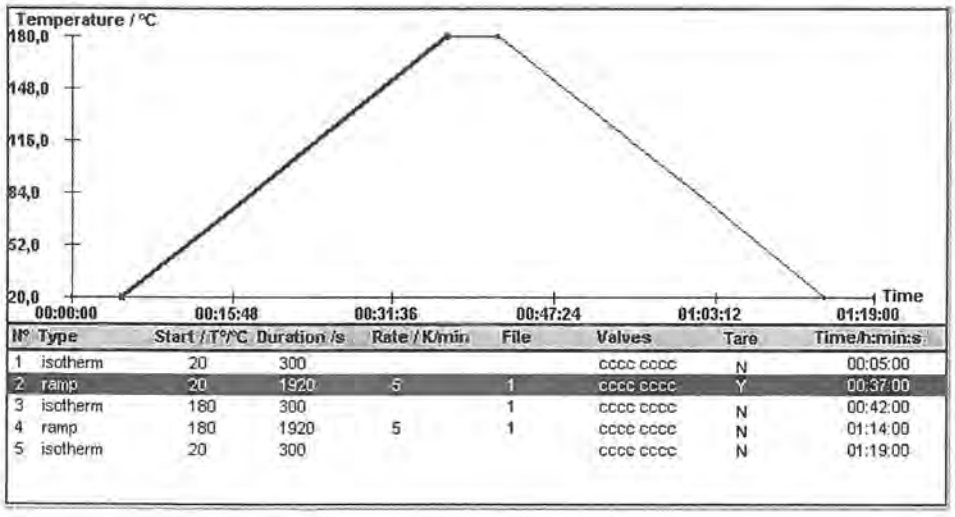
Remark	An experiment is a collection of scanning and isothermal sequences.

1.4.4.4.1. Simple cycle

The simplest cycle in thermogravimetry involves heating a sample continuously and then cooling the furnace rapidly so as to test the new sample or start a second heating procedure on the same sample:

- An isothermal level at the start temperature so as to produce a stable temperature in the furnace and stability in the TG signal before the start of heating for about 300 seconds.
- A tare on the TG signal.
- A scanning sequence from the initial to the final temperature in the test at the chosen scanning rate
- An isothermal level at the final temperature for 300 seconds.
- A cooling scanning sequence with its initial temperature as the one reached, and final temperature as the initial temperature.

The graph hereafter is a means of controling that parameters entered in the computer are correct.



N°	Type	Start / T°/°C	Duration /s	Rate / K/min	File	Valves	Tare	Time/h:min:s
1	isotherm	20	300			cccc cccc	N	00:05:00
2	ramp	20	1920	5	1	cccc cccc	Y	00:37:00
3	isotherm	180	300		1	cccc cccc	N	00:42:00
4	ramp	180	1920	5	1	cccc cccc	N	01:14:00
5	isotherm	20	300			cccc cccc	N	01:19:00

Figure 17: Simple cycle

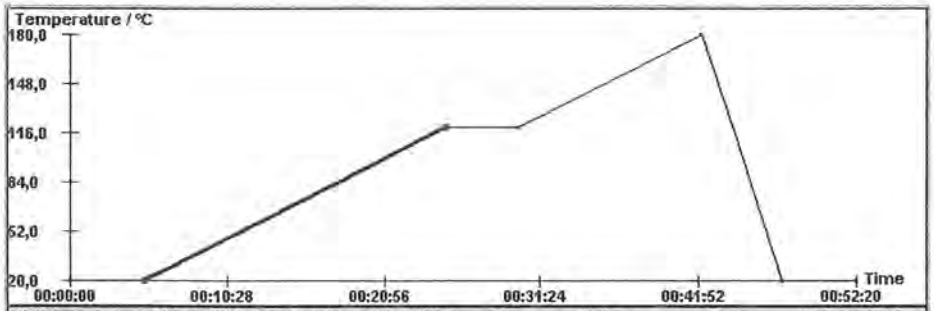
WARNING No command from the ***Valve*** window (cccc cccc) ***Gas 1*** is passing. To switch on ***Gas 2*** activate valve 1 (occc cccc).

1.4.4.4.2. Staged cycle

The staged cycle provides for carrying out heating or cooling in various stages. For instance, two types of reaction (dehydration and decomposition) are possible for a TG experiment:

- An isothermal level at the start temperature for 300 seconds.
- A scanning sequence from the initial temperature to the intermediate temperature (end of dehydration for instance) at an initial scanning rate.
- An isothermal level at the intermediate temperature for 300 seconds.
- A tare on the TG signal.
- A scanning sequence from the intermediate temperature to the final temperature (end of decomposition for instance) at a second scanning rate.
- A scanning sequence from the final temperature to the start temperature at a cooling rate.

Working from these two examples more complex cycles can be produced depending on the experiment's requirements. 200 sequences are available to carry out this work.



N°	Type	Start / T°/°C	Duration /s	Rate / K/min	File	Valves	Tare	Time/h:min:s
1	isotherm	20	300			cccc cccc	N	00:05:00
2	ramp	20	1200	5	1	cccc cccc	N	00:25:00
3	isotherm	120	300		1	cccc cccc	N	00:30:00
4	ramp	120	720	5	1	cccc cccc	Y	00:42:00
5	ramp	180	320	30		cccc cccc	N	00:47:20
6	isotherm	20	300			cccc cccc	N	00:52:20

Figure 18: Staged cycle

WARNING The value for the cooling rate must be provided as positive.

1.5. Making use of the test

After entering the experimental conditions start scanning the temperature cycle and record the thermogramme

1.5.1. Thermogramme

Working from the first thermogramme recorded choose the re-plot as a function of either time or temperature by optimising the axes with the ***Zoom*** function. As a general rule preference is given to representing as a function of the more expressive temperature so as to situate the products transformation temperatures. However, if the cycle contains a succession of scanning sequences and isothermal levels representing as a function of time provides for an overall display of phenomena.

Two types of phenomena are shown up on a thermogramme such as the TG type:

1. Mass loss (the most frequent phenomenon) associated to the following transformations: dehydration, dehydroxylation, pyrolysis, decomposition, combustion...

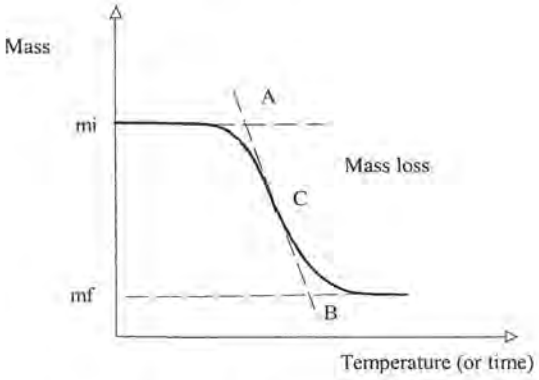


Figure 19: Mass loss

2. Mass gain generally associated to reactions such as oxydation, corrosion, passivation, adsorption.

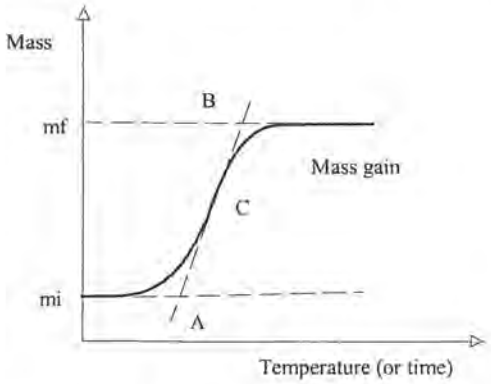


Figure 20: Mass gain

Mass loss is generally shifted toward the lower part of the thermogramme while mass gain is shifted toward the upper part of the thermogramme.

1.5.2. Determining a simple mass variation

In most experiments, the sample is transformed by heat, which is generally a simple mass variation or a mass loss:

The method used for determining mass variation and characteristic temperatures of the transformation comply with the international ***ISO*** standards in force or in draft.

1.5.2.1. Mass variation

Let m_i be the initial mass of the sample,

Let m_f be the final mass of the sample,

the variation in mass Δm in % is equal to:

$$\Delta m = \frac{m_i - m_f}{mi} x100$$

1.5.2.2. Characteristic temperatures

Define points A, B, and C in order to determine the characteristic temperatures of the transformation:

- A is the start point of mass variation and is the intersection between the initial base line and the tangent of the TG curve during mass variation.
- B is the end point of mass variation and is the intersection between the final base line after the transformation and the tangent of the TG curve during mass variation.
- C is the medium point of mass variation and is the intersection between the TG curve and the parallel to the abscissa axis drawn at the medium point between A and B. C generally corresponds to the inflexion point on the TG curve.

Characteristic temperatures T_A, T_B and T_C are given for the corresponding points.

1.5.3. Determining a multiple steps mass variation

Depending on the analyzed sample the thermogramme can show different distinct variations that may not be well separated. Two situations are possible:

1.5.3.1. Well separated mass variations

For well separated mass variations the method used for determining mass variation and characteristic temperatures is similar to the one previously described.

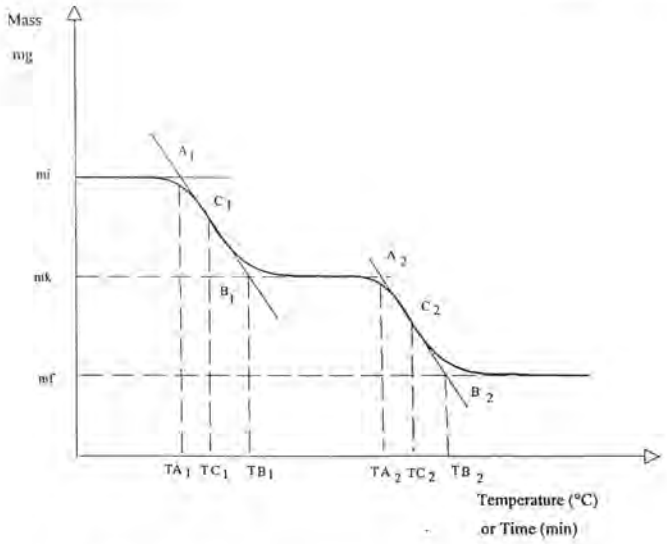


Figure 21: Well-separated mass variations

1.5.3.2. Mass variation

Let m_i be the initial mass of the sample,

Let m_k be the mass of the sample after the first transformation,

Let m_f be the final mass of the sample after the second transformation,

the first variation in mass Δm_2 in % is equal to:

$$\Delta m_1 = \frac{m_i - m_k}{m_i} x100$$

the second variation in mass Δm_1 in % is equal to:

$$\Delta m_2 = \frac{m_k - m_f}{m_i} x100$$

The remainder R produced by the end of the experiment is equal to (in %):

$$R = \frac{m_f}{m_i} x100$$

1.5.3.3. Characteristic temperatures

Define points A_1, B_1, and C_1 in order to determine the characteristic temperatures of the transformation of the first mass variation and A_2 , B_2 and C_2 for the second one.

Each mass variation is determined as described in the simple mass varation paragraph.

1.5.3.4. Poorly separated mass variations

If the TG curve does not show a stable base line between the two mass variations the method previously described for determining mass variation must be adapted.

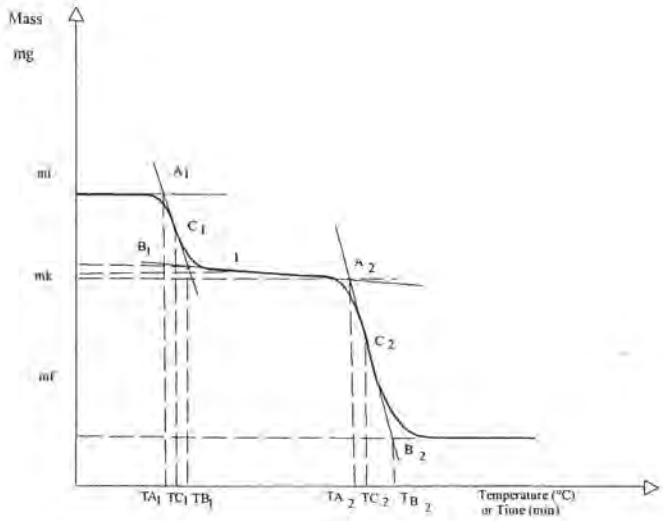


Figure 22: Poorly separated mass variations

Define the medium point I in order to determine the mass m_k:

1. Define B_1 with the intersection of the tangent of the TG curve during the first transformation and the tangent with the gentlest slope at the base line between two variations.
2. Define A_2 with the intersection of the tangent of the TG curve during the second transformation and the tangent with the gentlest slope at the base line between two variations.
3. Draw the parallel lines on the abscissa axis meeting B_1 and A_2 .
4. Draw the parallel median meeting the TG curve on I.

The method used for determining mass variations and characteristic temperatures is similar to the one previously described.

1.5.4. Temperature correction

The temperature of the sample is measured by the thermocouple linked to the TG rod.

The temperature is measured near the sample. However, a slight difference with the real temperature of the sample can be observed due to the thermal gradient and transfer through the crucible's wall.

Contrary to the DTA and DSC methods no standard is available for the TG method (except magnetic standards requiring a magnet in the furnace).

However, fusion of metal standards can be done as follows:

- Take an alumina crucible
- Arrange a thin alumina plate pierced at the center on the crucible
- Place a piece of standard above the hole in the plate so as the diameter of the sample is slightly higher than the hole's.
- Close the furnace and scan within the range standard's temperature of fusion.
- When the standard melts the liquid precipitates down the crucible's bottom causing a deviation in the balance.

Working with this curve determine with accuracy the real temperature of the sample and the correction to be added.

1.5.4.1. Standard materials used

Use the standards given in the table hereafter for carrying out this type of measurement:

Substance	Melting point (°C)	Réferences
Indium	156.598	ITS-90
Tin	231.928	NIST , ITS-90
Lead	327.45	NIST
Aluminium	660.32	ITS-90
Silver	961.78	ITS-90
Gold	1064.18	ITS-90
Nickel	1455	IPTS-1968

Reference : ISO norm 11357-1 (Annex A)

WARNING Only indium (NIST GM 758) and tin (NIST GM 758) are recognized as official standards for the DTA method. For the other metals choose a 4N purity (99,99%) or better 5N (99,999%).

WARNING If the metal crucible is used it first needs to be partly filled with alumina before arranging the sample so as to prevent any contact between the molten sample and the crucible (alloys may be formed).

WARNING The samples must be melted in an inert gas atmosphere, especially for a nickel sample (it may otherwise attack the alumina crucible).

However, depending on the range of temperature planned for analysis, inorganic and organic substances may be used for fusions and transitions :

SUBSTANCE	TEMPERATURE (°C)	REFERENCE
Potassium nitrate	127.7 (transition)	NIST GM 758
Potassium perchlorate	299.5 (transition)	NIST GM 758, 759

Silver sulfate	430 (transition)	NIST GM 758, 759
Quartz	573 (transition)	NIST GM 759, 760
Potassium sulfate	583 (transition)	NIST GM 759, 760
Potassium chromate	665 (transition)	NIST GM 759, 760
Barium carbonate	810 (transition)	NIST GM 760
Strontium carbonate	925 (transition)	NIST GM 760

From: ISO norm 11357-A (Annex A)

⚠ When using these substances special attention must be paid to exhibiting high vapour pressures.

⚠ In contrast, certain substances can break down if they are heated beyond their transition or fusion temperature.

⚠ It is thus VITAL to remain within the temperature measurement corresponding with the transformation given in the table.

1.5.5. Using the DTG derivative curve

Using the TG curve recorded the software can plot the DTG derivative with the various filterings corresponding with the level of the background noise of the TG curve (refer to the ***Setsoft*** software booklet).

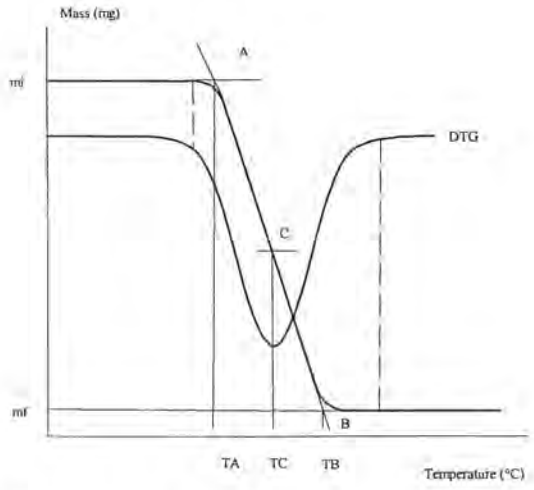


Figure 23: Single DTG

The DTG signal -equivalent to dm/dt- directly expresses the transformation rate and is used in studies in kinetics.

Plotting the DTG curve gives the inflexion point of the TG curve, which is characterized by the top and defines with great accuracy the start of the transformation.

Plotting the DTG curve is especially interesting for multiple transformations.

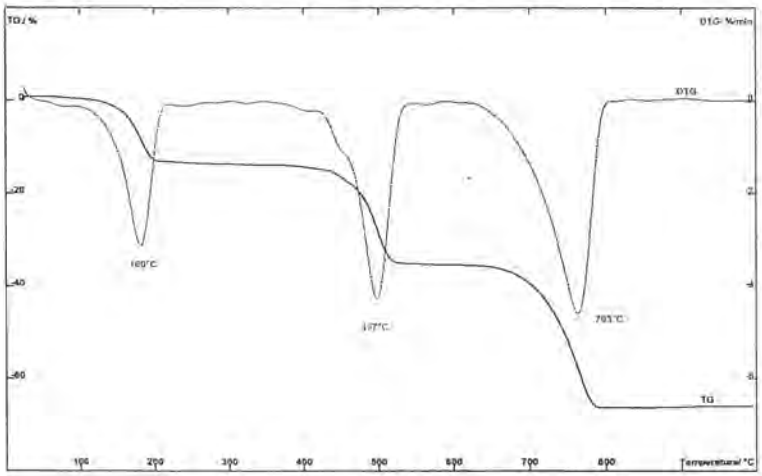


Figure 24: Multiple DTG

Detecting the various peaks of the DTG curve results in identifying the various transformations and more particularly the poorly separated ones.

2. DTA version

The *labsys*™ TG-DTA version associates a DTA rod connected to the balance module so as to measure the mass variation and the corresponding thermic effect simultaneously on the same sample. The DTA method also allows detecting transitions that do not produce mass viariation (such as fusion, crystallization,...).

The *labsys*™ DTA version gives only the thermal effect.

2.1. DTA rod description

The DTA rod consists of :

- A ceramic plate supporting two thermocouple housings for the measurement and reference crucibles, together with a housing for the temperature-control thermocouple in central section
- A ceramic shaft supporting the plate
- A connector at the end of the shaft
- A mark on the shaft indicating the type of rod.

The accepted arrangement is that the side designed to take the crucible with the sample, named the ***sample*** side is fitted to the front opposite the rod. The ***reference*** side is designed to accomodate the crucible containing a thermally inert substance is fitted to the rear.

The shaft is a four-wired stem containing the measurement and reference thermocouples, as well as the temperature-control thermocouple.

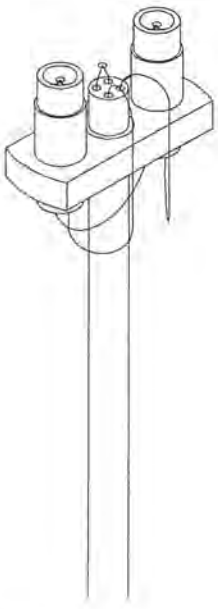


Figure 25: DTA rod upper part

Remark The connectors provide for a very easy way of changing DTA rods. ***Do not forget to check that the rod is properly centered.***

2.2. Selecting the DTA rod

Depending on the temperature under study two types of DTA rods are available, using different properties for the thermocouples :

1. Ambient version + 1200°C in platinel (green mark). This version, although limited in temperature range, is more sensitive and is recommended for experiments at low and average temperatures.
2. Ambient version + 1600°C in platinum-platinum rhodium 10% (red mark).

⚠ However, when entering the experimental conditions into the computer, set the safety temperature at the selected rod's maximum operating temperature so as to prevent damage to the transducer, especially for the platinel rod. The safety temperature can be set at a lower value as a function of the sample analyzed (e.g. danger of decomposition) or as a function of the heat bearing of certain crucibles (e.g. aluminium).

Remark Refer to *Chapter 2 - 6 - Spare parts* in the ***Practical work/Maitenance*** booklet for information related to rod types.

2.3. Selecting the crucible

After selecting the type of DTA rod a crucible needs to be selected as a function of the sample to be analyzed and the type of test to be carried out. Three types of crucibles are available with different volumes:

- Alumina (20 and 100 mm^3)
- Platinum (20 and 100 mm^3)
- Aluminium (160 mm^3)

Selecting the crucible depends on the sample to be analyzed. As a general rule:

- If the sample is a metal or contains elements of metal choose the alumina crucible.
- If the sample is a mineral choose the platinum crucible.
- If the sample is organic either crucible can be used but the platinum crucible with the greater thermal conductivity is preferable.

Selecting the crucible's volume is a function of the mass of sample to be analyzed. As a general rule it is best to analyze a small mass of sample (20 to 50 mg) so as to minimise the effects within the product of a thermal gradient. However, if the thermal effect to be measured is small it is advisable to use the largest mass of sample.

⚠ The various recommendations given above cannot cover all the instrument's applications.

WARNING Before analyzing a new product there should be information available about the dangers of how it may corrode the crucible during heating or one of the possible transformations (fusion, decomposition, ...).

WARNING This is a vital choice as it determines the outcome of the experiment. Making the wrong choice can lead to damaging the crucible, and thereby to damaging the DTA rod.

Remark Refer to *Chapter 2 - 6 - Spare parts* in the ***Practical work/Maitenance*** booklet for information related to the references of crucibles.

2.4. Crimping the crucible

2.4.1. Tools

Aluminium crucibles can be crimped with a set of tools composed of 7 pieces (A to G). Various volumes in DTA and DSC crucibles can be crimped.

In most cases, it is better to crimp a stopper in order to:

- To limit overflowings,
- To introduce equivalent thermic characteristics (M x Cp, « émissivité ») between the reference crucible and the measure crucible.

⚠ The stopper must not be used when a risk of overpressure does exist, especially in case of:

- Kinetic of very quick reaction.
- Very high voltage vapour samples.

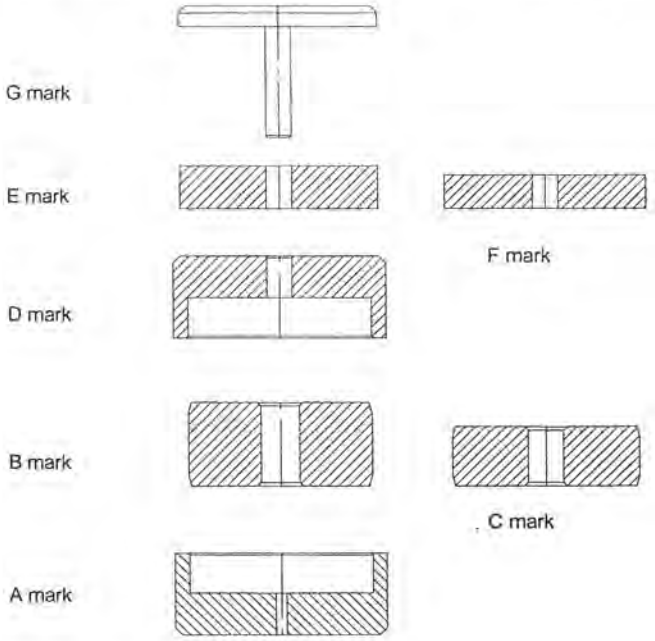
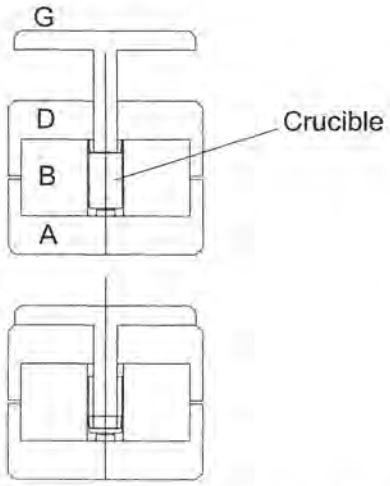


Figure 26: Crimping tools

2.4.2. TG-DTA

The TG-DTA test is generally carried out with an open crucible. However, in some cases (e.g. dehydration of gypsum in plaster) a non-tight closed crucible must be used to produce a better separation of thermal phenomena and to keep the vapour right above the sample.

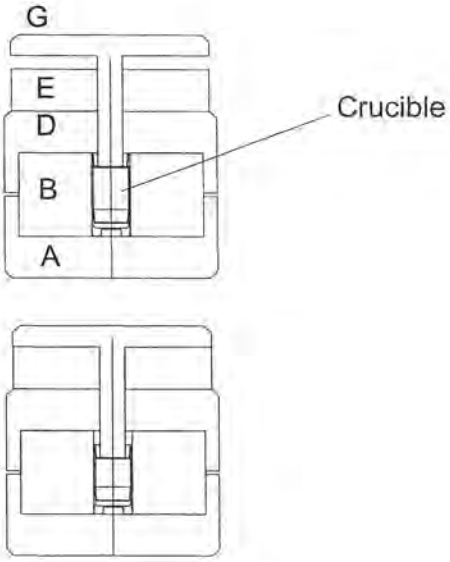
2.4.2.1. Filling up a low level



The diagram in *2.4.1.* shows the various sets of tools. The crimping is processed by a pressure of the hand on part G. G is also used to remove the crucible once crimped if stuck in parts B or C.

Figure 27: Filling up a low level

2.4.2.2. Filling up a high level



Remark Crimping a high level filling can also be used to add a second cork on a crucible crimping a low level.

Figure 28: Filling up a high level

2.5. Preparing the experiment

Once the rod and the crucible is selected (see previous section) and the necessary precautions are taken, the experiment requires various operations:

1. Weighing a sample
2. Arranging crucibles on the rod
3. Selecting the sweeping gas
4. Entering the experiment conditions
5. Open the water circuit.
6. Recording signals

2.5.1. Weighing a sample

The sample can be a liquid or a solid (powder, granule, film, ...). In both cases, the sample represents the product to be analyzed and must be carefully used.

Weigh the sample in the crucible, using a balance providing an accuracy of 0.01 mg. The mass depends on the type of analysis to be carried out and on the variation of the expected mass:

- If a gas-solid reaction is studied, use a thin layer of sample so as to have a good contact with the gas.
- If the thermic effect researched is low, use the most bigger sample mass as possible.
- To separate thermic effects close to each other in temperature, take a low mass of sample to decrease thermic gradient effect in the sample as well as to improve the separation of peaks.

⚠ If the sample is explosive, weigh only a few milligrams of sample.

2.5.2. Placing crucibles

- Bring the furnace down by operating the switch to reach the rod
- Place the crucible with the sample in the front side of the rod
- In the rear side, place a crucible that is the same type.
  The crucible could be:
  - empty, in case of a low mass sample or a high thermal effect measurement.
  - filled with an equal mass of alumina (previously calcinated) if the sample mass is important or the thermal effect to measure is low.

The ***reference*** crucible mainly compensates the thermic effect due to the specific heat of the sample.

In practice, the ***reference*** crucible remains empty when the low volume aluminium crucible is used. When the medium volume crucible is used, it may be useful to fill it with alumina.

If a liquid is analysed in a tight crucible it is recommended to use distilled water as a reference but the instructions for use given in the chapter refering to crucibles must be taken into account.

TG-DTA/DSC version

- Check that the balance is in its working area: the sensor must be perfectly vertical.

- Bring the furnace down.

TG-DTA/DSC version

- If necessary, mechanically equilibrate the balance in order to be in the most sensitive range.
  - 2 measure ranges: +/-200mg et +/- 2000mg
  - The range can be chosen and checked in the software window ***Direct programming***, the value ***Untared Mass*** only, is taken into account for the choice of the range.
  - Initial and final values must be between –200 and +200 mg. It means that the **expected** mass loss or mass gain must be taken into account.

2.5.3. Selecting the sweeping gas

The *labsys*™ offers various possibilities:

- Use an inert sweeping gas (argon, nitrogen, helium): the sweeping gas is used to prevent the sample from oxidizing (with opened crucible)

WARNING If a reactive gas is to be used in the balance, make sure that the various parts of the instrument, and more particularly the balance module and the thermocouple, will not corrode.

- Use an active sweeping gas (oxygen, hydrogen): the sweeping gas is used to investigate the sample/sweeping gas reaction with an opened crucible.

⚠ Before investigating a reaction between a sample and a reactive gas, make sure that the transducer is not likely to corrode or or be damaged due to a violent reaction.

- Use an inert gas and then a reactive gas: in some investigations (determination of induction time for oil for instance), first, the sample must be protected under inert gas, and then the inert gas is replaced by an oxidizing gas (air, oxygen) in order to oxidize the sample.

WARNING Use gases having a close density (argon and oxygen for instance). Indeed, the flow of both gases must be adjusted so as when changing the gas, the Heat flow signal is not disturbed. Use the device for automatic commutation of gases as this operation is performed via the computer.

2.5.4. Entering experimental conditions

This part of the experiment is also detailed in the software booklet which provides information related to the test to be carried out from the computer.

In this paragraph, additional instructions on the experiment itself are given:

- Scanning and sequencing
- PID actions
- Safety temperature
- Control of the eletrovalve

2.5.4.1. PID actions

The regulation of the *labsys*™'s furnace is done via a type K thermocouple. PID coefficients for regulation must be entered in the computer so as to regulate the furnace.

PID values are expressed in:

- °C for P (Proportional)
- Seconds for I (Integral)
- Seconds for D (Derivative).

P	180
I	500
D	20

These values apply to the whole temperature range of the furnace.

2.5.4.2. Safety temperature

Entering a safety temperature is vital for protecting the transducer, the sample and the crucible, depending on the experiments to be carried out.

In general, the following values are to be recommended:

- If the work is performed over the whole temperature range set the value for the safety temperature at the maximum operating temperature plus 20°C.
- If protection is required for the sample under analysis so as to prevent decomposition, oxidation, etc or for a crucible as a function of its temperature capacity, set the value at the safety temperature chosen.

Temperature scanning automatically stops at the selected temperature should there be a problem or previous errors.

2.5.4.3. Control valve

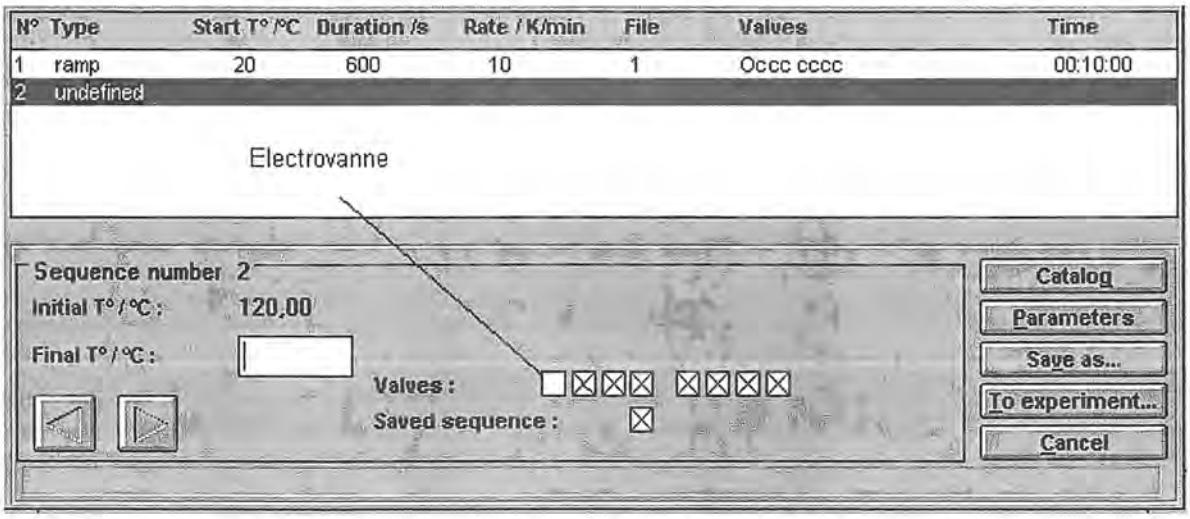


Figure 29: Control electrovalve

2.5.4.4. Scanning and sequencing

Before starting the experiment a sample scanning cycle needs to be prepared. To do this the software offers a sequence-gathering table which carries out heating and cooling operations, as well as periods of constant temperature.

In practice there are two types of sequences:

3. For a scanning sequence, supply the initial and the final temperature, as well as the scanning rate during this sequence.
4. For an isothermal sequence, supply the level temperature (°C) and the length of the level (second).

WARNING The maximum scanning rate for temperature is 50°C/mn.

Remark An experiment is a collection of scanning and isothermal sequences.

For a proper understanding of how it works here are a few examples of experiments with a TG:

2.5.4.4.1. Simple cycle

The simplest cycle in thermogravimetry involves heating a sample continuously and then cooling the furnace rapidly so as to test the new sample or start a second heating procedure on the same sample:

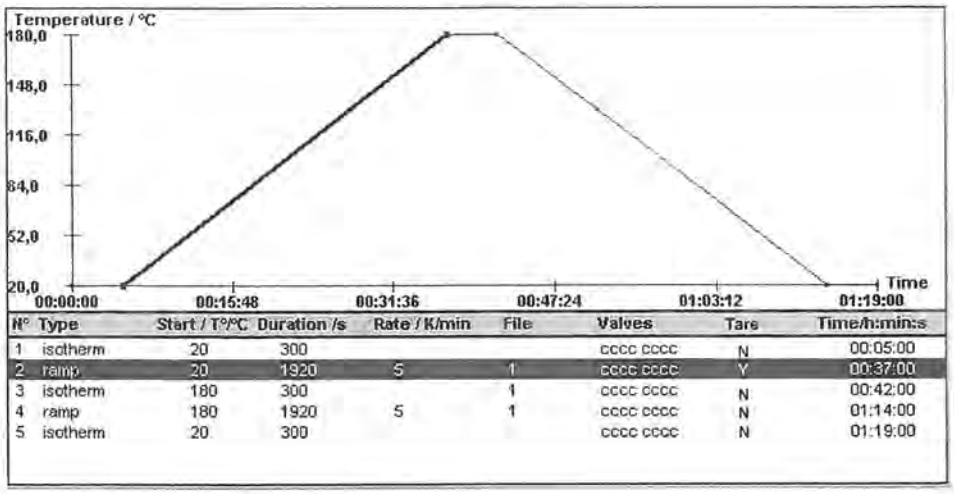
- An isothermal level at the start temperature so as to produce a stable temperature in the furnace and stability in the TG signal before the start of heating for about 300 seconds.

TG-DTA/DSC version

- A tare on the TG signal.

- A scanning sequence from the initial to the final temperature in the test at the chosen scanning rate
- An isothermal level at the final temperature for 300 seconds.
- A cooling scanning sequence with its initial temperature as the one reached, and final temperature as the initial temperature.

The graph hereafter is a means of controling that parameters entered in the computer are correct.



N°	Type	Start / T°/°C	Duration /s	Rate / K/min	File	Valves	Tare	Time/h:min:s
1	isotherm	20	300			cccc cccc	N	00:05:00
2	ramp	20	1920	5	1	cccc cccc	Y	00:37:00
3	isotherm	180	300		1	cccc cccc	N	00:42:00
4	ramp	180	1920	5	1	cccc cccc	N	01:14:00
5	isotherm	20	300			cccc cccc	N	01:19:00

Figure 30: Simple cycle

WARNING No command from the ***Valve*** window (cccc cccc) ***Gas 1*** is passing. To switch on ***Gas 2*** activate valve 1 (occc cccc).

Remark Dans la version DTA/DSC, il n'y a pas de colonne tare

2.5.4.4.2. Staged cycle

The staged cycle provides for carrying out heating or cooling in various stages. For instance, two types of reaction (dehydration and decomposition) are possible for a TG experiment:

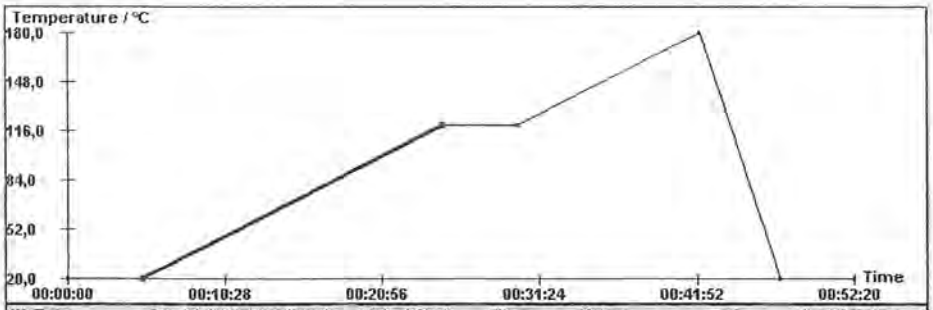
- An isothermal level at the start temperature for 300 seconds.
- A scanning sequence from the initial temperature to the intermediate temperature (end of dehydration for instance) at an initial scanning rate.
- An isothermal level at the intermediate temperature for 300 seconds.

TG-DTA/DSC version

- A tare on the TG signal.

- A scanning sequence from the intermediate temperature to the final temperature (end of decomposition for instance) at a second scanning rate.
- A scanning sequence from the final temperature to the start temperature at a cooling rate.

Working from these two examples more complex cycles can be produced depending on the experiment's requirements. 200 sequences are available to carry out this work.



N°	Type	Start / T°/°C	Duration /s	Rate / K/min	File	Values	Tare	Time/h:min:s
1	isotherm	20	300			cccc cccc	N	00:05:00
2	ramp	20	1200	5	1	cccc cccc	N	00:25:00
3	isotherm	120	300		1	cccc cccc	N	00:30:00
4	ramp	120	720	5	1	cccc cccc	Y	00:42:00
5	ramp	180	320	30		cccc cccc	N	00:47:20
6	isotherm	20	300			cccc cccc	N	00:52:20

Figure 31: Staged cycle

Remark The value for the cooling rate must be provided as positive.

2.6. Making use of the test

After entering the experimental conditions start scanning the temperature cycle and record the thermogramme

2.6.1. Thermogramme

Working from the first thermogramme recorded choose the re-plot as a function of either time or temperature by optimising the axes with the ***Zoom*** functions. As a general rule preference is given to representing as a function of the more expressive temperature so as to situate the products transformation temperatures. However, if the cycle contains a succession of scanning sequences and isothermal levels representing as a function of time provides for an overall display of the phenomena.

Various types of phenomena such as mass variation and thermal effects are shown on a TG-DTA thermogramme (see the figure below):

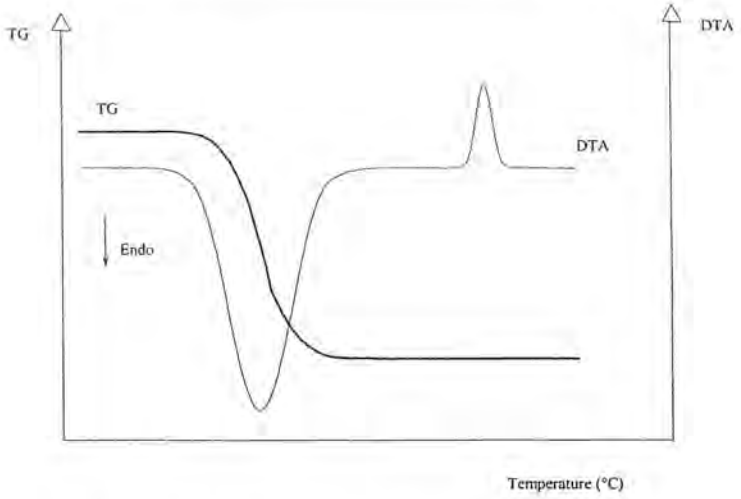


Figure 32: TG-DTA thermogramme

1. Phenomena associating mass variation and thermal effects ; either mass loss (dehydration, dehydroxylation, pyrolysis, decomposition, combustion, etc.) or mass gain (oxidation, corrosion, adsorption, etc).
2. Phenomena deprived of mass variation but detected via an endothermic effect (fusion, phase transition, glass transition, etc.) or via an exothermic effect (crystallisation).

For the TG signal, refer to *1.5* in order to determine characteristic temperatures and calculations for mass variations. The DTA signal is more specifically analyzed in the coming sections.

The common practice is to direct the endothermic peaks towards the bottom of the thermogramme and the exothermic peaks towards the top.

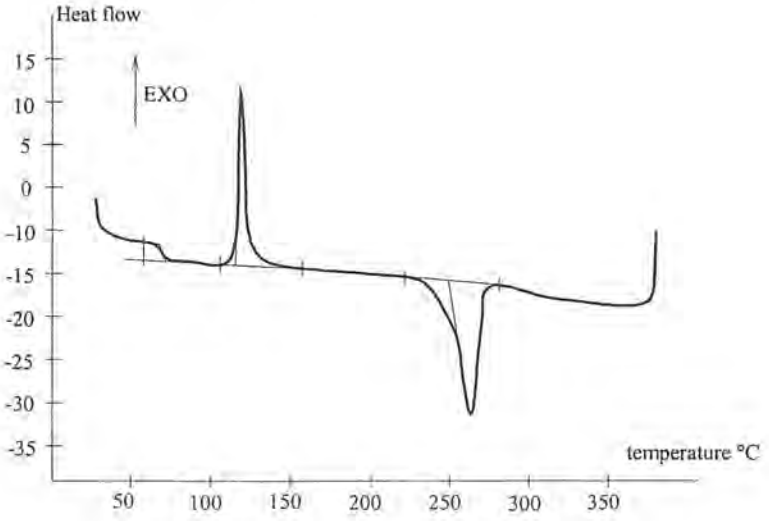


Figure 33: Endothermic and exothermic peaks

Remark The first operation in making use of a thermogramme involves identifying the various transformations and specifying them as endothermic or exothermic effects and relating them to the different mass variations.

2.6.2. Determining the transformation temperatures and/or times (DTA signal)

Three types of transformation are distinguished in this chapter :

1. Endothermic transformation of the type fusion or phase transition
2. Exothermic transformation of the type crystallisation or reaction
3. Glass transition

The methods used for determining the transformation temperatures (or times) comply with the international ***ISO*** standards in force or in draft.

2.6.2.1. Endothermic transformation

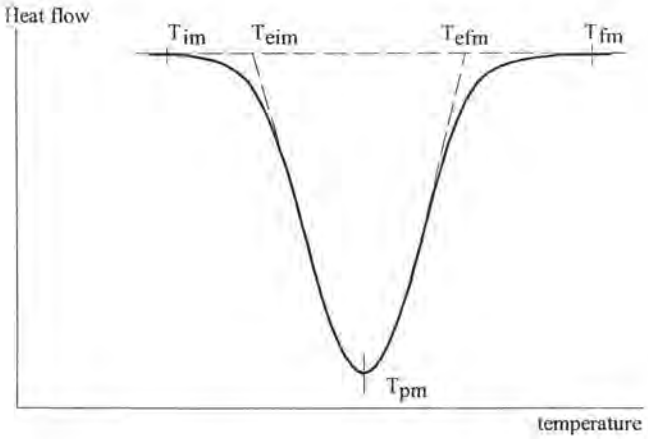


Figure 34: Endothermic transformation thermogramme

The accepted practice is to determine the following temperatures (or times) :

- Temperature T_{im} (or time t_{im}) at the peak start corresponding with the peak's take-off in relation to the base-line plotted between the start and the end of the peak
- Temperature T_{eim} (or time t_{eim}) corresponding with the ***onset*** temperature, i.e. the intersection between the base-line and the tangent at the peak's inflexion point in the increasing phase
- Temperature T_{pm} (or time t_{pm}) corresponding with the top of the peak.
- Temperature T_{efm} (or time t_{efm}) corresponding with the ***endset*** temperature, i.e. the intersection between the base-line and the tangent at the peak's inflexion point in the decreasing phase.
- Temperature T_{fm} (or time t_{fm}) at the peak end corresponding with the peak returning to the base-line.

In the special case of a pure, crystalline substance the fusion temperature is measured at the ***onset*** temperature T_{eim}.

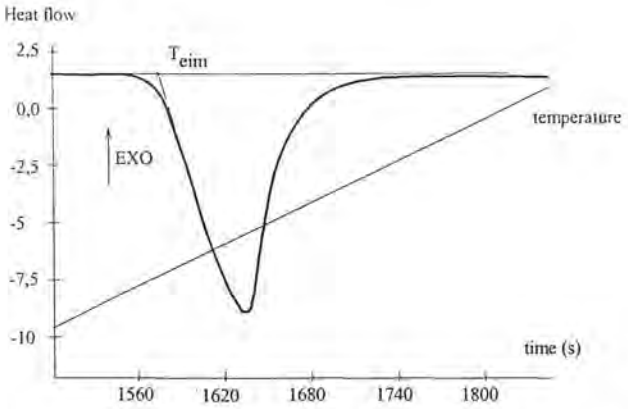


Figure 35: Thermogramme of the fusion of a pure substance

Remark For semi-crystalline substances, like numerous polymers, the fusion (or softening) temperature is measured at the T_{pm} temperature on the peak top.

Refer to *Chapter 1* in the ***Practical Work/Maintenance*** booklet for additional information.

2.6.2.2. Exothermic transformation

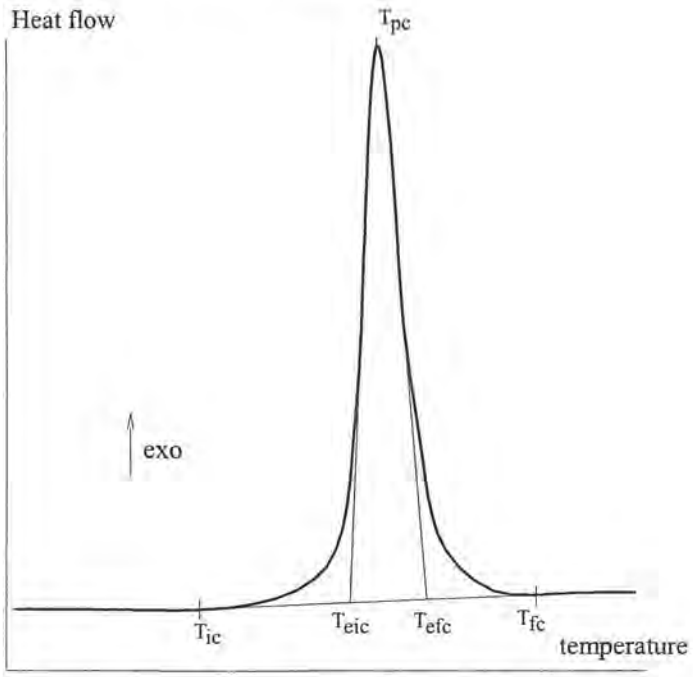


Figure 36: Thermogramme of an exothermic transformation

The accepted practice is to determine the following temperatures (or times) :

- Temperature T_{ic} (or time t_{ic}) at the peak start corresponding with the peak's take-off in relation to the base-line plotted between the start and the end of the peak.
- Temperature T_{eic} (or time t_{eic}) corresponding with the ***onset*** temperature, i.e. the intersection between the base-line and the tangent at the peak's inflexion point in the increasing phase
- Temperature T_{pc} (or time t_{pc}) corresponding with the the top of the peak
- Temperature T_{efc} (or time t_{efc}) corresponding with the ***endset*** temperature, i.e. the intersection between the base-line and the tangent at the peak's inflexion point in the decreasing phase
- Temperature T_{fc} (or time t_{fc}) at the peak end corresponding with the peak returning to the base line

Remark In the same way as for fusion the crystallisation temperature in a pure, crystalline substance is measured at the ***onset*** temperature T_{eic} .

Remark For a semi-crystalline substance it is measured at the T_{pc} temperature on the peak top.

2.6.2.3. Glass transition

The present state of knowledge accepts that glass transition corresponds with the progressive change in the features of a solid to those of a viscoelastic liquid.

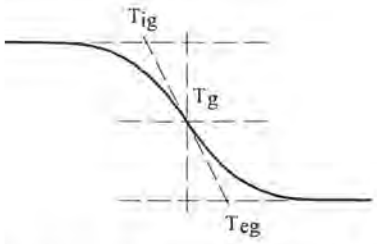


Figure 37: Glass transition without relaxation time

As this involves a progressive transformation glass transition is distinguished by three specific temperatures:

1. The temperature at the start of transition T_{ig} given by the intersection between the base-line (before the transition) and the tangent at the inflexion point (line on the largest slope).
2. The temperature at the end of transition T_{eg} given by the intersection between the base-line (after the transition) and the tangent at the inflexion point.
3. The conventional temperature for glass transition T_g produced by the intersection of the curve and the centre line between the two base-lines.

If the sample shows any signs of relaxation before or after glass transition, proceed as described in the following diagram :

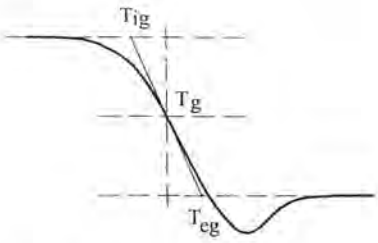


Figure 38: Glass transition with relaxation time

2.6.3. Temperature correction

Studying the temperature correction is easier with the coupling of the balance and theDTA rod than with teh TG rod only.

Measuring the sample's temperature is performed by the thermocouple fitted under the crucible containing the sample.

Although this measurement is done near the sample a small difference may be noted with the sample's real temperature due to the thermal gradient and the time for the heat to cross the crucible wall.

Temperature correction will vary according to :

- The temperature.
- The scanning rate used.
- The type of crucible involved.
- The type and rate of sweeping gas.

Standard materials with known fusion or transformation points are required to carry out this temperature correction.

For a semi-crystalline substance it is measured at the T_{pc} temperature on the peak top. In the same way as for fusion the crystallisation temperature in a pure, crystalline substance is measured at the ***onset*** temperature T_{eic} .

Remark To ascertain if temperature correction is needed :

- Bring about the fusion of a known standard within the temperature range of the transformation being studied.
- Compare the value measured with the one given in the literature.

2.6.3.1. Standard materials used

Metals are prepared for determining temperature calibration:

Substance	Melting point (°C)	Réferences
Indium	156.598	ITS-90

Tin	231.928	NIST , ITS-90
Lead	327.45	NIST
Aluminium	660.32	ITS-90
Silver	961.78	ITS-90
Gold	1064.18	ITS-90
Nickel	1455	IPTS-1968

Reference : ISO norm 11357-1 (Annex A)

WARNING Only indium (NIST GM 758) and tin (NIST GM 758) are recognized as official standards for the DTA method. For the other metals choose a 4N purity (99,99%) or better 5N (99,999%).

WARNING If the platinum crucible is used (or any other metal crucible) it first needs to be partly filled with alumina before arranging the sample so as to prevent any contact between the molten sample and the crucible (alloys may be be formed).

WARNING The samples must be melted in an inert gas atmosphere, especially for a nickel sample (it may otherwise attack the alumina crucible).

However, depending on the range of temperature planned for analysis, inorganic and organic substances may be used for fusions and transitions :

SUBSTANCE	TEMPERATURE (°C)	REFERENCE
Potassium nitrate	127,7 (transition)	NIST GM 758
Potassium perchlorate	299,5 (transition)	NIST GM 758, 759
Silver sulfate	430 (transition)	NIST GM 758, 759
Quartz	573 (transition)	NIST GM 759, 760
Potassium sulfate	583 (transition)	NIST GM 759, 760
Potassium chromate	665 (transition)	NIST GM 759, 760
Barium carbonate	810 (transition)	NIST GM 760
Strontium carbonate	925 (transition)	NIST GM 760

From: ISO norm 11357-1 (Annex A)

⚠ When using these substances special attention must be paid to exhibiting high vapour pressures.

⚠ In contrast, certain substances can break down if they are heated beyond their transition or fusion temperature.

⚠ It is thus VITAL to remain within the temperature measurement corresponding with the transformation given in the table.

2.6.3.2. Experimenting

Choose at least three standard materials comprising the temperature zone which will be used for analyzing the samples.

Set the experimental conditions to be used for analyzing the samples especially :

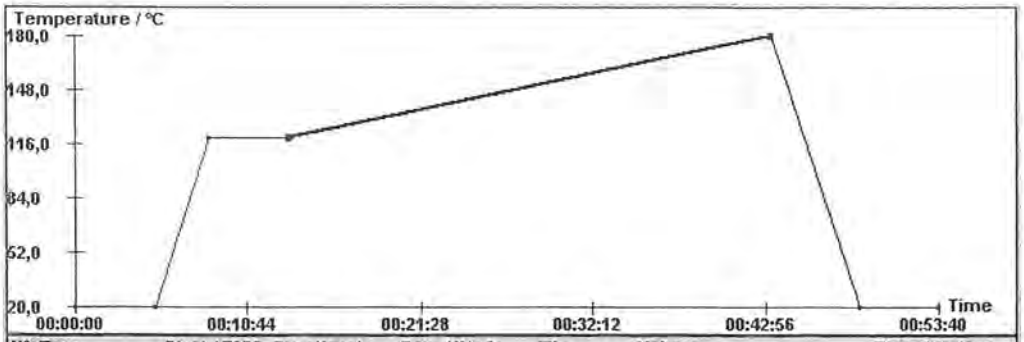
- Type of crucible.
- Properties and flow-rate of the sweeping gas.
- Temperature scanning rate.

For each standard material:

- Weigh about 50 mg of substance into a crucible.
- Arrange the crucible on the ***sample*** side of the DTA transducer. Arrange an identical, empty, crucible on the ***reference*** side.
- Close the furnace and switch on the sweeping gas(if used).
- Prepare the scanning cycle so as to get the substance molten.

Remark In practice scan the furnace's temperature rapidly (30°C/mn) up to above 30°C before fusion. After an isothermal, stabilising level record the fusion at the chosen rate.

- Finally, scan the furnace's cooling.
- Record the corresponding thermogramme and re-plot the part corresponding with the standard's fusion as a function of temperature. Plotting the curve is a means of controlling that the sample does not show mass variation during fusion, that is to say it remains stable.
- Repeat the operation for each material, each time adapting the temperature range for measuring fusion and transition.



N°	Type	Start / T°/°C	Duration /s	Rate / K/min	File	Valves	Time/h:min:s
1	isotherm	20	300			cccc cccc	00:05:00
2	ramp	20	200	30	1	cccc cccc	00:08:20
3	isotherm	120	300		1	cccc cccc	00:13:20
4	ramp	120	1800	2	1	cccc cccc	00:43:20
5	ramp	180	320	30		cccc cccc	00:48:40
6	isotherm	20	300			cccc cccc	00:53:40

Figure 39: Example of scanning cycle

WARNING Expand the temperature range for analyzing fusion when the scanning rate increases.

WARNING A second fusion of the sample is recommended after cooling and this second thermogramme provides useful information.

Remark The first fusion does, in fact, often provide a compact shape to the sample, which is more helpful for the heat exchange with the transducer.

2.6.3.3. Temperature correction for a fixed scanning rate.

For each fusion peak determine the ***onset*** temperature T_{eim} as defined in *2.6.2.1*:

Given:

- T_{eim}, . the measured ***onset*** temperature.
- T_{fi} , . the sample i's real melting point.
- $dT_i = T_{eim} - T_{fi}$, the temperature correction.

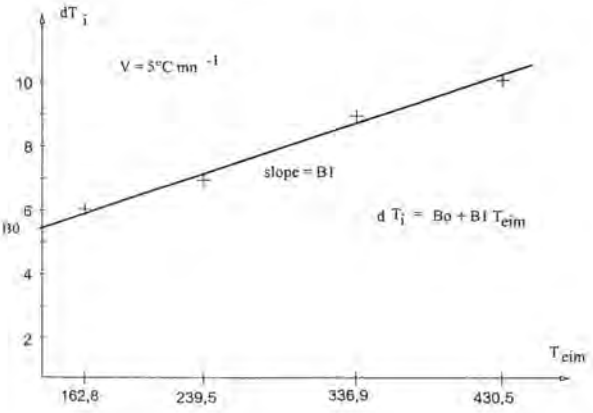


Figure 40: Temperature correction for a fixed scanning rate

Draw up a table (T_{eim} , T_{fi} , dT_i) and plot the variation $dT_i = f(T_{eim})$.

Express this variation in the form of a straight line: $dT_i = B_0 + B_1 . T_{eim}$

Determine B_0 and B_1 by using a regression programme.

Enter the values B_0 and B_1 on to the software's ***Parameters*** page for temperature correction.

Re-set the values B_2 and B_3

WARNING This relationship provides for correcting any temperature for the analysis interval considered and by always using the same scanning rate.

2.6.3.4. Temperature correction for various scanning rates

The software allows the correction parameters to be calculated automatically. Refer to the *Temperature correction* section in the ***Setsoft*** base software booklet.

If analyzing the sample has to be done at various temperature-scanning rates the fusion of the standard materials needs to be studied at various scanning rates V_i

In practice carry out experiments for each standard at a minimum of three different rates whose values encompass the values of the rates to be used for the sample.

Calculation method:

- Draw up a table (T_{eim} , T_{fi} , V_i , dT_i)
- Using the method of the least squares or a regression programme determine the coefficients B_0, B_1 and B_2 for the correcting relation:
  $dT_i = B_0 + B_1 . T_{eim} + B_2 . V_i$

In practice, if N is the number of tests carried out, calculate the following sums:

A	ΣT_{eim}
B	ΣV_i
C	ΣdT_i
D	ΣT_{eim}^2
E	$\Sigma T_{eim} . V_i$
F	$\Sigma T_{eim} . dT_i$
G	ΣV_i^2
H	$\Sigma V_i . dT_i$

Here the coefficients are produced by the relations :

$B_0 = (J/W)$

$B_1 = (K/W)$

$B_2 = (L/W)$

Or :

$W = N (DG - E^2) - A^2G + 2ABE - DB^2$

$J = C (DG - E2^2) - F (AG- EB) + H (AE - DB)$

$K = N (FG - HE) - A (CG - BH) + B (CE - FB)$

$L = N (DH - EF) - A (AH - EC) + B (AH - DC)$

The temperature correction thus determined applies for any temperature and scanning rate for the range under study.

Enter the values B_0, B_1 and B_2 on to the software's ***Parameters*** page for temperature correction.

The coefficient B_3 is re-set for the instrument used.

WARNING During the experiments for determining temperature correction check or initially re-set the values B_0, B_1, B_2 and B_3.

2.7. Energy calibration

Although the DTA technique is above all a qualitative method, there is a facility, by use of the standards, for calibrating the DTA transducer so as to transform the electrical signal S (in microvolts) into thermal power P (in milliwatts). Heat related to thermal effect can thus be linked to mass variation that really produced a reaction during transformation. The coefficient of calibration D is then determined as :

$S = K . P$

This coefficient of calibration K varies with various parameters :

- The sample shape and mass.
- The properties of the DTA transducer.
- The experimenting temperature.
- The properties of the crucible.
- The properties and flow-rate of the sweeping gas.

2.7.1. Measuring the heat of fusion for a pure substance

The thermogramme corresponding with the fusion of a pure substance is represented in the following diagram (also refer to *Chapter 1* in the ***Practical Work/Maintenance*** booklet):

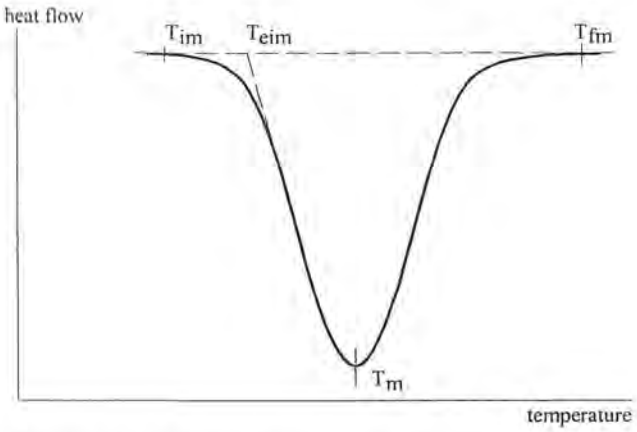


Figure 41: Fusion of a pure substance

The heat of fusion for the sample analyzed is produced by integrating the area under the peak between the peak's start T_{im} and end T_{fm} temperatures without initial calibration, and the ordinate being expressed in µV and the abscissa in seconds, the peak's area is expressed in µV.s. Integrating the peak is done via the ***Integration*** function on the base software after choosing the type of base-line. For a fusion peak a straight base-line is used between the temperatures T_{im} and T_{fm}.

2.7.2. Standard materials used

Paragraph *2.6.3.1* provides a table of metal standards for determining temperature correction.

The same standards may be used for energy calibration as they are thermally stable and offer the facility of providing numerous, successive tests without modifying their specifications.

Their fusion heat contents are used for energy calibration.

Substance	Melting heat content (J / g)	Melting T°C	Réferences
Indium	28,5	156.598	ITS-90
Tin	60,22	231.928	NIST , ITS-90
Lead	24,72	327.45	NIST
Aluminium	395.5	660.32	ITS-90
Silver	104.8	961.78	ITS-90

Gold	64.5	1064.18	ITS-90
Nickel	300	1455	IPTS-1968

WARNING Only tin (NIST SRM 2220) and zinc (NIST SRM 2221a) are recognized as standards certified for energy calibration. For the other substances the values given are taken from the literature.

Remark It should be noted that, for the same substance, significant differences may be observed over the value of the fusion heat content

2.7.3. Experimenting

Choose one or several standards based on the transformation temperature range under study.

The experimental conditions are identical to those described in *2.6.3.2.*

Plot the fusion curve as a function of time or temperature.

Remark In practice temperature and energy calibrations are carried out with the same experiment, on the same fusion peak of the metal standard.

2.7.4. Calibration with a single standard

If the transformation takes place within a limited temperature range a single coefficient of calibration can be used when choosing the standard with the melting point closest to the sample transformation temperature.

Let H be the fusion heat content of the metal standard chosen (in J / g).

Let m be the mass of standard analyzed (in g).

Let S be the area of the fusion peak (in µV . s).

Then the coefficient of calibration at the standard's melting point is given by:

K = (S/H) * (1/m) in microvolt per watt. K is better expressed in µV/mW.

For any peak area A (in µV . s) , combined with the corresponding transformation Q (in Joules) the formula is :

Q = A/K

2.7.5. Calibration with various standards

In practice calibration with a single standard is not very accurate as the coefficient of calibration varies with temperature.

Various metal standards are recommended so as to plot a variation curve of the coefficient of calibration as a function of temperature.

The substances shown in *1.5.4* can be used.

Choose at least five standards to produce correct determining.

Let H be the fusion heat content of the standard i (in J / g), let m_i be the mass of standard analyzed (in grammes), let S_i be the area of the fusion peak (in $\mu V \cdot s$), then the coefficient of calibration K_i at the standard's melting point T_{eim} is given by:

$K_i = (S_i/H_i) * (1/m)$ in $\mu V/W$.

A table (T_{eim}, K_i) can be done and the variation $K = f(T_{eim})$ can be plotted.

This calibration curve reveals the instrument's coefficient of calibration at any temperature.

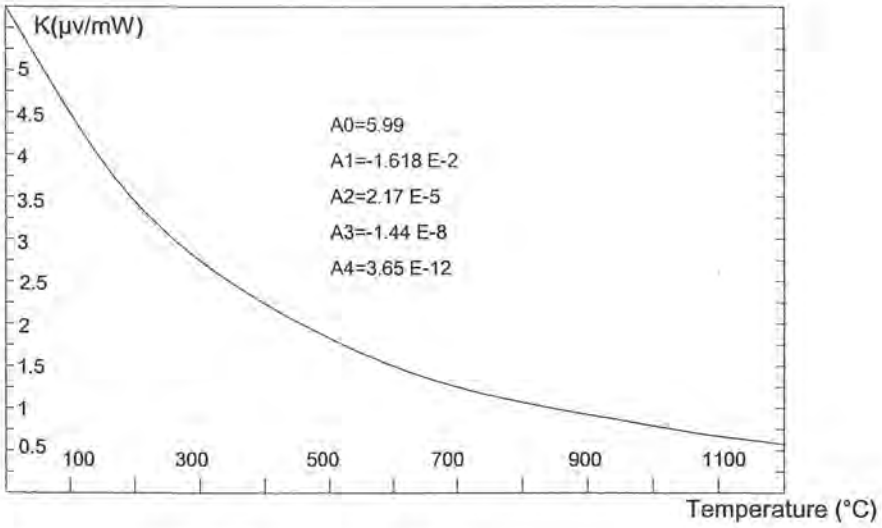


Figure 42: 1200°C argon gas DSC rod

This variation is best put in the form of a polynomial function of the fourth degree :

$K = A_0 + A_1 \cdot T_{eim} + A_2 \cdot T_{eim}^2 + A_3 \cdot T_{eim}^3 + A_4 \cdot T_{eim}^4$

A regression software is needed for this work.

The coefficients A_0, A_1, A_2, A_3 and A_4 thus determined are entered on to the software's ***Parameters*** page for automatically transforming the DTA signal.

Remark Using the calibration curve does not guarantee the accuracy of the results.This is linked to the performance of the transducer used as well as the standards chosen for calibration.

Remark As a general rule, for a DTA transducer which is not designed for quantitative measurements, the accuracy for heat measurement is of the order of 10%.

Remark For quantitative measurements the DSC-type transducers are recommended.

3. DSC plate-type version

The TG-DSC plate-type version consists of a DSC plate-rod connected to the balance module so as to measure the mass variation and the thermal effect of the same sample -with a similar quantity- simultaneously. The DSC method can also detect transitions without variation in mass (fusion, crystallisation, ...).

The *labsys*™ DTA version gives only the thermal effect

3.1. DSC Plate

The DSC rod consists of :

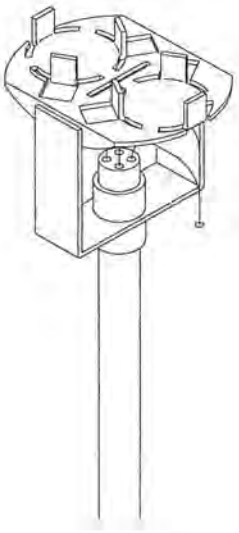


Figure 43: DSC rod upper part

- A machined, metal plate containing two housings for the sample and reference crucibles.
- A temperature-control thermocouple in the plate's central section.
- A ceramic shaft designed to accommodate the various thermocouples
- A connector at the end of the shaft.
- A mark on the shaft indicating the rod type.

The accepted arrangement is that the side designed to take the crucible with the sample, named the ***sample side*** is fitted to the front opposite the rod. The ***reference*** side designed to take the crucible containing a thermally inert product is fitted to the rear.

Remark The connectors provide for an easy way of changing DSC rods. As the connectors on the DTA rods are identical moving from the DSC technique to the DTA technique is immediate.

WARNING The temperature-control thermocouple is the same for the three DSC rods (in Pt-Pt Rh 10%). The safety temperature thus needs to be clearly set for each rod as a function of their maximum temperature so as to prevent damage to the transducer (especially the 800°C and 1200°C transducers). This safety temperature may be set at a lower value as a function of the sample being analyzed (e.g. may decompose) or a function of the heat capacity of certain crucibles (e.g. aluminium).

3.2. Choosing the plate-type DSC rod

Based on the temperature range under study as well as the sensitivity required three types of plate-type DSC rod are available using the properties of various thermocouples:

1. The version for ambient / 800°C DSC transducer in chromel-constantan has the highest sensitivity and is recommended for experiments at average temperature and for highlighting small thermal effects.
2. The version for ambient / 1200°C DSC transducer in chromel alumel has a slightly lower sensitivity to the former but provides for analyses over a wider temperature range.
3. The version for ambient / 1600°C DSC transducer in platinum-platinum rhodium 10 % is designed for high-temperature experiments. Its sensitivity is much lower than those of the previous transducers.

WARNING The chromel used in the manufacture of the 1200°C DSC rods oxidises at an average temperature of 1000°C and the constantan used in the 800°C-DSC version oxidises at an average temperature of 500°C. This transducer is thus best used when being swept by an inert gas and when working in an oxidizing atmosphere.

3.3. Choosing the crucible

After choosing the type of DSC rod a crucible needs to be selected as a function of the sample to be analyzed and the type of test to be carried out. Three types of crucible are available with an identical volume of 100 mm^3 including the cover. Choosing which crucible depends on the sample to be analyzed. As a general rule :

1. The aluminium crucible can be used up to 500°C. It is recommended for analyzing organic substances, polymers, for studying dehydration in minerals (plaster, gypsum, etc.). Clamping the cover on to the sample improves the DSC transducer's selectivity. This crucible can generally not be re-used.

2. The alumina crucible is generally used for all types of materials, especially metals.

WARNING Certain minerals may attack the alumina.

3. The platinum crucible is generally used for analyzing minerals.

WARNING Be cautious with substances containing silicium.

Remark As a general rule it is best to analyze a small mass of sample (20 to 50 mg) so as to minimise the effects within the sample of a thermal gradient.

If the thermal effect to be measured is small:

- Choose the most sensitive transducer.
- Increase the mass of sample.
- Increase the temperature scanning rate.

WARNING The various recommendations given above cannot cover all the instrument's applications.

WARNING Before analyzing a new product there should be information available about the dangers of how it may corrode the crucible during heating or one of the possible transformations (fusion, decomposition, ...) or of the possible overflow. This is a vital choice as it determines the outcome of the experiment. Making the wrong choice can lead to damaging the crucible, and thereby to damaging the DSC rod.

3.4. Crimping the crucible

3.4.1. Tools

Refer to *2.4.1.*

3.4.2. DSC

3.4.2.1. Filling up a low level

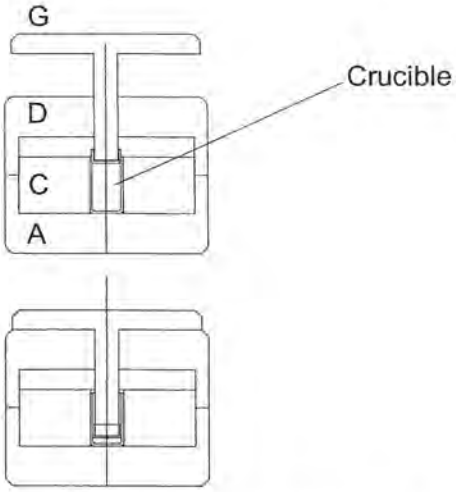


Figure 44: Filling up a low level

3.4.2.2. Filling up a high level

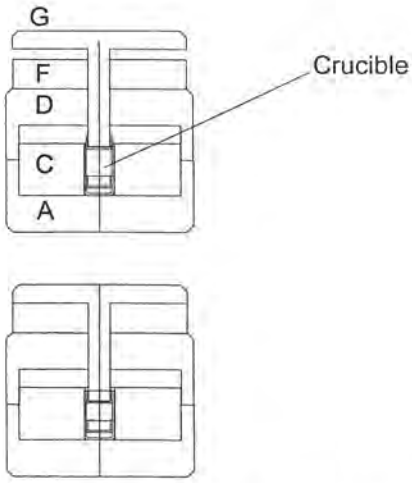


Figure 45: Filling up a high level

Remark Crimping a high level filling can also be used to add a second cork on a crucible crimping a low level.

3.5. Preparing the experiment and Making use of the test

Refer to §. 2.5. et 2.6.

WARNING When using 800°C and 1200°C rods at high temperature it is best to protect them with a stream of inert gas so as to prevent the plate from oxidising.

Remark The same rule applies for correcting the temperature with the DSC transducers using the same standard materials.

Remark The DSC rod needs to be calibrated using various standards (refer to *2.7*) to determine the calibration curve and calculate the coefficients of the calibration polynomial.

Remark The calibration curves can vary with the properties of the crucible and especially with the properties of the gas

4. Coupling with a mass spectrometer

4.1. Parts of the process

This describes the coupling of a ***BALZERS*** mass spectrometer supplied by **SETARAM**. For any other type of spectrometer, the coupling delivered by **SETARAM** must be adjusted.

4.1.1. Mass spectrometer

The description and the functioning mode of the analyzer are described in the booklet supplied by the manufacturer.

4.1.2. Capillary

The capillary allows working at athmospheric pressure in the thermobalance and with a vacuum of eabout 10^{-6} mbars in the mass spectrometer.

- The capillary -made of fused silica- is protected by a Teflon pipe. The assembly is surrounded by an insulating heating sleeve.
- The sleeve is 1 m long and the capillary diameter is 0.23 mm.
- The capillary rapidly transfers (about 100 ms) a sample representative ofthe gazeous mixing from the thermobalance in the ion source: le ratio of partial pressures of the various constituants is maintained.
- The capillary and the mass spectrometer are already connected.

4.1.3. Connection to the thermoanalyzer

The spectrometer-analyzer connecting part is mounted at outlet of the heating sleeve. The end is protected by a tight metal sleeve.

Before connecting the capillary to the thermoanalyzer, make sure it is not obturated. In that case the spectrometer itself is used and the characteristic peaks of the ambient to be detected are checked.

Otherwise, if the capillary is obturated refer to the Balzers booklet. The capillary at the connection end must be 45 mm long (refer to .....

4.1.4. Connection to the capillary

The balance nose or standard DTA/DSC transducer must be replaced by a nose provided with a connection allowing the introduction of the capillary in the specific area and ensures tightness in the system.

The nose of the spectrometer coupling is provided with a tee at the gas outlet.

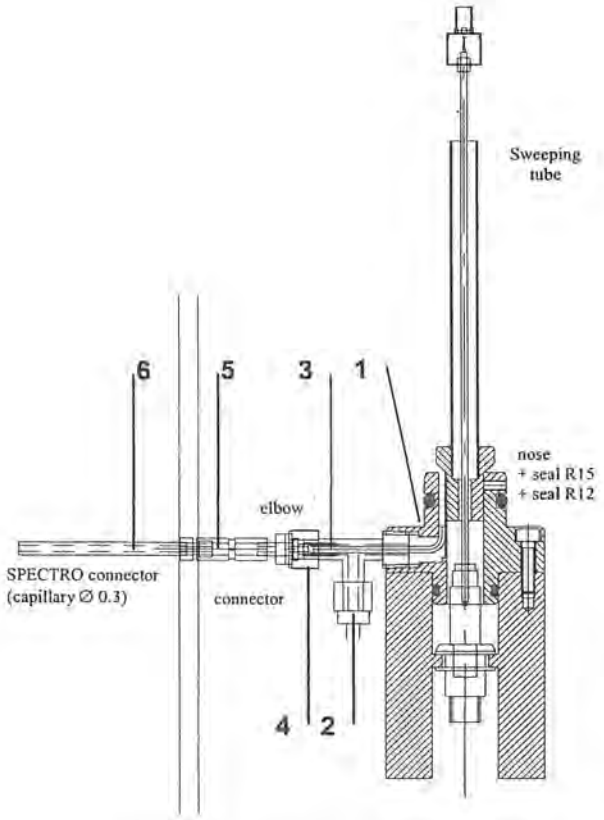


Figure 46: Spectrometer coupling nose

1. Bring the furnace up.
2. Remove the front cover (refer to *Chapter 1 -5*.
3. Disconnect the inlet (1) and outlet (2) gas pipes.
4. Remove the two sweeping gas half-tubes (refer to Chapter *1 -5*).
5. Remove the standard nose: unscrew the two locking bolts and pull the nose upward ; resistance comes from the seal (for a DTA or DSC rod it has already been removed).
6. Place the new nose and ensure that there is a seal.
7. Reconnect the gas inlet (1) and outlet (2) pipes.
8. Place the sweeping gas half-tubes.
9. Introduce the capillary in the by-pass connection (3). The capillary itself (quartz part) must be introduced down to the curved part of the connection (3).
10. Screw the coupling bolt (4) on the nose.

If the instrument has been directly bought with the Spectrometer option do not pay attention to instructions given in the following paragraph from 3 to 8.

4.1.5. Changing the capillary

Refer to Figure 46

1. The capillary goes through a ferule connection (5). Unscrew it, remove the ferule and keep it. The same ferule is to be found on the spectrometer side (spectrometer spare parts).
2. Remove the adjusting part (6) which is inserted in the Teflon tube.

3. Change the capillary on the spectrometer side: refer to the corresponding booklet.
4. Push the capillary through the Teflon tube and in the adjusting part (6). Let about 80 mm long out.
5. Slide the ferule (5) and connector (4) on the capillary and screw the two bolts manually.
6. Close the assembly with the protecting sleeve.
7. Switch the spectrometer on and observe the evolution of internal pressure, screw the two bolts with the tools supplied until pressure starts decreasing (then stop tightening to prevent the ferule and capillary from being damaged).

4.1.6. Utilisation

Refer the the ***Practical work/Maintenance*** booklet for selecting the appropriate rod, crucible ane preparing the experiment.

Refer to the ***Coupling of a mass spectrometer*** software booklet to get the instructions for use.

SETARAM : excellence in thermal analysis

LABSYS™ : low cost series of multi-module thermal analyzers

- DSC131 : -150 to 700°C (heat flux sensor)
- DTA, TG/DTA : ambient to 1600°C
- DSC, TG/DSC : ambient to 1600°C
- TMA : ambient to 1000°C

SETSYS : top of range in thermal analyzers

- DSC141 : -150 to 600°C (power compensation)
- DTA, TG/DTA : -150 to 2400°C
- DSC, TG/DSC : -150 to 1600°C
- TMA, DLTMA : -150 to 2400°C

micro DSC : high sensitivity DSC and calorimetry

- micro DSCIII : -20 to 120°C ("batch and flow")
- micro DSCVII : -45 to 120°C ("batch")

CALVET PRINCIPLE DSC

- DSC 121 : -120 to 830°C
- DSC Robotic Sytem : -120 to 830°C

CALVET CALORIMETERS

- BT 2.15 : low temperature calorimeter from -196 to 200°C
- MS 80 : standard calorimeter from ambient to 200°C
- HT 1000 : high temperature calorimeter from ambient to 1000°C
- C 80 : mixing and reaction calorimeter from ambient to 300°C
- Titrys : titration calorimeter from ambient to 75°C
- calorimeters based on your analysis needs

96 LINE : high temperature and large volume thermal analyzers

- MULTI-HTC 96 : DSC and calorimetry
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  DSC detectors up to 1600°C
- TG 96 : thermogravimetry
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- DHT 96 : dilatometry
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2

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PRACTICAL WORK MAINTENANCE

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CONTENTS

1. REVISIONS TABLE

C	22/06/99	Conformity with the BT norms Compilation of TG-TGATD/DSC and ATD + DSC	C/LABTGTPA	C. PARAZZA	K. DAVAT	JL. DAUDON

CHAPTER 1 - PRACTICAL WORK

1. Introduction

The ***Practical Work*** Chapter relates to operations with the thermobalance and coupling with the DTS and DSC transducers and is written for people discovering these techniques as well as for students wanting to become familiar with these techniques and the measuring facilities available.

Initial reference will be made to the ***Commissioning*** and ***Utilisations*** chapters, especially to the paragraphs dealing with temperature and energy calibration of the transducers.

This chapter only touches upon the applications of the TG, TG-DTA and TG-DSC techniques.

The user may also refer to the following works :

TITLE	AUTHOR (YEAR)	EDITOR (COUNTRY)
Thermal Analysis (3rd Edition)	W. WENDLANDT (1986)	John Wiley and Sons (USA)
Thermal Analysis	B. WUNDERLICH (1990)	Academic Press (USA)
Thermal Analysis Techniques and Applications	E. L. CHARSLEY and S. B. WARRINGTON (1991)	Royal Society of Chemistry (UK)
Thermal Characterization of Polymeric Materials	E. A. TURI (1981)	Academic Press (USA)
Thermal Analysis of Foods	V. R. HARWALKAR and C. Y. MA (1990)	Elsevier (UK)
Pharmaceutical Thermal Analysis	J. L. FORD and P. TINNINS (1989)	Ellis Horwood Limited (UK)

2. Definitions and Vocabulary

The definitions and vocabulary used in this chapter have been published by the International Confederation for Thermal Analysis (ICTA) in a compilation entitled *For better thermal analysis and calorimetry* (John 0. Hill , Publisher).

Remark Furthermore the definitions concur with the ISO standards published by the International Standardization Organization.

2.1. Differential Thermal Analysis (DTA)

Differential Thermal Analysis is a technique in which the difference in temperature between the sample and the reference is measured as a function of time or temperature when the temperature of this sample is scanned in a controlled atmosphere.

2.2. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry is a technique in which the heat flow (thermal power) of the sample is measured as a function of time or temperature when the temperature of this sample is scanned, in a controlled atmosphere.

In practice what is measured is the difference in heat flow between a crucible containing the sample and a reference crucible (the latter is generally empty, but may also contain a material which is thermally inert in the temperature range being studied).

2.3. Thermogravimetric Analysis (TG)

The thermogravimetric analysis is a technique in which the mass of a sample is measured as a function of time or temperature when the temperature of this sample is scanned in a controlled atmosphere.

2.4. Vocabulary used

- The symbol T is used for the expression in degrees Celsius (°C) or in Kelvin (K) .
- The symbol t is used for the expression in seconds (s), minutes (min) or hours (h).
- The symbols m for mass and W for weight are recommended.
- The heating (or cooling) scanning rate is expressed by the derivative dT/dt . In practice, as this involves an average value during heating, it is represented by V and is expressed in $°C.mn^{-1}$ or $K.mn^{-1}$.
- The ordinate of the DTA curve is expressed in microvolts and corresponds with the temperature difference ΔT .

- The ordinate of the DSC curve corresponding with the difference in heat flow must be expressed as ***d(ΔQ)/dt*** rather than dH/dt, given that ***Q*** represents a quantity of heat, while ***H*** represents a heat content. The difference in heat flow is expressed in milliwatts.(m***W***).

Refer to *Chapter 2 - 1.5.* and *2.5.* in the ***Commissioning/Utilisations*** booklet for the various types of thermogrammes, together with temperature and energy calibrations.

3. Examples of practical work

Various examples of practical work refering to various applications are given as a way of getting to know the TG, TG-DTA and TG-DSC methods.

Each example of practical work is distinguished by :

- How the application is presented.
- How the test is carried out.
- How use is made of the calorimetric curve.
- How the data is processed.

3.1. TG rod : Decomposing the calcium carbonate $CaCo_3$

3.1.1. Presentation

Calcium carbonate $CaCO_3$ decomposes in calcium oxide CaO releasing carbon dioxide CO_2 :

$CaCO_3 \rightarrow CaO + CO_2$

Decarbonation starts around 700°C. However, transformation temperature changes if CO_2 pressure varies above the sample.

Under CO_2 sweeping transformation starts at a higher temperature (around 900°C). Conversely, under vacuum, transformation temperature decreases to 450°C. In the example below, transformation is studied under neutral gas (argon).

3.1.2. Experimenting

3.1.2.1. Samples and experimenting conditions

1. Use an alumina crucible 400 µl adapted to the TG rod
2. Weigh precisely about 300 mg of calcium carbonate
3. Arrange the crucible on the TG rod in its housing
4. Press the control button on the instrument's front panel to close the furnace
5. Start sweeping helium at a rate of about 1 litre per hour
6. Prepare the scanning cycle to perform the sample's decomposition

In practice, enter the following experimenting conditions in the software:

1. Scanning from 20°C to 1000°C at 10°C/mn
2. Rapid cooling from 1000°C down to 20°C at 30°C /mn

The cycle can be repeated to check that the substance is completely decomposed. The second curve is also often used as base line or « blank ».

3.1.2.2. Interpreting the TG curve

Re-plot the curve produced as a function of temperature, optimising the choice of the axes (use the ***Zoom*** function). It is recommended to plot the curve in % (see Figure 1).

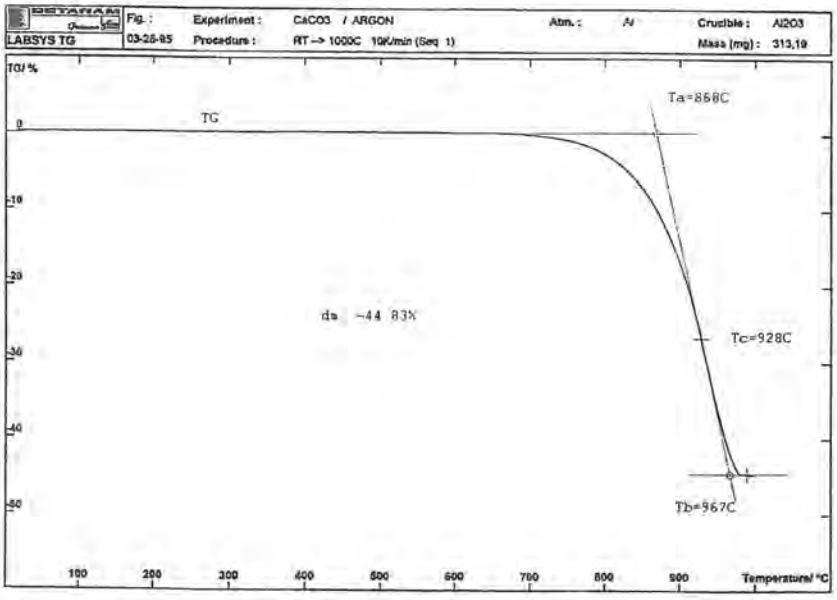


Figure 1 : TG curve

Decarbonation starts at about 600°C and stops at about 1000°C.

To determine the corresponding variation in mass select the start and end of the mass variation via the ***Mass Variation*** function.

E.g.: $\Delta m = -44.83\%$

Let us determine the characteristic transformation temperatures as described in *Chapter 2 - 1.7.* in the ***Commissioning/Utilisations*** booklet:

In the example : $T_A = 868$ °C

$T_B = 967$ °C

$T_C = 928$ °C

It is obvious that the standard imperfectly defines the start of the transformation. Plotting the DTG derivative and the TG curve defines this area much better. Select both plottings on the screen, optimising the axes. The DTG curve is expressed in %/min (see Figure 2).

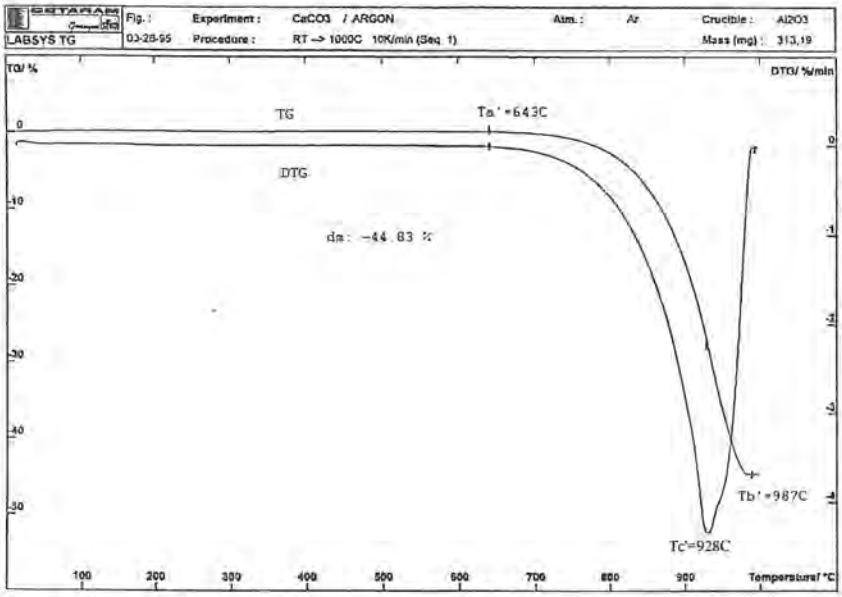


Figure 2: DTG derivative

The DTG curve shows a peak. Using the peak, the start, top and end of the peak can be determined when moving the cursor on the screen. Project the points vertically onto the TG cruve to have A', B'and C' with their respective temperatures in the example:

$T_{A'} = 643$ °C

$T_{B'} = 987$ °C

$T_{C'} = 928$ °C

C and C', showing the inflexion point of the TG curve are located at the same place. A' and B' are the calculation limits of mass variation.

3.2. 1200°C TG-DTA rod : Dehydrating and decomposing calcium oxalate

3.2.1. Presentation

Calcium oxalate is a hydrated substance CaC_2O_4, H_2O. When heated various transformations occur:

- The water molecule separates at around 200°C:
  $CaC_2O_4, H_2O \rightarrow Ca\ C_2O_4 + H_2O$

- The calcium oxalate decomposes in calcium carbonate, releasing carbon monoxide at around 500°C:
  $CaC_2O_4 \rightarrow CaCO_3 + CO$

- The calcium carbonate decomposes in calcium oxide, releasing carbon dioxide at around 700°C:
  $CaCO_3 \rightarrow CaO_3 + CO_2$

Thermogravimetry identifies the various transformations. The thermogravimetric and DTA techniques give the corresponding thermal effects.

With calcium oxalate, the DTA method can focus on modifications in the transformations depending on the atmosphere used.

Indeed, the second transformation that releases CO shows an equilibrium between Co and CO_2 (Boudouard equilibrium) with oxygen :

$CO + 1/2\ O_2 \leftrightarrow CO_2)$

If oxygen pressure is changed, the equilibrium is thus changed. In the example supplied, investigations on transformations in calcium oxalate are carried out under neutral gas (argon) and oxidizing gas (air).

3.2.2. Experimenting

3.2.2.1. Samples and experimenting conditions

1. Use an alumina crucible adapted to the DTA rod
2. Weigh precisely about 40 mg of calcium oxalate
3. Arrange the crucible on the ***sample*** side of the DTA transducer (an empty alumina crucible is used as reference)
4. Press the control button located on the instrument's front panel to close the furnace
5. Start selected sweeping gas at a rate of about 1 litre per hour. If using a neutral gas (such as argon) purge before operation the sample chamber so as to clear off the remaining oxygen: neutral gas is scanned at a rate of about 30 litres/hour for approximately 20 mn, and then scan a rate of 1 litre/hour.

Prepare the scanning cycle:

- Scanning from 20°C to 1000°C down to 20°C at 30°C/mn
- Rapid cooling from 1000°C down to 20°C at 30°C/mn

The cycle can be repeated to check that the substance is completely decomposed. The second curve is also often used as base line or « blank ».

3.2.2.2. Interpreting the TG and DTA curves

3.2.2.2.1. Calcium oxalate under argon

Analyzing calcium oxalate under argon shows 3 very distinct transformations on the TG and DTA curves (see Figure 3):

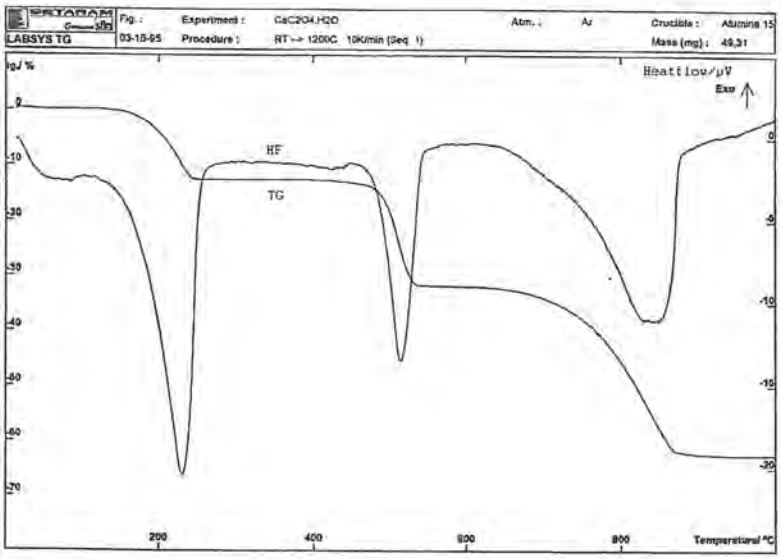


Figure 3: Calcium oxalate under argon

1. Calcium oxalate dehydrates between 100°C and 250°C.
2. Calcium oxalate decomposes in calcium carbonate between 450°C and 550°C.
3. Calcium carbonate decomposes in calcium oxide between 650°C and 850°C.

Plotting the DTG derivated curve shows that the DTA endothermic peak and the DTG peak are linked (see Figure 4).

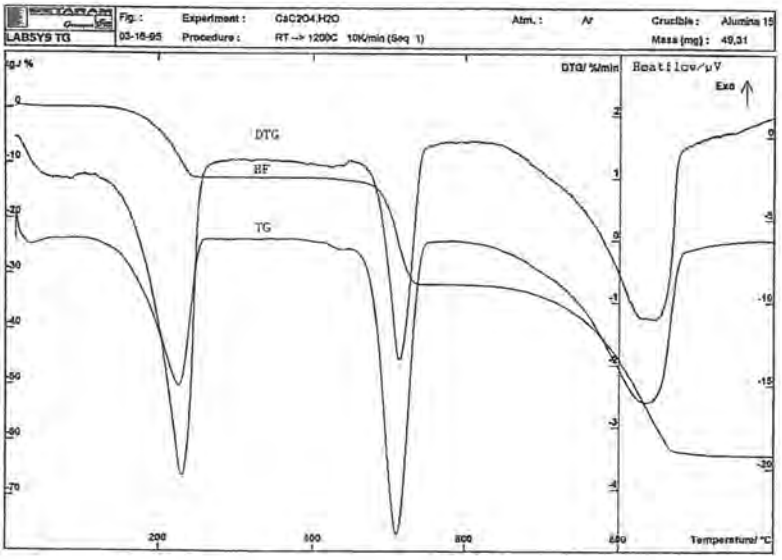


Figure 4: Plotting the DTG derivated curve

For each transformation plot the TG, DTA and DTG curves for the selected area.

3.2.2.2.2. *Dehydrating calcium oxalate*

Once the curves corresponding with this transformation are plotted optimising the ***Zoom*** function, select the TG curve to calculate the mass loss.

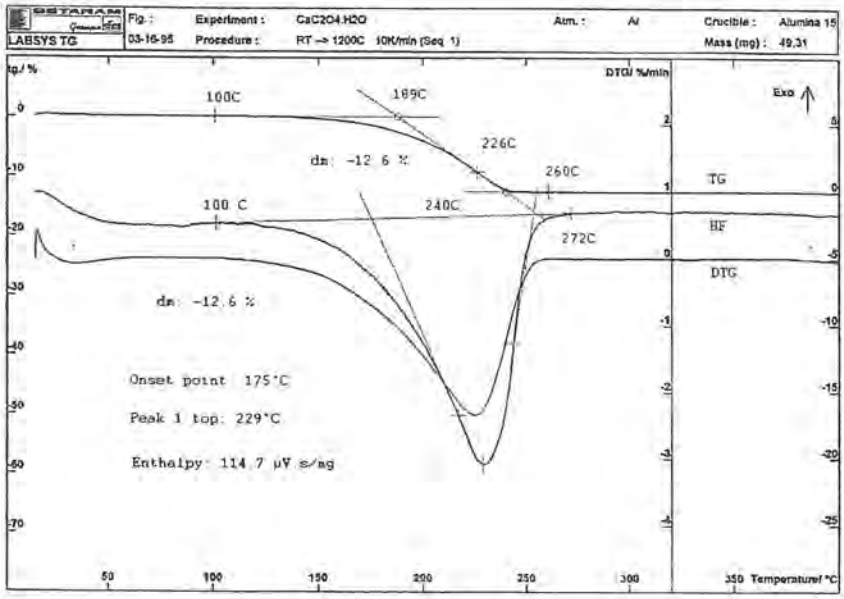


Figure 5: Dehydrating calcium oxalate

Select the start and end of the mass loss with the ***Variation in mass*** function (the DTG peak precisely defines the limits) between 100 °C and 275 °C.

Mass loss resulting from the separation of the water molecule is equal to :

$\Delta m_1 = -12.63\ \%$

Calculating the characteristic temperatures for the TG curve result in the following values:

$T_A = 189\ °C$ $T_B = 240\ °C$ $T_C = 226\ °C$

Defining temperatures on the DTA curve give values equivalent to the DTG curve:

$T_i = 100\ °C$ $T_f = 272\ °C$ $T_p = 229\ °C$

If the DTA rod is calibrated the peak integration is possible. However, this operation is better performed with the DSC-plate rod.

3.2.2.2.3. Decomposing calcium oxalate in calcium carbonate

Once the curves corresponding with the second transformation are plotted and optimized the ***Zoom*** function, select the TG curve to calculate the mass loss.

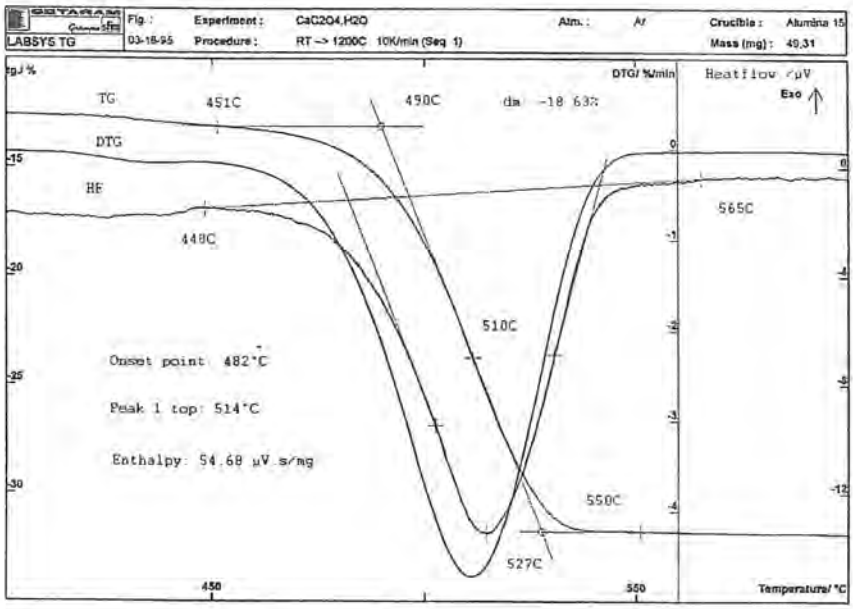


Figure 6: Decomposing calcium oxalate in calcium carbonate

Select the start and end of the mass loss using the ***Variation in Mass*** function, between 445 °C and 550 °C.

Mass loss produced by decomposition and separation of CO is equal to:

$\Delta m_2 = -18.63\%$

Calculating the characteristic temperatures for the TG curve result in the following value:

$T_A = 490$ °C $\qquad T_B = 527$ °C $\qquad T_C = 510$ °C

Defining temperatures on the DTA curve gives values equivalent to the DTG curve:

$T_i = 448$ °C $\qquad T_f = 565$ °C $\qquad T_p = 514$ °C

3.2.2.2.4. Decomposing calcium carbonate in calcium oxide

Once te curves corresponding with the third transformation are plotted and optimized the ***Zoom*** function, select the TG curve to calculate the mass loss.

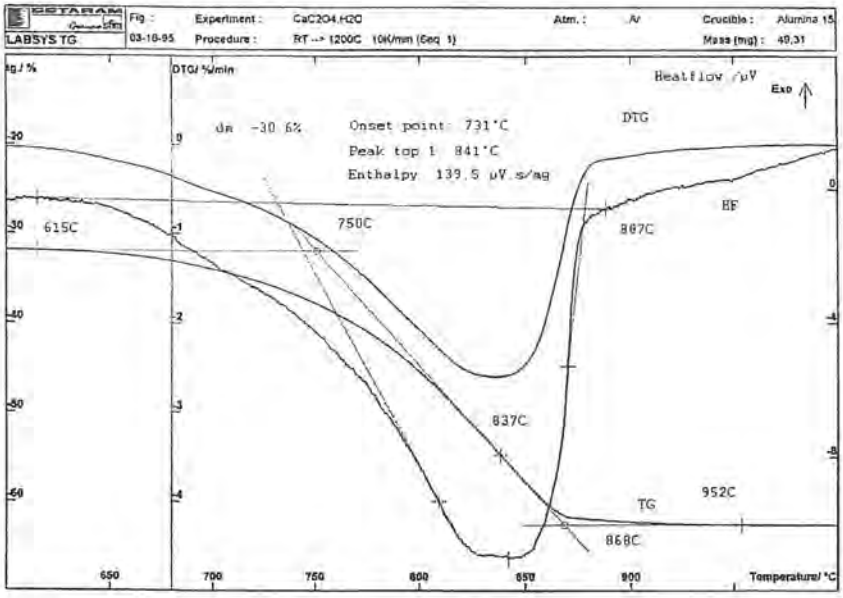


Figure 7: Decomposing calcium carbonate in calcium oxide

Select the start and end of the mass loss using the ***Variation in Mass*** function, between 615°C and 900°C.

Mass loss produced by decomposition and vaporisation of CO_2 is equal to $\Delta m_1 = -30.6\%$

Calculating the characteristic temperatures for the TG curve result in the following values:

$T_A = 750\ °C$ $T_B = 868\ °C$ $T_C = 837\ °C$

Defining temperatures on the DTA curve gives values equivalent to the DTG curve:

$T_i = 615\ °C$ $T_f = 887\ °C$ $T_p = 841\ °C$

3.2.2.2.5. Calcium oxalate under air

Analyzing calcium oxalate under air shows three distinct transformations on the TG and DTA curves. However, the second transformation shows a significant difference as the thermal effect becomes exothermic (endothermic under argon) (see Figure 8).

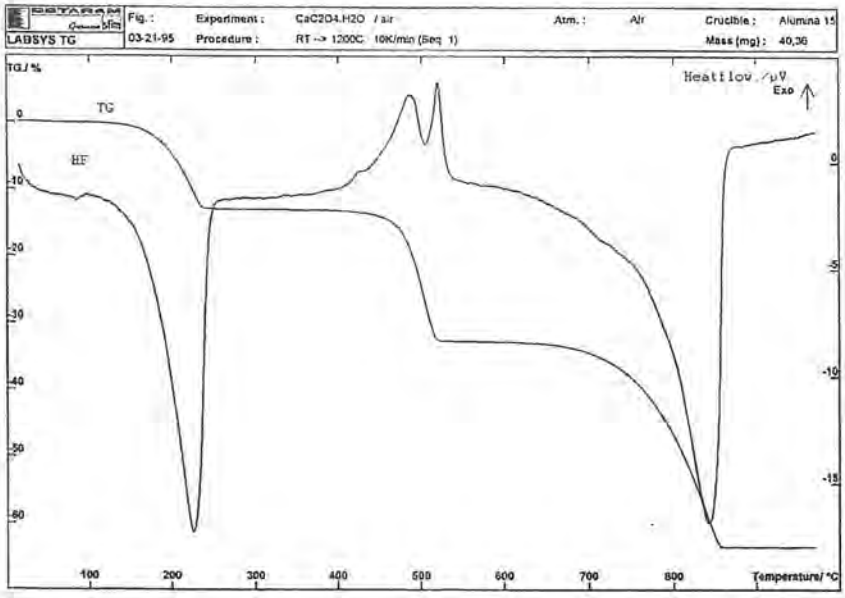


Figure 8: Calcium oxalate under air

Oxygen modifies the decomposition of oxalate in calcium carbonate, not the mass, but the thermal effect because of the reaction between CO and O_2 :

$$CO + \frac{1}{2} O_2 \leftrightarrow CO_2$$

Decomposing carbonate in calcium oxide shows a sharper thermal effect because the rate of the reaction is higher.

The various mass loss and characteristic temperatures for DTA and TG curves can be gathered to be compared with the values obtained in the previous experiment.

3.2.2.2.6. *Dehydrating calcium oxalate*

See Figure 9

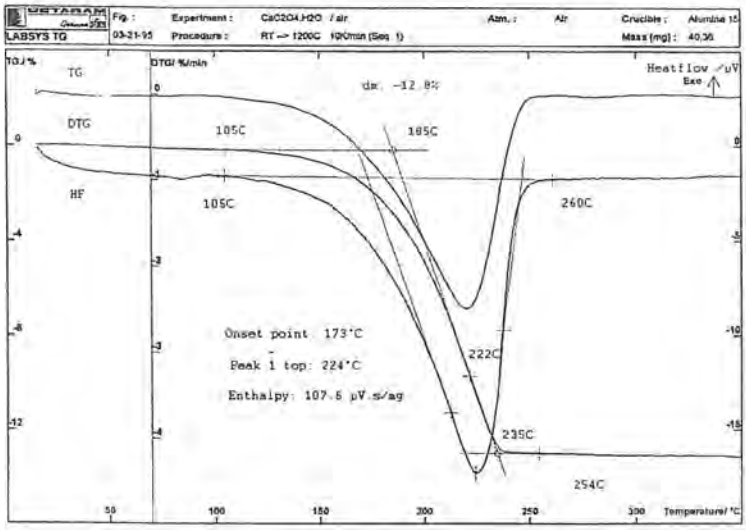


Figure 9: Dehydrating calcium oxalate

$\Delta m_1 = -12.8\%$

$T_A = 185\ °C$ $T_B = 235\ °C$ $T_C = 222\ °C$

$T_i = 105\ °C$ $T_f = 260\ °C$ $T_p = 224\ °C$

3.2.2.2.7. *Decomposing calcium oxalate in calcium carbonate*

See Figure 10

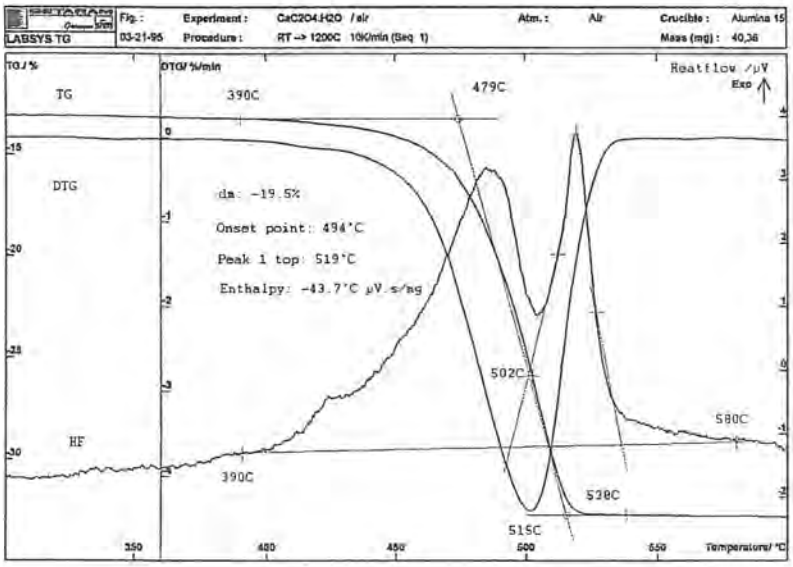


Figure 10: Decomposing calcium oxalate in calcium carbonate

$\Delta m_2 = -19.5\%$

$T_A = 479\ °C$ $T_B = 515\ °C$ $T_C = 502\ °C$

$T_i = 390\ °C$ $T_f = 580\ °C$ $T_p = 519\ °C$

3.2.2.2.8. Decomposing calcium carbonate in calcium oxide

See Figure 11

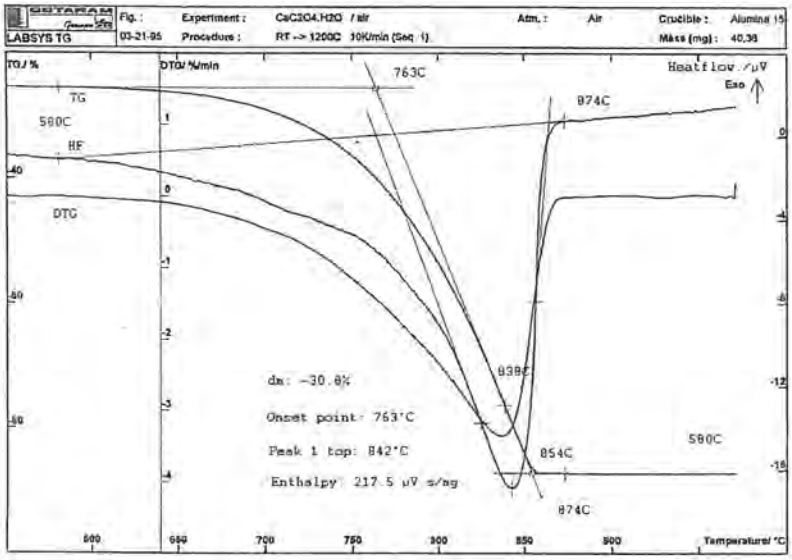


Figure 11: Decomposing calcium carbonate in calcium oxide

$\Delta m_3 = -30.8\%$

$T_A = 763\ °C$ $T_B = 854\ °C$ $T_C = 838\ °C$

$T_i = 580\ °C$ $T_f = 874\ °C$ $T_p = 842\ °C$

3.3. 1200°C DTA rod : Studying Tin-Lead alloys

3.3.1. Presentation

Tin-lead alloys have the special feature of forming a eutectic mixture titrating 62% of tin and 38% of lead. This eutectic melts around 180°C . As pure metals tin melts at 232°C and 327°C.

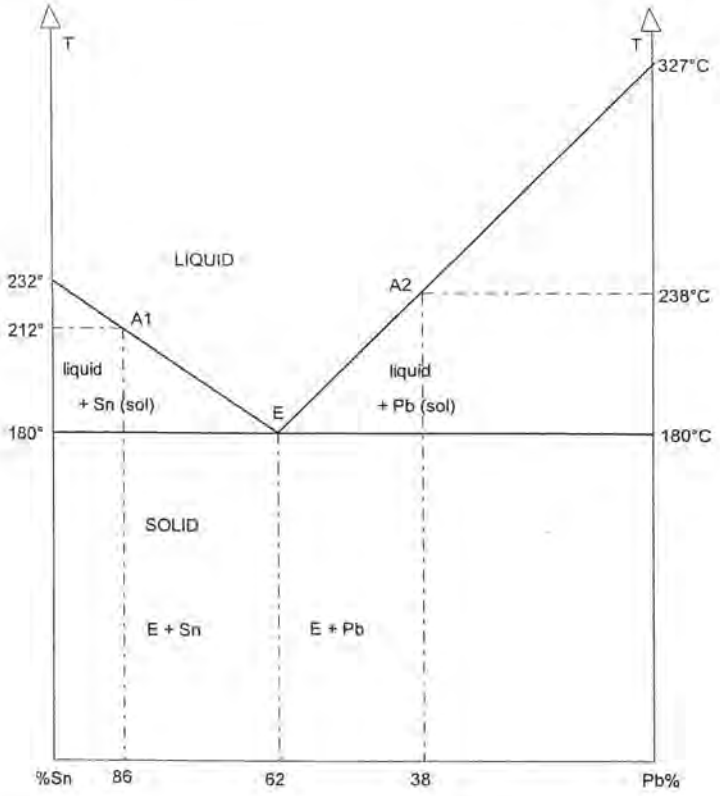


Figure 12 : Tin / Lead phase diagram

The experiments to be carried out consist of plotting the following DTA curves :

- Pure tin.
- Alloy before eutectic composition : 86% tin, 14% lead.
- Eutectic composition : 62% tin, 38% lead.
- Alloy after eutectic composition : 38% tin, 62% lead.
- Pure lead.

The curves produced must provide for distinguishing the specifying points on the phase diagram, i.e.:

- Melting point for tin, lead, eutectic.
- Start and end points for fusion of the alloys 86 Sn/14 Pb and 38 Sn/62 Pb.

Understanding the measurement of fusion in a pure substance requires recalling the measuring principle.

To explain the measurement let us take the example of fusion.

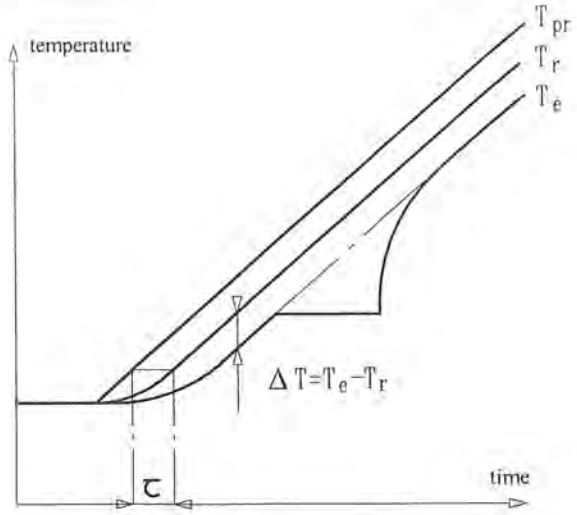


Figure 13 : Fusion curve

Various temperatures are to be considered :

- T_{pr} : furnace's scanned temperature.
- T_r : temperature of the reference crucible.
- T_e : sample's temperature.

During temperature scanning the sample's temperature lags behind the scanned temperature. When fusion of the sample takes place, as transformation does not vary, the sample's temperature stays constant throughout the transformation.

When the last crystal has melted this temperature tries to catch up with the other temperatures and to follow the same pattern.

If the difference in temperature T_e - T_r is represented a peak is produced which distinguishes the sample's fusion by the DTA.

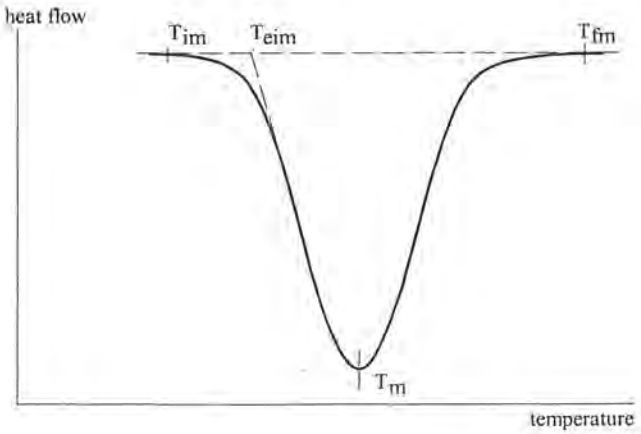


Figure 14 : Fusion peak by the DTA method

3.3.2. Experimenting

3.3.2.1. Samples and experimenting conditions

- Use alumina crucibles
- With pure metals weigh a single fragment of about 50 mg.
- With alloys prepare the mixture. Here initial fusion is needed so as to produce the final composition.
- Arrange the crucible containing the sample on the ***sample*** side of the transducer
- Put an identical crucible as a reference containing an equivalent mass of previously dehydrated alumina
- Close the furnace
- Prepare the scanning cycle so as to cause the sample's fusion

In practice enter the following experimenting conditions into the computer :

1. Scanning from 20°C to 150°C at 30°C/min
2. Isothermal sequence at 150°C for 5 min
3. Scanning at 5°C/min up to :
   - 250°C for pure Sn
   - 230°C for Sn 86 / Pb 14
   - 260°C for Sn 38 / Pb 62
   - 350°C for pure Pb
4. Cooling scanning down to 20°C at 20°C/min
5. Record the DTA signal for each sample

3.3.2.2. Interpreting the DTA curves

3.3.2.2.1. Pure tin

Re-plot the DTA curve between 150°C and 300°C by using the ***zoom*** function.

The curve may be plotted as a function of time or temperature The plot as a function of time provides for displaying the effect of fusion on the sample's temperature curve.

From the 150°C to 225°C , the base-line on the DTA curve is stable. When the first crystals of tin begin to melt the signal deviates from the endothermic side with a sharp angle. When all the crystals of tin have melted the DTA signal returns towards the initial base-line.

To measure the fusion temperature select on the screen the start and end of the peak via the ***Integration*** function. The tangent to the turning point on the rising DTA peak is plotted giving the melting point (***Onset*** temperature) where it intersects with the base-line.

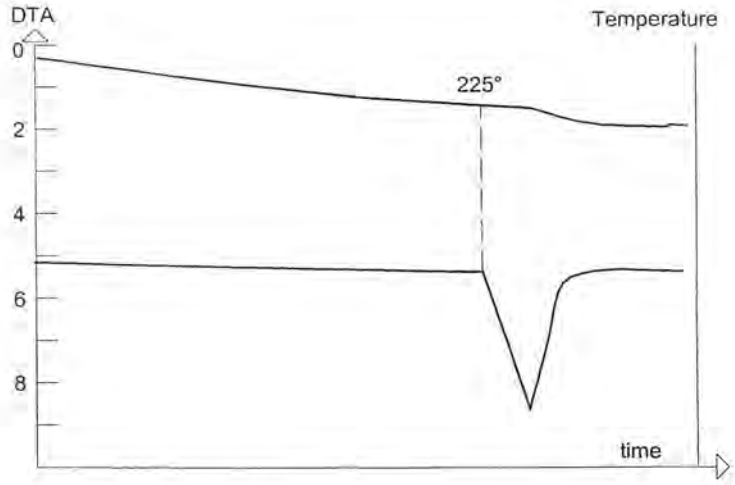


Figure 15 : Fusion of tin

3.3.2.2.2. Alloy of 86% tin

Re-plot the DTA curve between 150°C and 300°C.

Fusion of the eutectic mixture starts of 180°C, translating by a sharp angle. The eutectic mixture behaves like a pure substance but with a melting point lower by 50°C in relation to tin.

The end of fusion for the eutectic is translated by the top of the first peak, and the DTA signal then decreases. But the excess crystals of tin start dissolving in the eutectic liquid, and a new endothermic peak is observed. When there are no longer any crystals of solid tin, fusion is over and point A1 on the phase diagram is thus determined. This temperature (212°C) corresponds with the second maximum on the DTA curve.

Select the start and end of the peak. The ***Integration*** function produces the plot of the tangent at the turning point giving the first melting point. To produce th second temperature point the index on to the curve's second peak and read the temperature.

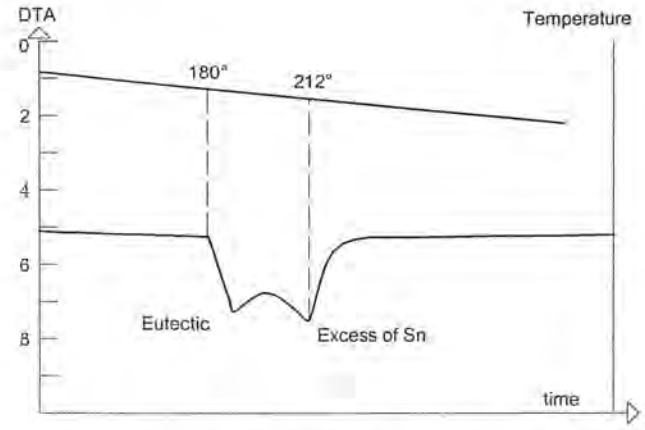


Figure 16 : Fusion of Sn 86%

3.3.2.2.3. Eutectic mixture of 62% tin

Re-plot the DTA curve between 150°C and 250°C.

The DTA curve produced is similar to the one for pure tin. It only shows a single endothermic peak, translating into the fact that this mixture behaves like a pure substance. Proceed as for tin so as to determine the eutectic's melting point.

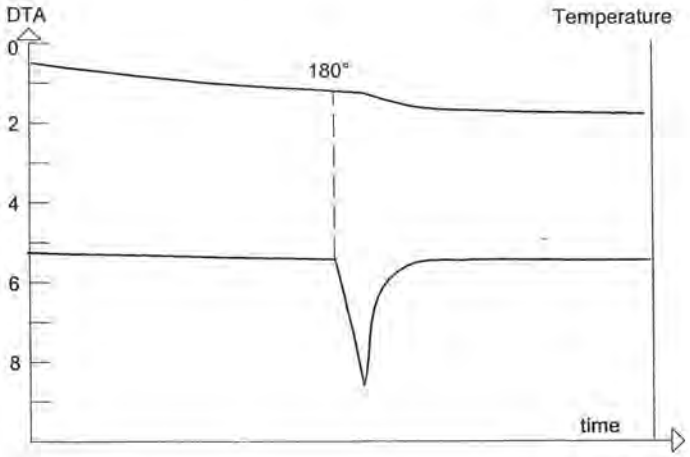


Figure 17 : Fusion of eutectic

3.3.2.2.4. Alloy of 38% tin

Re-plot the DTA curve between 150°C and 300°C.

Compared with the previous examples this alloy contains an excess of lead in the eutectic mixture. The start of fusion still begins at the same temperature of 180°C, corresponding with the eutectic's fusion. At the end of the eutectic's fusion there is a more pronounced return to the base-line than for the alloy of 86% Sn. A second, rather flattened peak is then recorded, corresponding with the fusion of the excess lead which has dissolved in the eutectic liquid. The temperature corresponding with the disappearance of the last crystals of lead is around 235°C; this is point A2 on the phase diagram, measured at the top of the second peak.

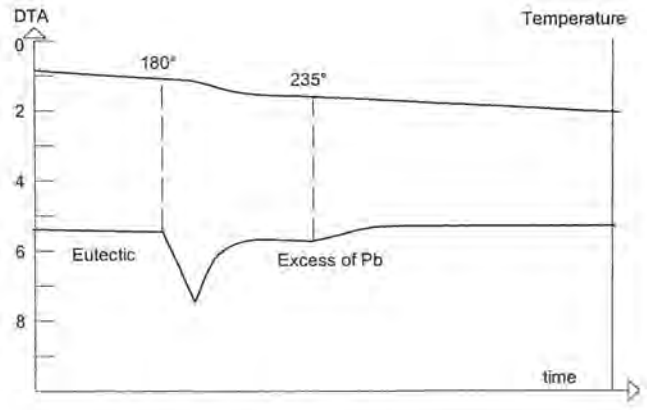


Figure 18 : Fusion of Sn 38%

3.4. 800°C DSC rod : Proportioning gypsum in cement.

3.4.1. Presentation

Gypsum is used for preparing plaster products. It is also found in small quantities in cement.The residual presence of gypsum causes the cement to set quicker. Based on what the cement is to be used for the amount of gypsum present must be known.

To distinguish the gypsum, which is dihydrated calcium sulphate $CaSO_4$, $2H_2O$, studying the dehydration provides qualitative and quantitative information. With pure gypsum heating such a substance leads to the following reactions:

- $CaSO_4$, $2H_2O \rightarrow CaSO_4$, $1/2\ H_2O + 3/2\ H_2O$, i.e. the formation of plaster (hemihydrate).

The plaster itself dehydrates and leads to the formation of anhydrite:

- $CaSO_4$, $1/2\ H_2O \rightarrow CaSO_4 + 1/2\ H_2O$

All that needs to be known is the dehydration heat of gypsum in plaster so as to be able to proportion the gypsum in types of industrial cement. Analyzing pure gypsum will provide the amounts of dehydration heat of gypsum in plaster, as well as plaster in anhydrite, and enable the quantity of gypsum in an industrial cement to be specified.

3.4.2. Experimenting

It is assumed that the DSC transducer has been calibrated for temperature and energy before starting the experiment (refer to the corresponding paragraphs in the chapter "Operations".

3.4.2.1. Samples and experimenting conditions

1. Use the aluminium crucibles with a cover
2. Weigh a sample of gypsum ($CaSO_4$, $2H_2O$) (about 25 mg)
3. Close the crucible with the cover using the press. Clamp the cover on to the sample.
4. This type of closure ensures that there is a certain amount of water vapour pressure above the gypsum during heating, so as to keep the two dehydrations quite distinct.
5. Arrange the crucible on the " Measurement " side of the transducer. An empty, closed, aluminium crucible is used as reference.
6. Close the furnace.
7. Prepare the following scanning cycle :
   - Isothermal sequence at 20°C for 5min.
   - Scanning from 20°C at 250°C at 5°C/mn.
   - Cooling scanning from 250°C to 20°C at 20°C/mn.

8. Repeat the same test with one (or several) cement sample(s) with a greater mass (about 50 mg).

3.4.2.2. Interpreting the DSC curves

Re-plot the curves produced with gypsum and cement as a function of temperature, making the optimum choice of the axes (use the zoom ***function***).

3.4.2.2.1. Gypsum

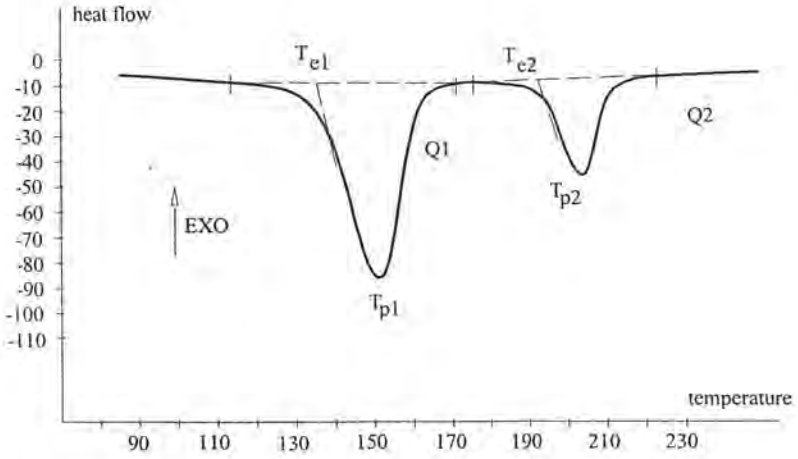


Figure 19 : Analyzing gypsum

Analyzing gypsum reveals two, quite distinct endothermic effects, corresponding with :

1. The dehydration of gypsum into plaster between 120°C and 170°C.
2. The dehydration of the plaster formed into anhydrite between 180°C and 225°C.

Let us make use of each of these peaks:

⇒ Dehydration gypsum→plaster

Select the start and end of the first peak with the ***Integration*** software. Carry out integration, which provides various results :

- The ***onset*** temperature Te_1 corresponding with the base-line's intersection with the tangent at the dehydration peak's turning point.
- The temperature Tp_1 at the top of the dehydration peak.
- The gypsum's dehydration heat Q_1..

The example supplied gives the following values :

(The example supplied corresponds with a type of clinker containing 5% gypsum).

⇒ Dehydration gypsum →plaster

Refer to *3.4.2.2.1* and proceed in the same way.

Let the following terms be :

$T'e_1$ et $T'p_1$ the corrected temperatures corresponding with the onset and the top of the peak

Q'_1 , the heat in J/g corresponding with the first dehydration peak

In the example supplied :

$T'e_1$ = 142,5°C $T'p_1$ = 150,2°C Q'_1 = 21,8 J/g

Remark Notice that the temperatures $T'e_1$ and $T'p_1$ are close to the temperatures Te_1 and Tp_1 measured with pure gypsum.

⇒ Dehydration plaster→anhydrite

Refer to *3.4.2.2.1* and proceed in the same way.

Let the following terms be :

- $T'e_2$ and $T'p_2$ the corrected temperatures corresponding with the onset and the top of the peak.
- Q'_2 , the heat in J/g corresponding with the second dehydration peak.

In the example supplied:

$T'e_2$ = 172,4°C $T'p_2$ = 185,9°C Q'_2 = 5,8 J/g

3.4.2.2.3. Determining the gypsum content in cement

Let the following terms be :

The gypsum content G in the cement sample is given by :

$$G = \frac{Q'_1 \, x100}{Q_1}$$

$Te_1 = 137,6\ °C$ $Tp_1 = 151,6\ °C$ $Q_1 = 430,9\ J/g$

⇒ Dehydration plaster → anhydrite

Select the start and end of the second peak with the ***Integration*** peak.

Carry out integration, which provides the following results :

- The ***onset*** temperature Te_2 of the plaster's dehydration peak.
- The temperature Tp_2 at the top of this peak.
- The plaster's dehydration heat Q_2 .

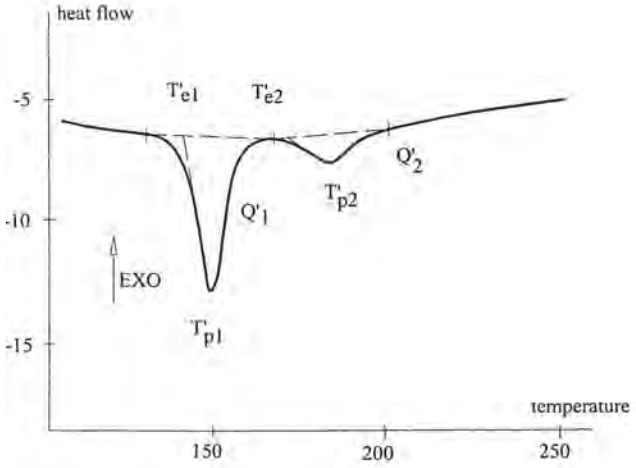
The example supplied gives the following values :

$Te_2 = 193,2°C$ $Tp_2 = 203,4\ °C$ $Q_2 = 146,9\ J/g$

Check that the ratio of the heat contents Q_1/Q_2 is close to 3 (in our example : 2,93)

i.e. equivalent to the ratio of the number of molecules of water lost at each dehydration (3/2 H_2O, then 1/2 H_2O).

3.4.2.2.2. Cement



Analyzing cement (see figure below) up to 250°C again reveals two distinct, endothermic effects corresponding with:

- Dehydration of the residual gypsum in plaster between 120°C and 170°C
- Dehydration of the plaster returned into anhydride, but possibly also the dehydration of the plaster present in the original cement sample.

Let us make use of each of these peaks.

which is, for the example supplied : G = 5.1 % , i.e. the proportion stated in the sample analyzed.

4. Coupling of a mass spectrometer

Selecting the rods and crucibles is refered to in *Chapter 1 - 3 - Examples of practical work.*

4.1. Parameters for the proper coupling

4.1.1. Choosing the carrier gas

The nature of the gas must be carefully chosen as samples can sometimes also contain various types of gas.

Remark A similar atomic mass unit may occur between the carrier gas and the gas produced by the sample, as for instance : N2 = CO = 28.

4.1.2. Adjusting the carrier gas rate

Very low rate: almost the whole amount of gas goes into the spectrometer and a small amount comes out of the thermoanalyzer (to be checked with a bubble meter) so as to avoid heating under partial vacuum, as the conditions of analysis may be modified.

This allows :

- an optimum research of the trace,
- an extension of the signal trail of the spectrometer (time between the end of the reaction (mass loss) and the return to the base line of the corresponding atomic mass unit).

High rate :

- allows an optimum decrease in the time of trail,
- dilutes the gases produced by the sample.

4.1.3. Sample mass

A small mass:

- allows an optimum time of trail,
- decreases the reaction time with gas (work with thin film),
- decreases the quantity of gas to be detected.

A large mass:

- increases the time of trail,
- increases the quantity of gas to be detected,
- may saturate the spectrometer.

4.1.4. Cold zone of the thermoanalyzer

The bottom of the furnace is not thermostated. Therefore, condensation may occur in there and not in the capillary. Recording via the vacuum jauge PKR (refer to the spectrometer booklet) lets us know if the decrease in atomic mass units occurs as supposed to or comes from obturated capillary due to condensation.

In the case of non condensable gas analysis at low temperature (lower than 200°C) the capillary may be introduced higher in the furnace.

4.2. Running an experiment

4.2.1. Using the spectrometer

Refer to the booklet supplied with the spectrometer;

4.2.2. Using the Setsoft software package

Please refer to the ***Setsoft*** base software booklet and the ***Coupling of a mass spectrometer*** booklet both supplied with the instrument.

CHAPTER 2 - MAINTENANCE

1. Introduction

The ***Maintenance*** chapter provides various items of information relating to the incidents which may occur to the instrument, the checks to be carried out, various remedies for the breakdowns, the list of error messages relating to the controller...

It is difficult to provide for all the incidents associated with the instrument's operation, especially those resulting from not complying with the instructions and information contained in this booklet.

2. Operating incidents

2.1. No warning light when running

When the instrument is switched on the running warning light on the instrument's front panel should come on.

If the warning light stays off:

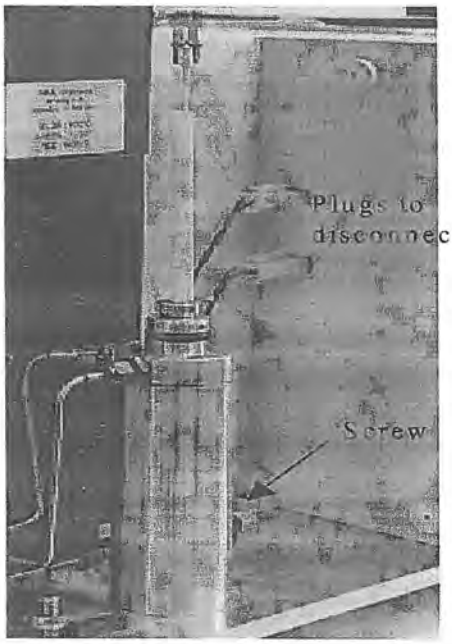
- Check that the mains cable is plugged.
- Check that the circuit breaker on the instrument's rear panel, is set at ***ON***.

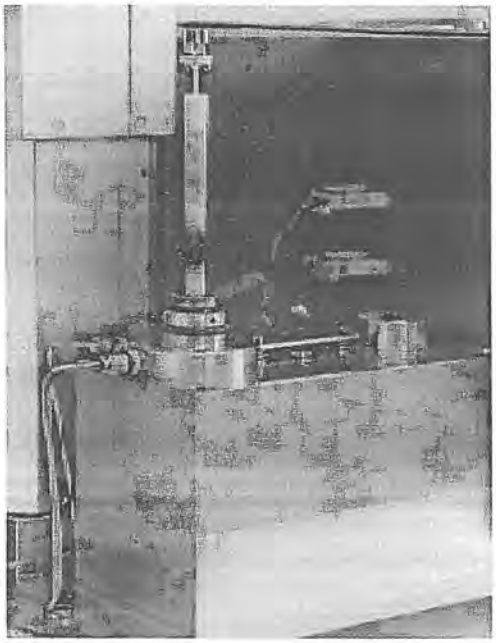
2.2. Opening of the instrument

The covering cap might be taken off the instrument for some interventions like changing or cleaning gas tubes or checking inner connections.

 Before any intervention, it is **IMPERATIVE** to stop the instrument and to disconnect the sector plug (principal power feeding).

- Lift the furnace up.
- Remove the front cover.
- Disconnect the 2 plugs on the right side of the sensor.
- Unscrew the screws which maintain the cover to the instrument's sides.
- And the screw on the right side of the sensor or behind the balance.





Plugs to disconnect

- Remove the cover in lifting it up vertically.

2.3. Locked lifting column

The lifting column is fitted with a thermal safety feature so as to prevent the fitting from overheating during repeated and closely timed operation.

When the column is worked too much the thermal safety fitting cuts in and blocks the column.

Wait for about ten minutes before being able to use the column again, which is the time required for the thermal safety fitting's bimetallic strip to cool down.

2.4. Interruption in gas circulation

If gas circulation is not done in the usual way (checked by measuring the gas flow at the outlet on the analysis chamber):

The pipe allowing the evacuation of the sweeping gas as well gas released from the experimental chamber may be closed because of the condensation of those gas (tar) in the coolest places.

To reach the gas pipework:

- Open the instrument (refer to the paragraph *2.2*).
- Dismount and clean the sweeping gas pipe with, for instance, a compressed jet air (it is also possible to put it in a solvant during several hours if it is an organic pollution. Dry carefully the sweeping gas pipe before putting it).
- Check that the pipework, at the entrance of the gas, in the rear face of the instrument, is not closed. For that, use a compressed jet air. Before, be sure to have removed the sweeping gas pipe.
- Dry it carefully before putting it.

If the phenomena is frequent:

- Increase the output sweeping gas in order to displace the condensation areea.
- Decrease the sample's size in order to limit the condensable gas volume.

2.5. Faulty temperature indication

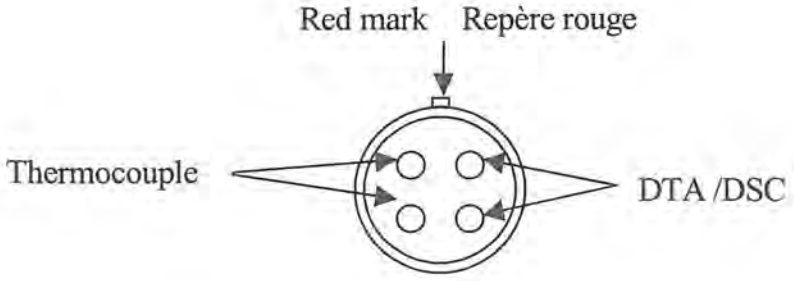
The furnace's temperature is provided by the temperature-control thermocouple fitted on the TG, DTA or DSC rod.

In case of broken thermocouple or measure chain, the indication temperature is 1740°C.

Two following messages will thus appear:

F1 temp. sensor failure
F1 above security temp.

- Dismount the sensor and check that the regulation thermocouple is not cut.
- For this, check the thermocouple continuity thanks to the ohmmeter betwwen the thermocouple connections in the sensor connector (see the figure hereafter).



Vue de dessous Bottom view

- A very low ohmic value must be found.
- If the thermocouple is broken, it is neccessary to change the sensor.

2.6. Faulty indication on the DTA or DSC signal

If the DTA or DSC signal permanently displays a saturation value equal to 2000 microvolts :

- Check the circuit ATD or DSC as described in the previous paragraph.
- If the thermocouples on the DTA or DSC rod have been cut off, the rod needs to be changed.

If during the experiment, crackling or excessive background noise appears on the plot of the DTA or DSC signal, the following checks can be carried out:

- Check around the DTA or DSC transducer that no connecting wires are touching each other or likely to touch each other during heating, if they have in some way been deformed.
- If this is the case straighten out the wires, taking care not to break them.
- Conduct a test in the same experimental conditions with two empty crucibles (new, if possible)
- If the crackling disappears this could be due to pollution of the crucible or a chemical attack on the crucible by the sample. In this case change the crucible and find a crucible with suitable properties for studying sample.
- Carry out a blank test (empty vessels) with a new rod so as to determine if the previous rod was defective.

2.7. Failure in furnace heating

If the furnace no longer heats up there may be various reasons for the breakdown and the following checks are offered in the search for a remedy :

1. If there is an error message on the screen (external safety, safety temperature exceeded,...) correct the error (no water circulating, raised column, thermocouple cut off, in correct parameter entered,...) and re-start the test.

2. Check on an ohmmeter that there is electrical continuity in the resistor by proceeding as follows.

- Raise the furnace to the top
- Switch off at the main circuit-breaker
- Take off the top cover at the four bolts fitted under the cover
- Disconnect one of the current feeds (black wire) on the block connector
- The ohmmeter should provide a reading for the resistance of around 1 ohm.

If the resistor has been cut off the furnace needs to be replaced. To do this proceed as follows:

- Stop the water circulation and disconnect the tubes after purging them.
- Remove the thermal safety fitting.
- Disconnect the two current feeds.
- Loosen the two bolts supporting the furnace.
- Remove the furnace.

Carry out the operations in reverse when fitting the new furnace.

WARNING Check and adjust the alignment one more time with the DTA/DSC support or the balance nose.

3. Error messages

Correct operation of the instrument via the controller is shown by the code ***System OK*** being displayed on the calculator's screen, especially on the ***Direct scanning*** screen.

Should the controller or the instrument malfunction, an error message displays on the screen to indicate the origin of the breakdown. These error messages are spread over various categories which are described in the following paragraphs.

3.1. "Controller system" error

ERROR MESSAGE
SYS UNDEFINED TRAP CALL
SYS Bus error
SYS Adress error
SYS Illegal instruction
SYS Divide by zero
SYS CHK instruction
SYS TRAPV instruction
SYS Privilege violation
SYS Trace vector
SYS OPCODE 1010 emulation
SYS OPCODE 1111 emulation
SYS FPCP Protocol violation
SYS FPCP format error
SYS Uninitialised int.
SYS Spurious interrupt
SYS FPCP Unordered condition
SYS FPCP inexact result
SYS FPCP divide by zero
SYS FPCP underflow
SYS FPCP Operand error
SYS FPCP overflow
SYS FPCP signaling NAN

If one of these error messages appears switch off the controller, then re-apply a voltage to it.

WARNING If the error message re-appears, SETARAM or its representative in the country needs to be contacted.

3.2. "Real-time clock" error

ERROR MESSAGE
Real-time treatment failure
Real-time watchdog detection

If one of these errors appears switch off the controller, then switch it on again, waiting a few seconds between the two actions.

WARNING If the error persits, the breakdown probably comes from the real-time clock circuit. Contact SETARAM or the nearest representative.

3.3. "Memory saving" error

ERROR MESSAGE
Parameters not memorized

This problem arises when the CS32 controller does not have a voltage applied for too long a period. All the "user" parameters are then re-set.

Re-initial the parameters with the software and leave a voltage applied to the controller for a few hours so that the batteries can be recharged.

3.4. "Port A" error

ERROR MESSAGE
Overrun error on port A
Parity error on port A
Framing error on port A
Receive break on port A
Time-out on transmiter A
Time-out on receiver A
Undefined reading variable on A
Undefined writing variable on A

One of these errors may appear during communication with the computer. Check that the communication flex between the computer and the controller is properly connected.

These error messages can also be seen when the computer is switched on after the controller or switched off when there is still a voltage applied to the controller. In these cases the error may be ignored by the user.

3.5. "Port B" error

ERROR MESSAGE
Overrun error on port B
Parity error on port B
Framing error on port B
Receive break on port B
Time-out on transmiter B
Time-out on receiver B
Undefined reading variable onB
Undefined writing variable on B
Undefined command

One of these errors may appear during communication with the computer. Check that the communication flex between the computer and the controller is properly connected.

This error message can also be seen when the computer is switched on after the controller or switched off when there is still a voltage applied to the controller. In this case the error may be ignored by the user.

3.6. "Temperature transducer" error

ERROR MESSAGE
F1 temp. sensor failure

These error messages correspond with a failure of the temperature transducer If the temperature transducer has been cut off replace it (change the rod).

3.7. "Signal saturation "error

ERROR MESSAGE
Heatflow 1 saturation

If there is saturation of the signal check the connection between the transducer and the controller.

3.8. "Safety temperature" error

ERROR MESSAGE
F1 above security temp.

These errors correspond with exceeding the safety temperature. Check the safety temperature initialisation and the latter's compatibility with the temperature programme Take into account that the set-point may be exceeded. Should there be poor temperature control the PID actions may also need to be checked..

3.9. "Fixed temperature" error

ERROR MESSAGE
Temp. set above sensor max.
Security set above sensor max.

These errors may appear at the start of an experiment. Check that the temperature programme (79) or the safety temperature does not contain a temperature value greater than one sustained by the temperature transducer.

3.10. "External safety" error

ERROR MESSAGE
Check external security

This message appears when the external safety fitting cuts in. If the external safety fitting is a water one top up or increase the water-circulation flow-rate. Check the connection between the controller's power control and the power module.

3.11. "Buffer saturation" error

ERROR MESSAGE
Acquisition buffer saturation.

If this message appears switch off the programmes within the windows environment operating with the SETARAM software.One of these is monopolising the Windows resources for too long. This involves losing data from the experiment taking place.

3.12. "Configuration"error

ERROR MESSAGE
Invalid or unknown apparatus

This message may appear following a fault in memory saving.

4. Cleaning

Avoid acid or other corrosive liquid splashing on to the bodywork.

 Before cleaning the instrument up, disconnect it from the electric network.

The instrument shall be cleaned up with water and soap.

 Under no circumstances, humidity must penetrate in the instrument.

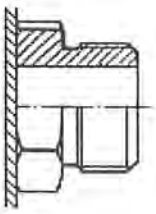
WARNING DO NOT USE computer cleansers (such as cleansing foams) as they can damage the painting of the cover.

5. Gas connections on the rear panel

Note This section refers to *Chapter 1 - 3.1 - Sweeping gas circuit* in the ***Commissioning/Utilisations*** booklet.

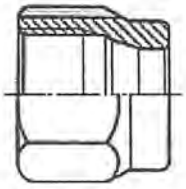
5.1. The SERTO parts

Basic component

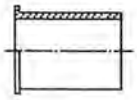


Compression ferrule

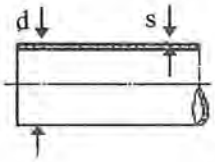
Connection nut



Stiffener sleeve

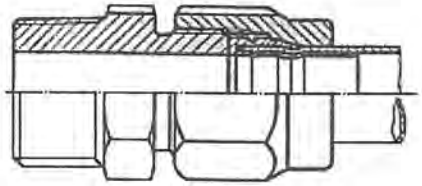


Polyurethane tube (PU 4x0,75)

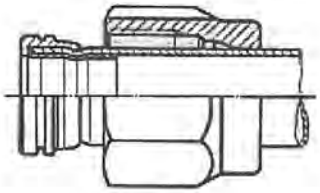


5.2. The union

Union installed

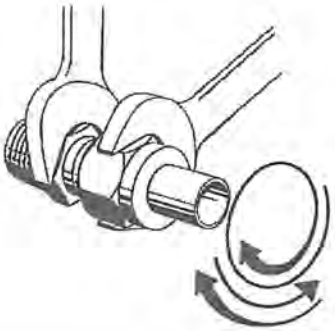


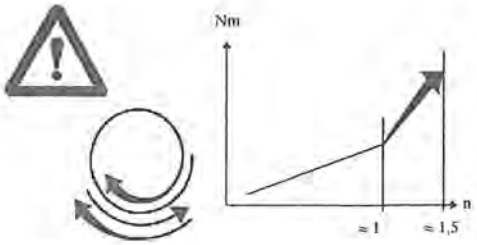
Union after dismantling



5.3. Mounting instructions

1. Cut the tube and place the stiffener sleeve.
2. Mount the compression ferrule and the nut on to the union.
3. Insert the tube as far as the stop.
4. Tighten the nut with a spanner until an increased resistance is felt.
5. Slacken off the nut slightly in order to relieve possible stresses.
6. Only now should the union be finally tightened against positive resistance.





6. Spare parts and consumables

6.1. TG Consumables

Désignation	Référence
2 incorporated crucible-holding rods	60/38297
5 alumina crucibles 400-microlitre	08/GG36492
2 platinum crucibles500-microlitre	08/GG36513

6.2. DTA Consumables

Désignation	Référence
1 DTA rod 1200°C (platinel)	60/37512
1 DTA rod 1600°C (PtRh 10%/Pt)	60/37513
10 Platinum crucible 100 µl for DTA	08/11299
10 Platinum cover	68/GG28206
10 Platinum crucible 20 µl for DTA	08/11298
10 Platinum cover	68/12342
20 Alumina crucible 100µl for DTA	08/11297
20 Alumina crucible 20µl for DTA	08/11296
40 Alumina cover	08/GG28204
4 Zircone crusible 100 µl for DTA	08/GG29892
4 Zircone cover	08/GG29893
100 Aluminium crucible 170 µl For DTA- 500°C maxi	08/GG33117
100 Aluminium cover	08/GG33118

6.3. Canne DSC

Désignation	Référence
1 DSC rod 800°C	60/37514
1 DSC rod 1200°C	60/37515
1 DSC rod 1600°C	60/37516
20 Alumina crucibles100 µl	08/GR29467
4 Platinium crucibles 100 microlitres	08/GR30092

10 Platinium cover	68/GR38397
100 Aluminium crucible 75µl - 500°C maxi	08/GAF37875
100 Aluminium cover	08/GAF37876

6.4. Spare parts

Description	Reference
2 alumina gas sweeping tube	60/38713
1 furnace	60/36130
1 low temperature calibration set	60/50194
1 high temperature calibration set	60/50195
1 electrovalve	03/50196
1 Crimping tool kit	08/GAF37776
5 R15 seals	04/38287
Polyethylene PE tube	04/50007
Panel mount union	04/37519
Flow adjusting valve	04/50114

SETARAM : excellence in thermal analysis

LABSYS™ : low cost series of multi-module thermal analyzers

- DSC131 : -150 to 700°C (heat flux sensor)
- DTA, TG/DTA : ambient to 1600°C
- DSC, TG/DSC : ambient to 1600°C
- TMA : ambient to 1000°C

SETSYS : top of range in thermal analyzers

- DSC141 : -150 to 600°C (power compensation)
- DTA, TG/DTA : -150 to 2400°C
- DSC, TG/DSC : -150 to 1600°C
- TMA, DLTMA : -150 to 2400°C

micro DSC : high sensitivity DSC and calorimetry

- micro DSCIII : -20 to 120°C ("batch and flow")
- micro DSCVII : -45 to 120°C ("batch")

CALVET PRINCIPLE DSC

- DSC 121 : -120 to 830°C
- DSC Robotic Sytem : -120 to 830°C

CALVET CALORIMETERS

- BT 2.15 : low temperature calorimeter from -196 to 200°C
- MS 80 : standard calorimeter from ambient to 200°C
- HT 1000 : high temperature calorimeter from ambient to 1000°C
- C 80 : mixing and reaction calorimeter from ambient to 300°C
- Titrys : titration calorimeter from ambient to 75°C
- calorimeters based on your analysis needs

96 LINE : high temperature and large volume thermal analyzers

- MULTI-HTC 96 : DSC and calorimetry
  calorimetric detectors up to 1500°C
  DSC detectors up to 1600°C
- TG 96 : thermogravimetry
  ambient to 1750°C
- DHT 96 : dilatometry
  1750°C and 2100°C versions

SYMMETRICAL THERMOGRAVIMETRY LINE

- TAG 24 : a line of symmetrical thermoanalyzers
  -150 to 2400°C
- TG-DSC 111 : the unique TG-DSC coupling
  -120 to 830°

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3

G/WINSOFTA

SETSOFT

INSTALLATION - ACQUISITION- PROCESSING - MANAGEMENT

SETARAM

GROUPE KEP INSTRUMENTATION • REGULATION

TABLE OF CONTENTS

1. REVISIONS TABLE

G	07/05/99		G/WINSOFTA	A. FOUILLAT	K. DAVAT	JL. DAUDON
REV	DATE	REV. PURPOSE	BOOKLET REF	REQUIRED BY	DONE BY	APPROVED BY

CHAPTER 1 - INSTALLATION AND MAPPING

1. Installation

1. 1. Preparation

1. 1. 1. Verification of hardware and software mapping

The software requires at least:

- A compatible IBM computer with a 80486DX2 / 66 processor or a higher performance.
- A hard disk with at least 20 Mo available.
- A 3½ 1.44 Mo floppy disk drive.
- A VGA or compatible screen.
- A minimum of 8 Mo of random access memory.
- MS-DOS™ 6.20 and Microsoft Windows™ 3.1 or a latest version.

1. 1. 2. Back up copies

Before the program is installed, back up copies of the SETARAM software package must be made with one of the following commands :

- ***Disk / Copy Disk*** in the Microsoft Windows™ manager file.
- The MS-DOS™ ***DiskCopy***.

1. 2. Installing the software package

Before using the software, three steps are to be followed:

1. Install the base software,
2. Install the software components previously bought,
3. Connect the instrument to the computer.

1. 2. 1. The base software

Installing the software first of all requires installing the base software (« Base software » floppy disk). Refer to paragraph 1.3 for the installation procedure (***Installing the base software***).

Although the base software is installed, acquisitions cannot be run. Only experiments given as examples can be treated.

Remark The installation programme verifies that a version of the software is not already installed on the station. If it is, the second installation performs the updating of the version originally installed if it is earlier than the version presently supplied.

1. 2. 2. Installing a software component

Three types of software components are to be distinguished:

- components for device
- collection software
- processing software

Each software component is supplied separately on a floppy disk, provided in addition to the base version.

Refer to Chapter 4, paragraph 11 (***Installing new software collection, treatments or apparatus***) for the installation procedure.

Remark Standard acquisition and treatment softwares are supplied with the base version and thus do not need to be installed.

1. 2. 3. Connecting an instrument to the computer

Once the base software and the software components are installed, the acquisition still cannot be run. Indeed, the instrument must be connected to the computer. Refer to Chapter 1, paragraph 3 (***Hardware Mapping***) for the connections.

1. 3. Installing the base software

1. 3. 1. Running the programme

1. Insert the #1 floppy disk (« Base Software ») into the floppy disk drive.
2. Select ***File / Run*** in the program or file manager.
3. Enter ***A:\SETUP.***
4. Follow the instructions appearing on the screen.

1. 3. 2. Installing

- **Choosing a destination directory**

  If the installation programme finds that an earlier version has already been installed, the version will be updated. Otherwise, the destination path is asked.

WARNING If no version is installed, installing the new version may take some time (a few minutes). Do not stop the installation procedure otherwise you may loose the experiments previously performed.

Figure 1: Destination directory

- **Copying files on the hard disk**

If the destination directory is correct start copying the files.

Figure 2 : Copying files on the hard disk...

When the first floppy disk is copied, the remaining disks are to be inserted one after the other.

Figure 3 : Insert the next disk !

- **Ending the installation**

The floppy disks are properly installed in the destination directory.

Figure 4 : The installation is complete

Click on ***OK*** to quit the installation programme. Re-start the computer so as to take all the modifications into account.

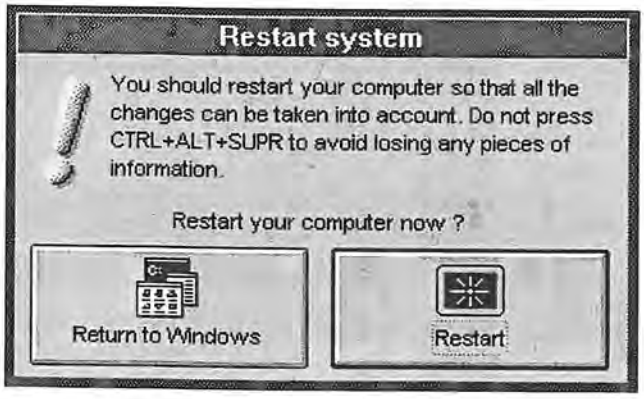


Figure 5 : Re-start the computer

WARNING If you select the ***Return to Windows*** button and try to run one of the SETARAM's softwares, it may not run properly.

WARNING Make sure no disk is in the drive.

1. 3. 3. Installation problems

Messages may appear on the screen if a hardware or software incompatibility is detected by the programme. If it is the case, please follow the instructions:

1. Click on ***OK*** to quit the installation program.
2. Solve the problem (follow the instructions displayed on the screen).
3. Re-run the program.

- **Files already used**

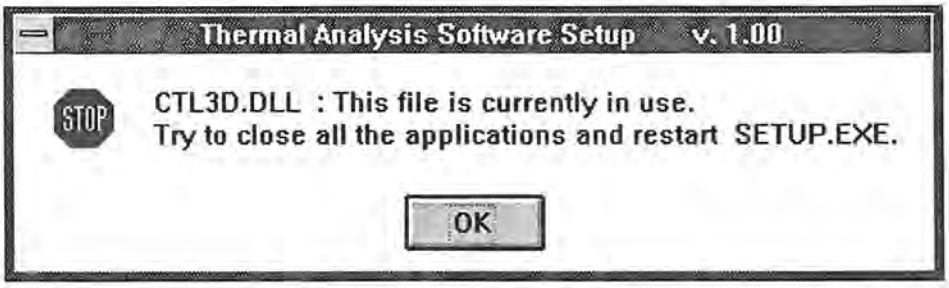


Figure 6 : File in use

One (or more) file(s) necessary for the installation is (are) already used. Try to close all the applications and restart SETUP.EXE.

Note If the SETARAM software package is already installed, check that the collection or processing database tools are not running.

- **Temporary directory already exists**

This may happen if the name of the directory you have created and the name of the temporary directory are the same. Click on ***Non***, name your directory differently and restart the installation.

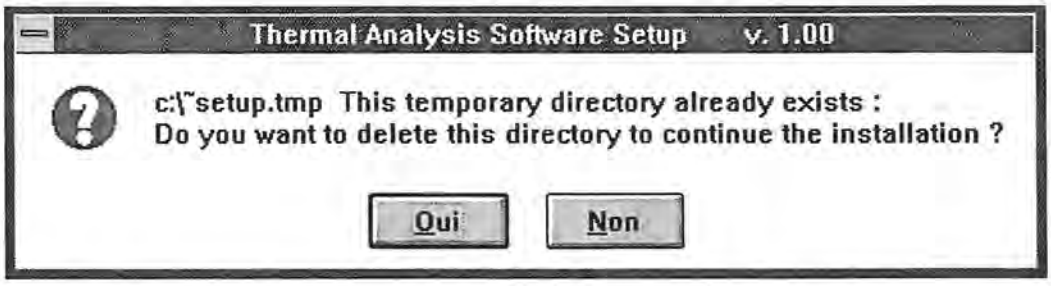


Figure 7 : Temporary directory

If the problem occurs in a former installation : click on ***Oui*** in order to continue the installation.

- **Installing an old version**

This can happen if you install a version of the SETARAM's software package which is earlier than the one installed on the system.

Figure 8 : An earlier version is already installed

- **Incomplete installation**

Figure 9: Incomplete installation

The above mentioned message appears on the screen after an error is made.

Try to rerun the installation but if the problem still exists, please contact **SETARAM**.

2. Running

2. 1. Acquisition software

Select the ***SETARAM*** file in the ***Program manager*** and double click on the ***Collection*** icon in order to run the acquisition software package.

Figure 10 : Running the acquisition icon

2. 2. Processing software

Go to the ***SETARAM*** file in the ***Program manager*** and double click on the ***Processing*** icon.

Figure 11 : Processing icon

2. 3. Database tools software

Go to the ***SETARAM*** group in the ***Program Manager*** and double click on the ***Database tools*** icon.

Figure 12 : Database Tools icon

3. Hardware Mapping

3. 1. Measurement device

A device can be used via a software only if it is connected to a communication port. Go to the ***Experiment / Setup / Device*** menu of the acquisition software package.

Then, a connection window opens and devices can be added or deleted (see Figure 13).

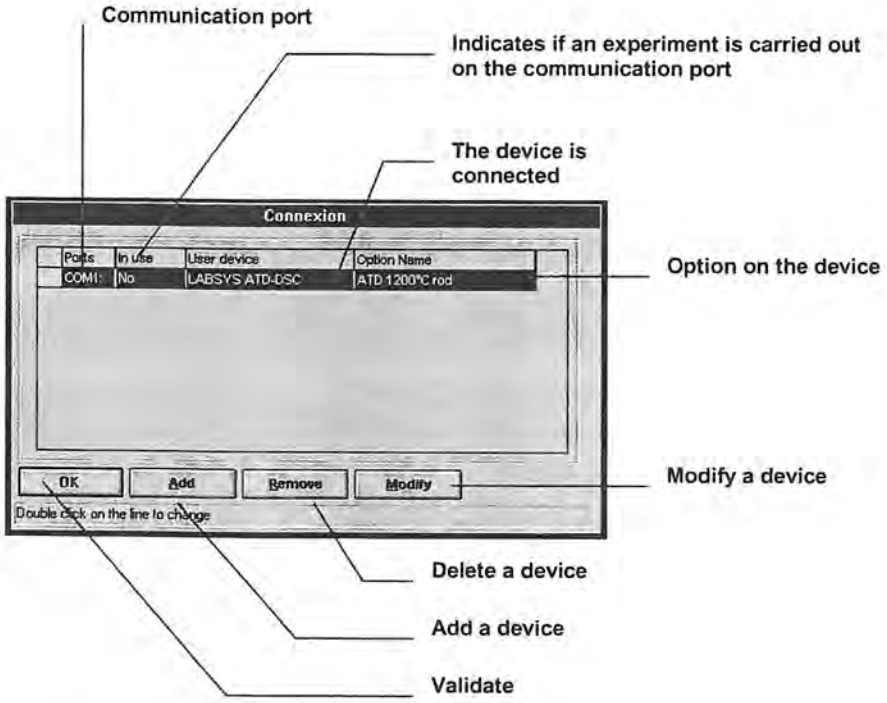


Figure 13: Add / delete devices

Click on ***Add*** for an additional device. A window opens and the device can be connected. (see Figure 15: The device is connected).

Remark If an experiment is performed on a connected device, the characteristics cannot be modified and the experiment cannot be stopped. ***Remove*** and ***Modify*** are unactivated.

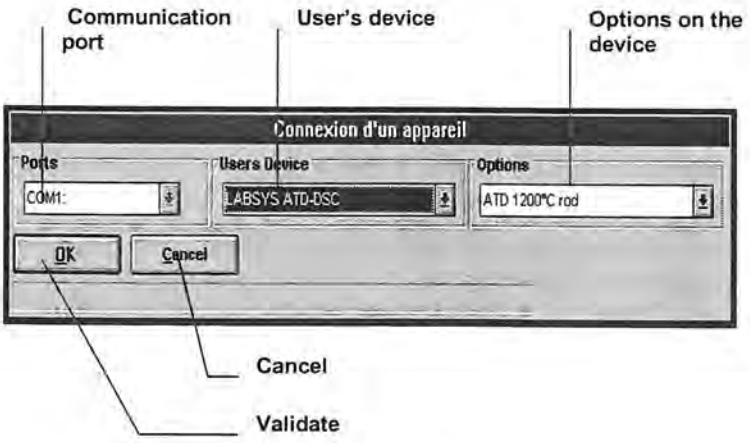


Figure 14: Connection of a device

Remark **Non connected** devices only are on the ***Users Devices*** pulldown list.

Once the connection is validated, the device is listed among the others connected devices and can be used by the thermal analysis software package.

Ports	In use	User device
COM1:	No	LABSYS ATD-DSC

Figure 15: The device is connected

Remark Re-select the device any time the option is physically changed in the instrument.

Remark Switch on the instrument before the correction.

Remark Some instruments may show a window where a set of coefficients specific to the instrument. The value for the coefficients are given by **SETARAM**.

4. General data

4. 1. Introduction

Data such as:

- User's names.
- Family of experiment.
- Sensors.
- Crucibles.

- Cells.
- Atmospheres.
- Etc...

can be entered via the ***Data*** menu of the acquisition program. Data can be helpful for the entering operation and can be used as a sort criterium in the experiment window catalog.

4. 2. Modifying

Values in the ***Atmospheres*** table can be modified for example: Select the ***Data / Atmospheres*** menu.

Figure 16 shows the various zones of the updating table.

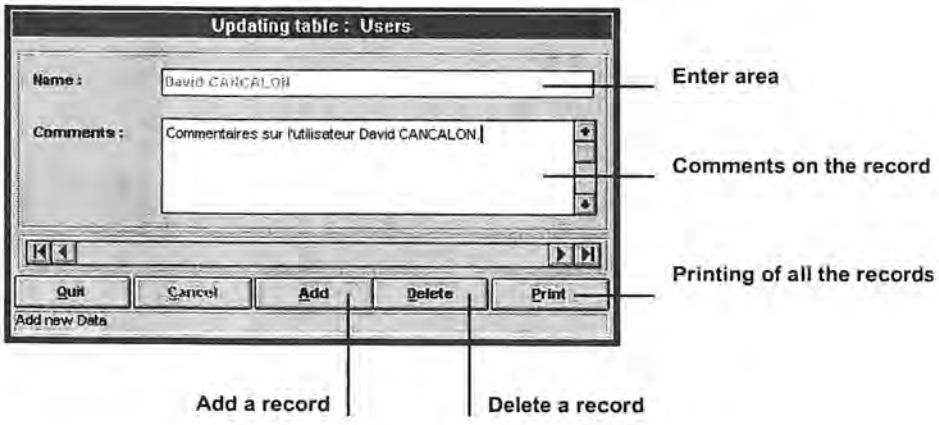


Figure 16: Updating data

5. Saving experiments

5. 1. Aim

The procedure mentioned below is used to save experiments that are stored in a computer aims at:

- Allowing the user to change his PC and keeping the experiments carried out previously.
- Keeping the experiments if the computer is out of order (by regular saving procedures).

However, it is not possible to save an experiment separately but only all of them.

5. 2. Principle

Two procedures are to be performed :

- A saving procedure for the experiments (on a floppy disk or on a network).
- A restoring procedure for the data.

WARNING These procedures must be carried out by someone who knows how to use the file manager, otherwise a wrong procedure can result in loosing all the experiments.

---

5. 3. Saving experiments

While installing, the user must enter the name of the directory where the softare will be installed. It is automatically the ***setaram.win*** directory.

The installation directory is composed of various sub-directories (such as access, courbes, exe, local, rapports).

It is compulsory to save:

- The entire content of the curve directory.
- The following files from the access directory: deplace.mdb, det_cp.mdb, dltma.mdb, dtg.mdb, etaljoul.mdb, set_util.mdb, standard.mdb et utilisat.mdb.

5. 4. Restoring experiments

To restore data, the software must first be installed on the PC where the experiments will be re-installed (follow the normal procedure used to install the base software).

WARNING The software version must be identical to the one installed on the PC where the saving procedure will be performed.

Then, delete the content of the curve directory and replace it by the files saved in this directory.

In the meantime, delete the following files: deplace.mdb, det_cp.mdb, dltma.mdb, dtg.mdb, etaljoul.mdb, set_util.mdb, standard.mdb and utilisat.mdh from the access directory and replace them by their saved version.

CHAPTER 2 - DATA COLLECTION

1. Defining and programming an experiment

1. 1. Software

1. 1. 1. Introduction

Thermal analysis of samples piloted by SETARAM devices are run by an acquisition software. The software is elaborated around a database and therefore experiments can be performed and a set of tools is available to help the user:

- Standard procedures can be defined.
- A catalogue including the management of experiments and stored procedures is kept (sorting and filtering depend on the device, the user, etc...).
- The user can program the device using a manual mode before or during an experiment and can preview the measured signals on a real time drawing screen.

Before running an experiment, several experimental conditions must be entered :

- Modify the experimental conditions of an experiment already performed.
- Modify a procedure that was previously stored on purpose.

1. 1. 2. Content of a procedure and an experiment

The table hereafter sums up the content of a procedure or an experiment :

	Procedure	Experiment
Name	Yes	Yes
Instrument	Yes	Yes
Context (user, family, crucible, etc...)	Yes	Yes
Heating procedure = n sequences	Yes	Yes
Parameters related to the whole experiment	Yes	Yes
Characteristics of the sample	No	Yes
Stored signals	No	Yes

To run an experiment from a procedure, the user only has to enter the characteristics of the sample.

1. 1. 3. Entering a procedure and an experiment

Once the ***Collection*** application is run via the corresponding icon, select the ***Experimentation / Data Collection*** menu.

The software is then arranged as follows :

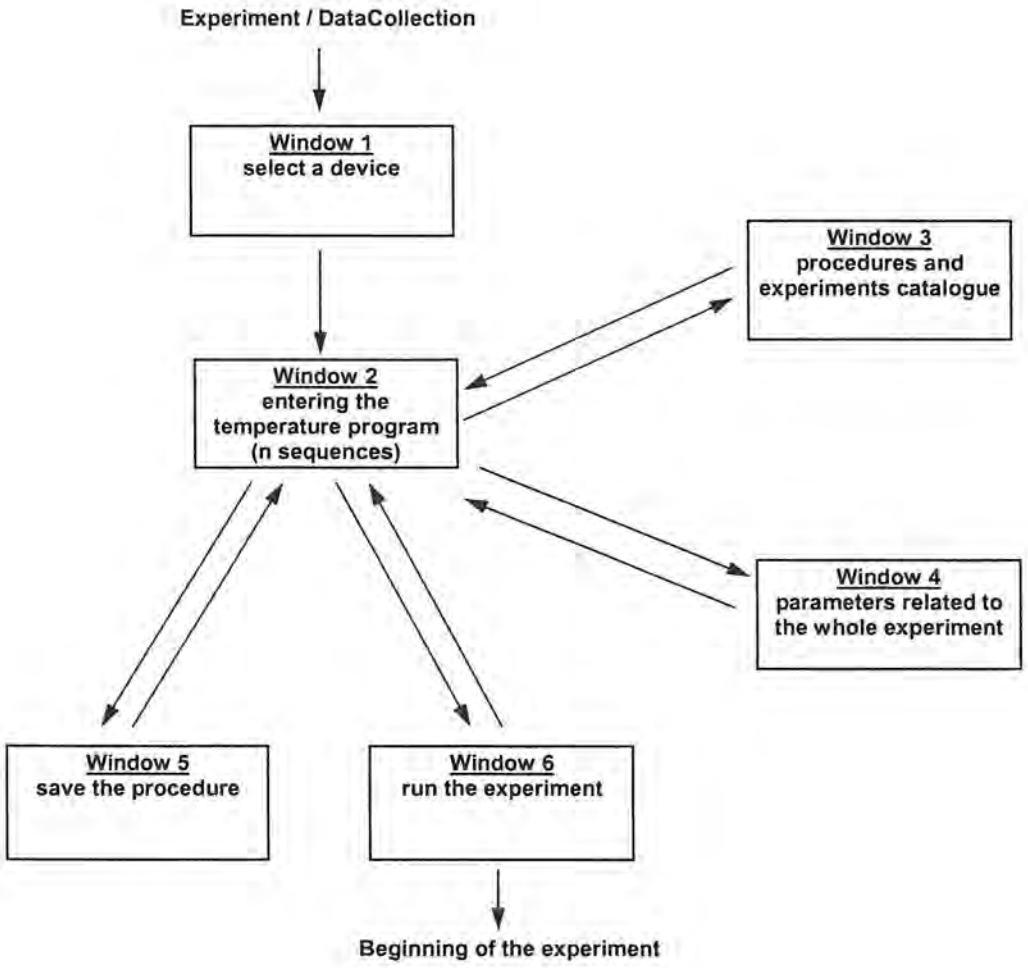


Figure 17 : Arrangement of the application

❑ **Entering a procedure**

1. Select the ***Experimentation / Data Collection*** menu. Window #1 opens and the device can be selected.
2. Once selected, window #2 opens and the temperature program can be entered.
3. If the automatically selected heating procedure is not adjusted and cannot be used to give a new procedure, click on ***Catalogue*** to open window #3.
4. Select an experiment or procedure in this window and click on ***OK*** to go back to window #2.

5. Once the temperature program is entered, click on ***parameters*** to open window #4.
6. Once these parameters are entered, click on ***OK*** to go back to the previous window.
7. Click on ***Save as*** to open window #5 and save the procedure.

❑ **Running an experiment**

Repeat the procedure mentioned in the previous paragraph until procedure #6 is reached and click on ***Save as*** to run the experiment.

❑ **Summary**

Let us complete the table used in section 1.1.2. by adding the number of the window where data related to the procedure or experiment are entered.

	Procédure	Experimentation
Name	Window #5	Window #6
Instrument	Window #1	Window #1
Context (user, family, crucible, etc…)	Window #5	Window #6
Instruction for temperature = n sequences	Window #2	Window #2
Parameters related to the whole experiment	Window #4	Window #4
Characteristics of the sample		Window #6

Remark A maximum of 199 sequences is available for a temperature program.

1. 2. Selecting a device (Window #1)

Once the temperature program is run and the ***Experimentation / Data collection*** menu is selected the selection window opens :

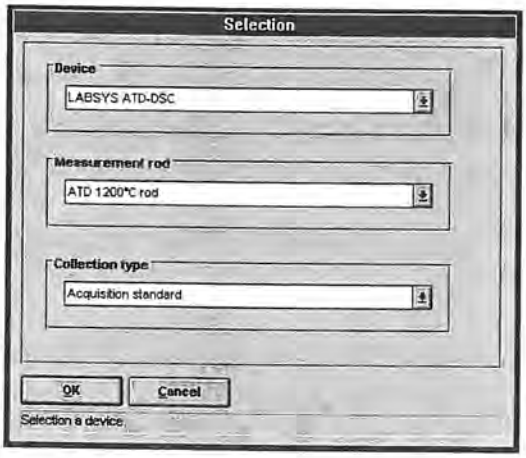


Figure 18 : Selection window of the device

Therefore the user can select:

- The measurement device (the list is adjusted to the devices available).
- The measurement module (the types of rods to be adjusted on the device are listed). When a device uses only one module, the module is automatically selected.
- The type of acquisition required.

Two buttons are available in the window:

- ***OK*** to validate the selection.
- ***Cancel*** to close the window.

Remark Before validating the selection, make sure that the selected device is connected ; if not, a message appears on the screen.

1. 3. Entering the temperature program (window #2)

Once the previous selection is validated, a window opens:

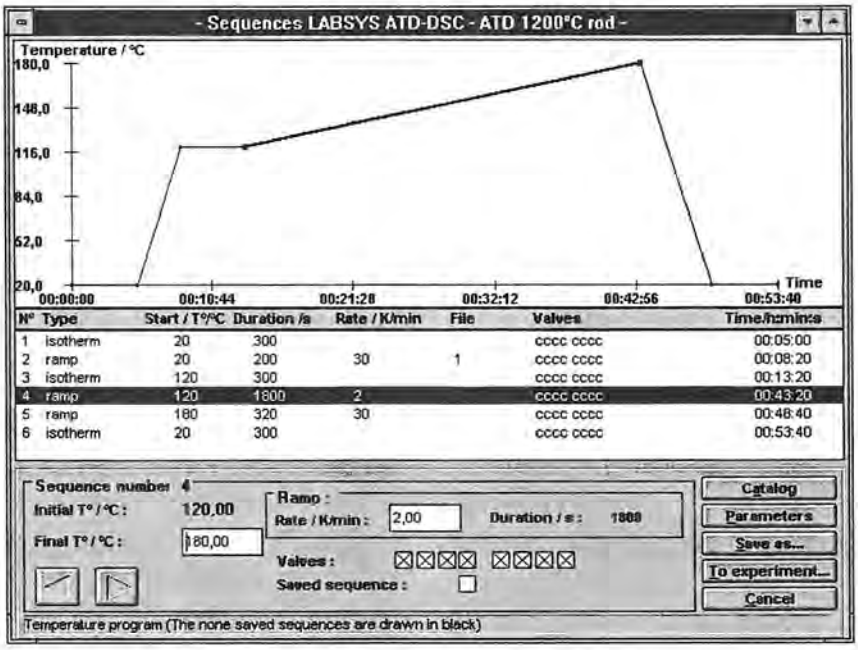


Figure 19 : Temperature program window

1. 3. 1. Content of the window

The window is made up of 3 parts and aims at entering the various sequences of the temperature program:

- The upper part shows a graphic of the temperature curve during the programming of the device.
- The centre part lists the various sequences programmed.
- The lower part aims at modifying the characteristics of the selected sequence.

The content of the window can be modified in order to:

- Enlarge the upper part and hide the centre: select the ***Display / Graphic full screen*** menu.
- Enlarge the centre part and hide the upper part: select the ***Display / List full screen*** menu.

1. 3. 2. Selecting a sequence

The characteristics of the selected sequence can be modified in the upper part. Indeed, the sequence can easily be identified in the list of sequences displayed in the centre part of the window as the corresponding line has a different color. Similarly, the sequence selected on the graphic is red and thicker.

Three possibilities are available to select a sequence:

- Click on the line to select the sequence directly.
- Click on the sequence to be selected among the list of sequences.
- Go to the selected sequence and move to the previous sequence via the  button or the ***Sequence / Reach / Previous*** menu, or move to the next sequence via the  button or the ***Sequence / Reach / Next*** menu, to the first sequence via the ***Sequence / Reach / First*** menu, or to the last sequence via the ***Sequence / Reach / Last*** menu.

1. 3. 3. Selecting several sequences

Several sequences can be selected to be modified simultaneously. Three possibilities are available:

- Press the mouse left button and move within the graphic to select sequences.
- Select them on the list (see the above mentioned instruction).
- Click on the sequences and press the ***Ctrl*** key to select them. The advantage of the method is that remote sequences can be selected as well.

1. 3. 4. Modifying the characteristics of a sequence

Select the chosen sequence and modify its characteristics in the lower part of the window:

- The temperature at the beginning of the sequence cannot be modified, except for the first sequence. This temperature can be changed if the temperature is modified at the end of the previous sequence.
- The temperature at the end of the previous sequence can be modified. If this temperature is equal to that at the beginning of the sequence, a frame named

Isotherm appears on the screen, otherwise a frame named ***Ramp*** is on the screen.

- The various valves (if the device has any) are localized. Click on them for any modification.
- A zone is available to save or remove the selected sequence.
- The zone can provide the user with a command grid such as tare, fan, power, etc. (depends on the type of device).

The value and length of time of the sequences can be entered in a zone available in the ***Isotherm*** frame.

The scanning rate of high and low temperatures can be entered in the ***Ramp*** frame and the value of the length of time for the ramp is indicated.

Remark Once the numerical value is entered, press on the ***Tab*** key to validate this value.

1. 3. 5. Modifying the characteristics of several sequences

Similar characteristics can be defined for several sequences. First of all, select the chosen sequences.

Then, the selected sequences are listed in the lower part:

Figure 20 : Several sequences are selected

The characteristics of the selected sequences can be modified (e.g. : click on a valve to modify its location on all the selected sequences).

1. 3. 6. Saving a sequence

The experiment is composed of several sequences. During the sequences, acquired points can either be saved or cancelled. Some sequences of an experiment can be stored. Therefore, the experiment can be selected to be stored either in one or several files. The identification number of the file is automatically computed when a user decides to save or to cancel the sequence. Two consecutive sequences can be saved in one or two files. Select the two of them at once and click on ***Saved sequences*** to save them in a single file. Select one file after the other and click on ***Saved sequences*** to save them in two separate files.

The second solution is interesting if a shorter acquisition time is required.

Indeed, the acquisition time is calculated so as the total number of points per stored signal is lower than 5,000 and the acquisition time is a multiple of .1 second.

Select a saved sequence and click on the ***Sequence / Informations*** menu in order to obtain this type of information.

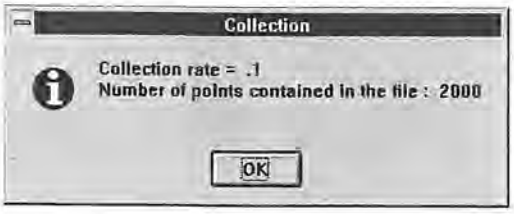


Figure 21 : Information about a sequence

The graphic sequences that are saved are blue or green, while the others are black.

1. 3. 7. Addding a sequence at the end of the program

The end of the temperature program must be reached. Two possibilities are available:

- Click on the graphic before the last sequence.
- Or move to the end of the program via the ▷| button.

An ***Undefined*** sequence is listed among other sequences. The final temperature of the sequence is to be entered and then from the value obtained, the isotherm duration or the ramp scanning rate is to be entered. The new sequence automatically provides for the characteristics used during the previous sequence.

1. 3. 8. Inserting a sequence during the program

Select the location of the new sequence before inserting it. Two possibilities are available:

- Select the location of the sequence and go to the ***Sequence / Insert a sequence*** menu.
- Or select the location on the graphic: locate the cursor to the next sequence, press the mouse left button and move toward the next sequence.

A sequence named ***Undefined*** appears and then repeat the action described in the previous paragraph.

1. 3. 9. Deleting a sequence

Select the sequence to be deleted and then activate the ***Edition / Cut*** menu. Several sequences can be deleted at once if selected before.

Remark The command can be cancelled via the ***Edition / Cancel cut*** menu.

1. 3. 10. Copying a group of sequences

One (or more) copy(ies) of a whole group of sequences can be done: select the sequences to be copied and go to the ***Edition / Copy*** menu. Then locate the cursor to the temperature program where the sequence is to be inserted. The copy is finally pasted either once via the ***Edition / Paste*** menu or several times via the ***Edition / Multiple paste*** menu (a window opens to specify the number of sequences to be pasted).

Remark All the sequences can be selected via the ***Edition / Select all*** menu. The multiple paste command can be cancelled via the ***Edition / Cancel*** menu.

1. 3. 11. Window buttons

Numerous buttons are available on bottom right:

- ***Catalog*** to open window #3.
- ***Parameters*** to open window #4
- ***Save as ...*** to open window #5.
- ***To experiment*** to open window #6.
- ***Cancel*** to close the window ; the ***Experiment / Close*** menu provides the user with the same command.

1. 3. 12. Zooming

The temperature program can be zoomed. Activate the ***Display / Zoom in*** menu and select the part of the plotting to be zoomed while pressing the mouse left button. Click on the ***Display / Zoom out*** menu to use automatic scales.

1. 4. Procedures and experiments catalog (window #3)

When the temperature program window opens, the program entered when the previous device was selected in window #1 automatically appears on the screen.

If the previous program is to be changed, another program, which was formerly entered, can be selected via the ***Catalog*** button:

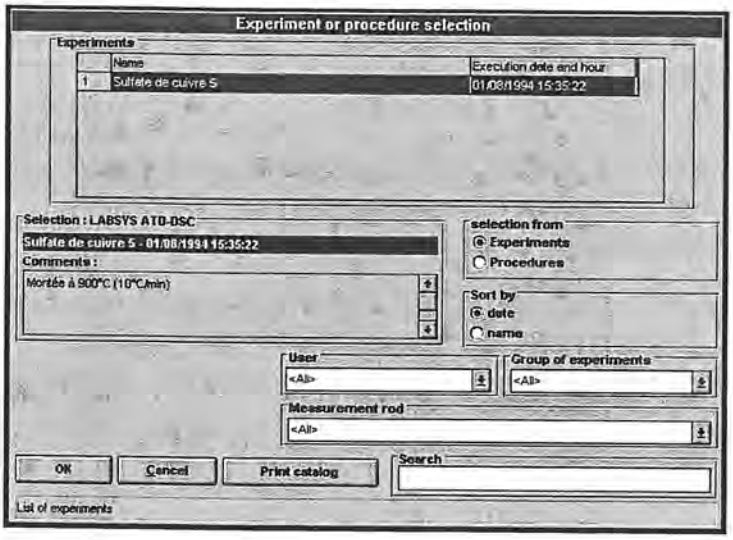


Figure 22 : Experiments and procedures catalog

An experiment that is already performed or a procedure already stored can be selected. Then, the temperature program and regulation parameters are loaded in the memory.

Various possibilities are available:

- Either procedures or experiments can be displayed.
- Listings can be sorted in alphabetical order or date.
- Listings can be filtered according to the user.
- Listings can be filtered according to the group of experiments.
- Keywords can be filtered by the name and comment fields (***search*** zone).
- Listings can be filtered by the measurement rod (if more than one rod is available per device).
- The comment of any experiment can be previewed.

Three buttons are available in the window:

- ***OK*** enters the conditions of the selected experiment or procedure.
- ***Cancel*** cancels the opening of the window. The ***Experiment / Close*** menu provides the user with the same command.
- ***Print catalog*** starts the printing of the catalog.

Remark When loaded, the selected experiment conditions can be modified. For example: if the experiment is carried out on a DSC 1200°C rod and the selected experimental condition is carried out on a DSC 1600°C rod, the temperature program may be lopped at 1200°C.

---

1. 5. Parameters related to the whole experiment (window #4)

When the temperature program is entered, several other parameters related to the experiment are to be entered.

The coefficients are entered in the ***parameters*** window via the ***Parameters*** button.

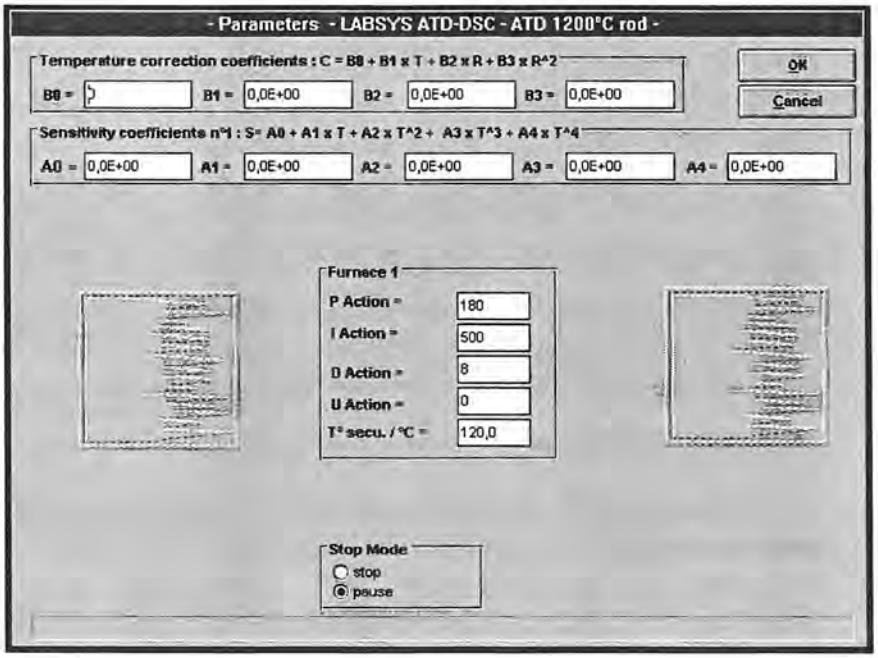


Figure 23 : Parameters related to the whole experiment

Item of information related to the type of devices are entered in this window:

- Coefficients for temperature correction.
- Coefficients for Heat flow correction (one or two series of coefficients, depend on the Heat flow signals acquired by the device).
- P, I, D, U values and the safety temperature for each furnace (furnace 1, and possibly furnace 2 and auxiliary furnace, depend on the device).
- Value of the auxiliary furnace temperature, if the device has any.
- Safety temperature of the sample if the temperature is measured (depends on the device).
- The temperature may be acquired either on the sample or on the furnace if both signals can be measured (depends on the device).
- The controller stop mode (either stop it or pause at the end of the experiment to keep it to the final temperature).
- The TMA range can be chosen if the instrument provides a measurement in TMA signal (depends on the device).
- The TG range can be chosen if the instrument provides a measurement in TG signal (depends on the device).
- The type of deformation of the sample can be selected : traction, flexion or compression if the instrument provides a measurement in TMA signal (depends on the device).
- The command for attenuating the Heat flow signal(s) can be selected (depends on the device).

- A tare for the TMA signal can be selected or not when starting the operation (depends on the device).

Note For a SETline range apparatus, other coefficients are necessary. Refer to the ***« Commissioning-SETline Utilisation/Practical Work »*** leaflet.

1. 6. Saving a procedure (window #5)

The temperature that has just been defined and the entered parameters can either be saved as a procedure or be immediately used to run another experiment.

Click on ***Save as*** in window #2 (temperature program window) to save both temperature and parameters as a procedure. Then a window opens:

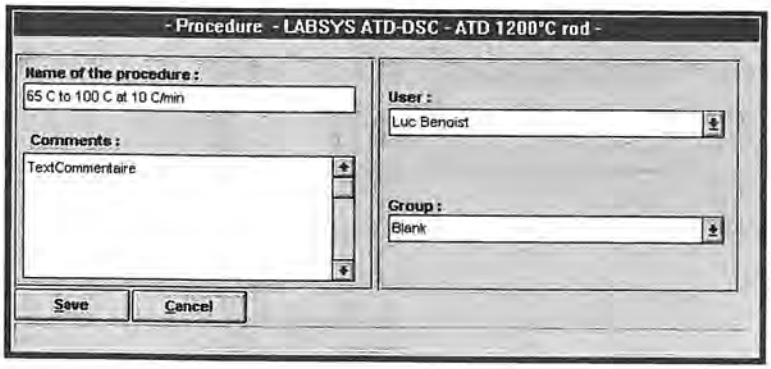


Figure 24 : Save a procedure

The user enters :

- The name of the procedure.
- A comment.
- The user's name.
- The group of the procedure.

The procedure will be easily identified among others once the above mentioned fields are entered (see *Procedures and experiments catalog (window #3) page 15*).

Two buttons are available:

- ***Save*** to save the procedure.
- ***Cancel*** to close the window.

1. 7. Starting an experiment (window #6)

Click on ***Experiment*** in window #2 (temperature program window) to start the experiment. The experiment window opens:

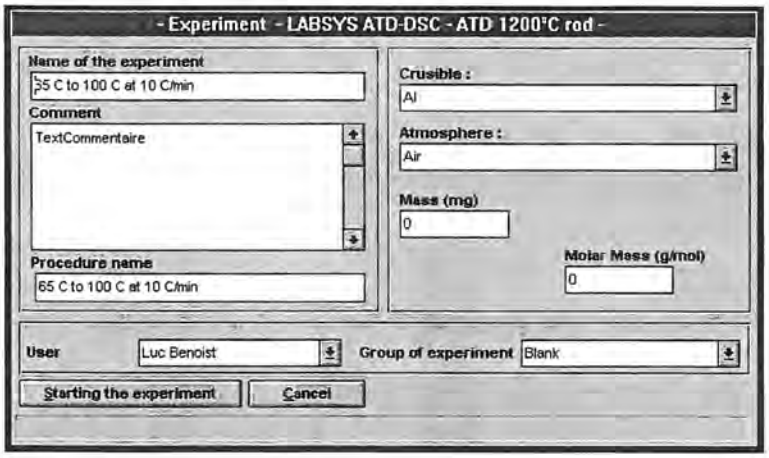


Figure 25 : Start an experiment window

The user enters:

- The name of the experiment.
- A comment related to the experiment.
- A short description of the heating procedure.
- The crucible used (this field might not be required for a few devices)
- The groupe of procedure.
- The atmosphere (this field might not be required for a few devices).
- The mass of the sample (this field might not be required for a few devices).
- The molar mass of the sample (this field might not be required for a few devices).
- The type of probe (this field might not be required for a few devices).
- The length of the sample (this field might not be required for a few devices).
- The section of the sample (this field might not be required for a few devices).

Two buttons are available:

- ***Starting the experiment*** to start the experiment.
- ***Cancel*** to close the window.

1. 8. Robotic system

For the DSC 121 RS instrument, the window described in the former paragragh is replaced by the following window:

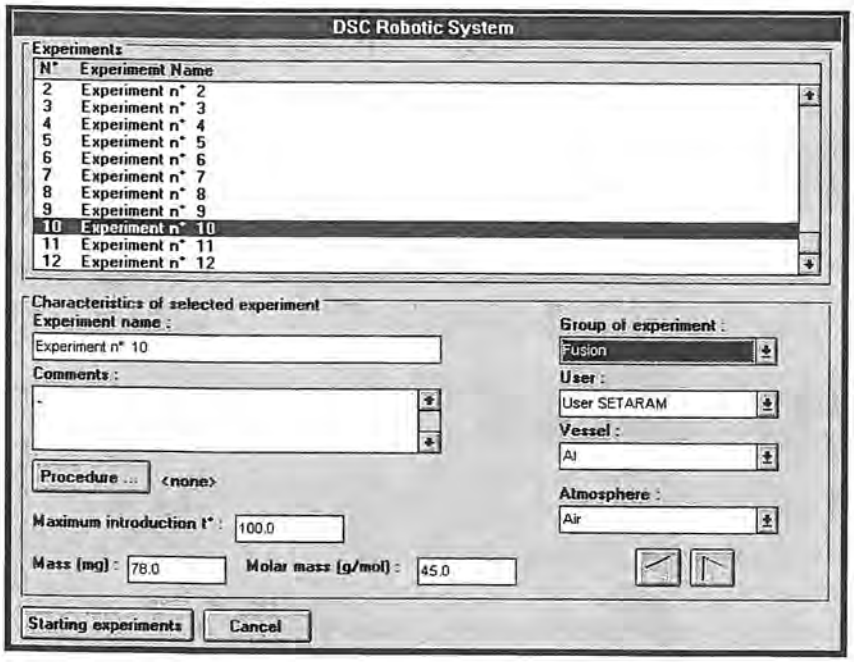


Figure 26: Entering the experimental conditions

Before opening this window, the number of samples to be analysed must be entered.

In this window various pieces of information can be entered such as:

- the name of the experiment
- a commentary about every experiment
- the type of vessel used
- the group of experiments
- the type of atmosphere
- the mass of the sample
- the molar mass of the sample
- the maximum temperature for introduction
- the heating procedure

Before opening the above described window, the heating procedures to be carried out on the samples must be previously saved (see *1. 6. - Saving a procedure (window #5)*).

The maximum temperature for introduction prevents the crucibles from being introduced at too high a temperature and from damaging the device. Before the introduction if the temperature is too high the system waits for the calorimetric transducer to be cooled down to the appropriate temperature.

If the same piece of information (same atmosphere for instance) has to be entered, the user may select the various samples among the list and enter the data only once.

1. 9. Entering several programs in parallel

1. 9. 1. Method

Several temperature programs can be entered in parallel and in various windows. Select several times the ***Experiment / Data collection*** menu in order to open several windows providing for entering the temperature program (window #2). Then, the commands in the menu are activate in the selected window. The window that were previously opened are listed at the end of the ***Window*** menu.

The window can be rearranged via the ***Window / Cascade, Window / Tile*** and ***Window / Arrange icons*** menus.

1. 9. 2. Interaction between windows

When several temperature program windows are open, items from one window can be copied into another:

- Select the sequences to be copied in the same window.
- Activate the ***Edition / Copy*** menu.
- Select the location of the item to be inserted on the target window
- Activate the ***Edition / Paste*** menu.

Remark While copying sequences, temperature or scanning rate of the copied sequences may be lopped if they are too high for the device used in the target window.

---

1. 10. Printing

1. 10. 1. Printing the current experiment conditions

Select the ***Experiment / Print procedure*** menu to print the temperature program while not completely entered:

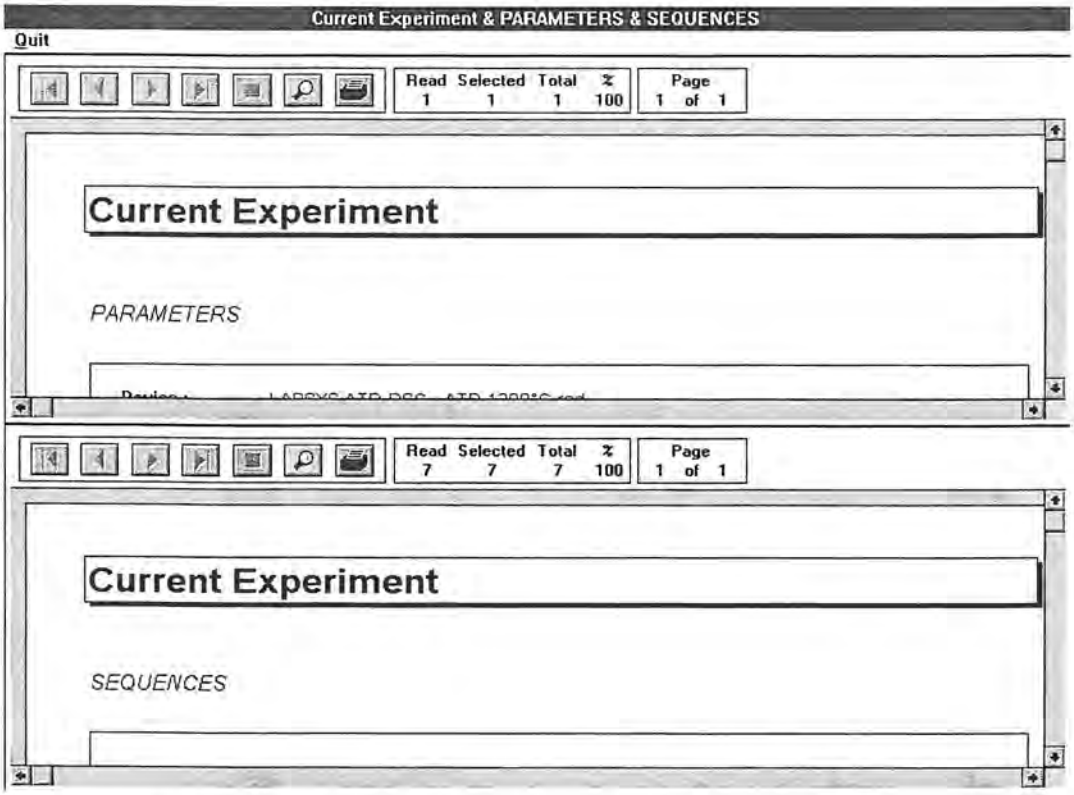


Figure 27 : Experimental conditions printing window

The window is made up of two parts (use lifts to move within the two parts) :

- The upper part sums up the data entered in window #4 (parameters related to the whole experiment).
- The lower part displays the sequences of the temperature program entered in window #2.

Click on to print one of the two zones.

Click on ***Quit*** to close the window.

1. 11. Annex : commands of the menu

1. 11. 1. Experiment Menu

- **Data collection...**

  Experimental conditions of a procedure or experimentation are entered (see Selecting an instrument (Window #1) *page 14*).

- **Close**

  To close the temperature program (see Window buttons *page 19*).

- **Print procedure**

  To print the experimental conditions while they are entered (see Printing the current experiment conditions *page 25*).

- **Setup...**

  Printer and device mapping (see Equipment mapping *page 5)*

- **Quit**

  To quit the application.

1. 11. 2. Edition Menu

- **Cancel**

  To cancel the last command (copying or deleting a sequence) (see Selecting a device (Window #1) *page 14*).

- **Cut**

  To delete one (or more) selected sequence(s) (see Deleting a sequence *page 18).*

- **Copy**

  To copy one (or more) sequence(s) (see Copying a group of sequences *page 19*).

- **Paste**

  To paste one (or more) sequence(s) (see Copying a group of sequences *page 19*).

- **Multiple paste**

  Multiple paste of one (or more) sequence(s) (see Copying a group of sequences *page 19*).

- **Select all**

  To select all the sequences.

1. 11. 3. Display Menu

- **Real time drawing**

  To open the real time drawing (see Real Time Drawing *page 22*).

- **Direct programming**

  To open the direct programming window (see Direct Programming *page 32*).

- **Zoom in**

  To zoom on the temperature program (see Real Time Drawing *page 22*).

- **Zoom out**

  To display the temperature program using automatic scales (see Zooming *page 14*).

- **List full screen**

  To list sequences on a full screen (see Content of the window *page 15*).

- **Graphic full screen**

  To display the graphic on a full screen (see Content of the window *page 15*).

1. 11. 4. Sequence Menu

- **Insert a sequence**

  To insert a new sequence (see Inserting a sequence during the program *page 18*).

- **Reach**

  To reach the first, the previous, the next or the last sequence (see Selecting a sequence *page 16*).

- **Information**

  Information about a saved sequence (see Saving a sequence *page 17*).

1. 11. 5. Data Menu

- **Users**

  To add new users.

- **Group of experiments**

  To enter new groups of experiments.

- **Crucible**

  To enter new crucibles.

- **Vessel**

  To enter the types of vessels

- **Atmosphere**

  To enter new types of atmosphere.

- **Probe material**

  To enter the the probe material. Used for TMA only.

1. 11. 6. Window Menu

- **Cascade**

  To rearrange the window in cascade mode.

- **Tile**

  To rearrange the window in tile mode.

- **Arrange icons**

  To rearrange icons.

- **At the end of window menu**

  To list the open program windows.

2. Real Time Drawing

2. 1. Introduction

The constant evolution of signals can be previewed from the device. The Real time drawing can be previewed at any time (before, during and after an experiment).

The ***Display / Real time drawing*** menu of the acquisition program gives access to the real time drawing window. Then, select the chosen device in the sub-menu displayed on the screen. Figure 27shows the various zones of the window.

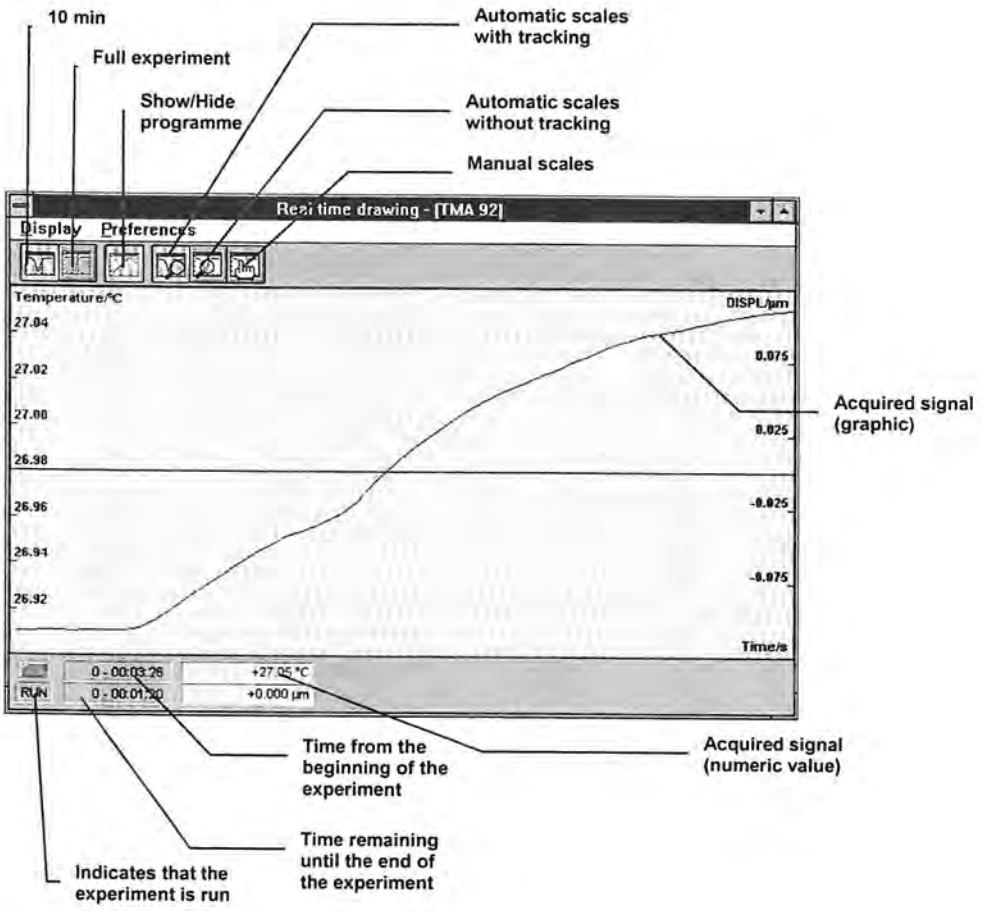


Figure 28: Real time drawing window

Remark Points for real time drawing are really acquired when the experiment starts or when the first window is displayed. When the option or the experiment is changed, the screen is automatically rebooted.

2. 2. Definition of the preview period

2. 2. 1. Previewing the last 10 minutes

The preview mode for the last 10 minutes is available via the ***Display / Last 10 minutes*** menu, whether an experiment is being performed or not.

In this mode, the part that is previewed moves to the left one minute every minute. As a result, the last 9 minutes, at least, are still on the screen. Scale of the time axis remains the same.

2. 2. 2. Previewing the whole experiment

This mode is available via the ***Display / Full experiment*** menu only when the experiment is being performed.

In this mode, the part that is previewed shows the experiment from its very beginning. Scale of the time axis is automatically readjusted when the duration of the experiment is modified.

2. 3. Making up

2. 3. 1. Colors

Backcolors of the screen and curves can be modified via the ***Preferences / Colors / ...*** menu. A window is displayed and a new color can be selected among a wide range of selected colors; a personal touch can also be added.

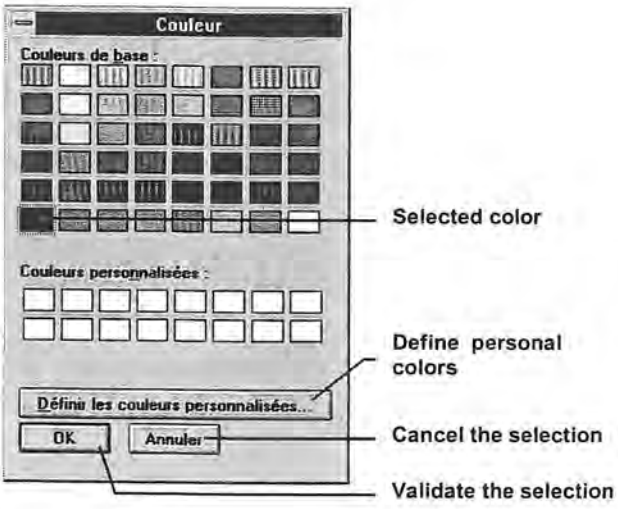


Figure 29 : Select a color in the real time drawing window

2. 3. 2. Scales

Three modes are available:

- Automatic mode without tracking.
- Automatic mode with tracking.
- Manual mode.

❑ **Automatic mode without tracking**

Select the ***Preferences / Scales / Automatic without tracking*** menu to obtain the automatic scale mode. Scales are automatically calculated according to a range of displayed signals. Scales may frequently be modified. This mode calculates to the nearest decimal point.

❑ **Automatic mode with tracking**

Select the ***Preferences / Scales / Automatic with tracking*** menu to obtain the automatic scale mode. Scales are calculated according to a range of signals acquired when the real time drawing window is open or from the beginning of the experiment. Scale ranges can only increase in this mode.

❑ **Manual mode**

Select the ***Preferences / Scales / Manual*** menu to obtain the manual mode. Scales are defined by the ***Preferences / Scales / Scales definition*** menu. Figure 30 (hereafter) is an example of the definition of scales.

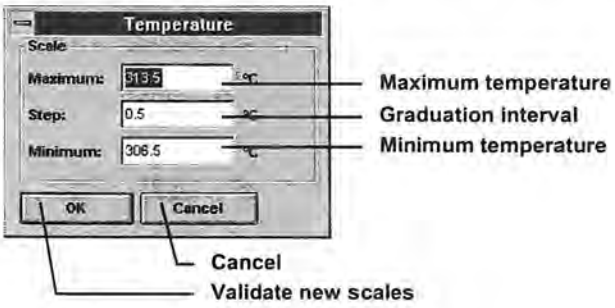


Figure 30 : Manual scales are defined

Remark The value of the interval entered by the user may not be respected. Indeed, as wording never overlap, some of them may not be displayed on the screen.

2. 3. 3. Display options

❑ **The temperature program is previewed**

The software automatically displays the temperature program on the temperature axis. However, click on the ***Preferences / Program*** menu to delete or reactivate temperature.

❑ **The window is always displayed**

The real time drawing window can constantly be displayed on the screen (even when another application is open for instance). Click on the ***Display / Always on top*** menu.

❑ **Full screen**

On the screen, the numerical display zone can be unactivated and replaced by a graphic. Click on the ***Display / Full screen*** menu to activate or unactivate this zone.

3. Direct Programming

3. 1. Introduction

Instantaneous values from the device can be previewed and checked by the direct programming window.

Click on the ***Display / Direct programming*** menu of the acquisition program to open the direct programming window. The method used to choose the device - and possibly its option- is described in the real time drawing window (see *Real time drawing page 22*).

WARNING A few actions occurring in the direct programming window may disturb an experiment. Be very careful !...

Figure 31 (hereafter) shows the various zones in this window:

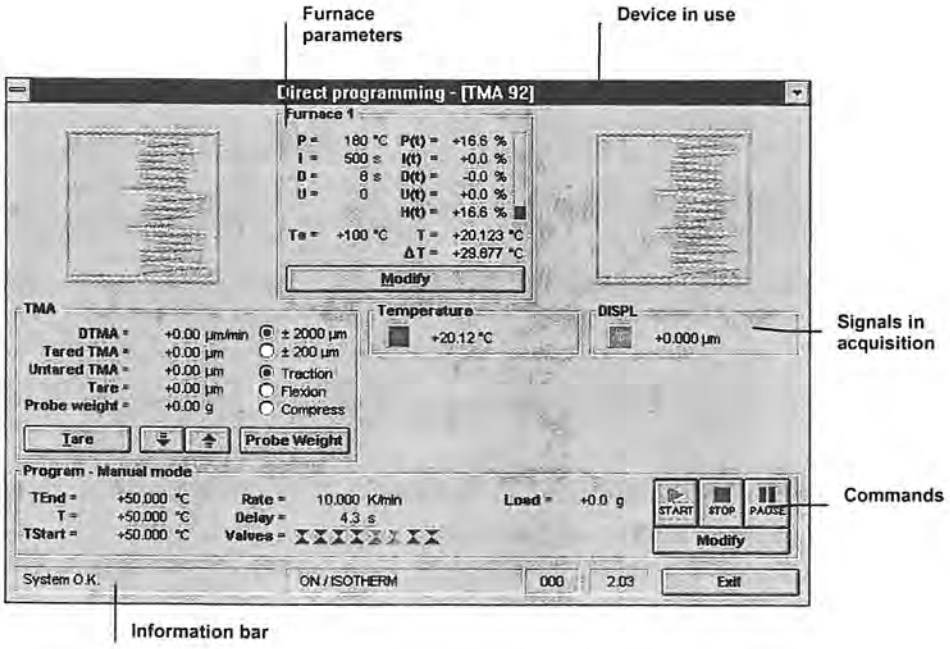


Figure 31 : Direct programming window

3. 2. Information bar

Information about the programmer mode (on or off), the running sequence number, the version of the controller, etc. are rapidly found on the information bar.

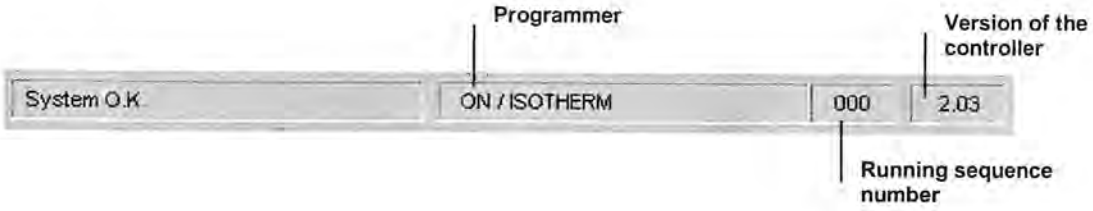


Figure 32 : Information bar

3. 3. Furnace parameters

3. 3. 1. Description

PIDs parameters, safety temperature, etc. are displayed together in the same zone.

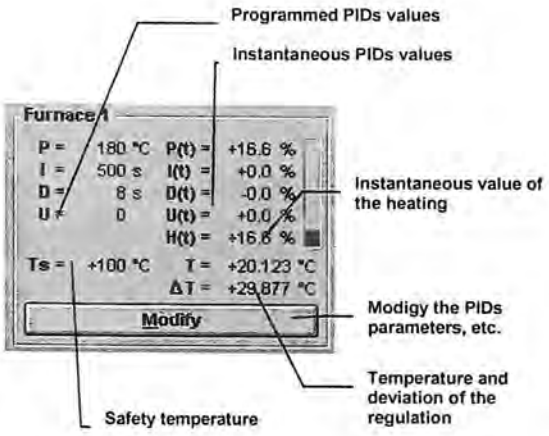


Figure 33 : Description of furnace parameters

3. 3. 2. Modification of PIDs and safety temperature

Click on ***Modify*** to change the PIDs and the safety temperature of the furnace. Then, a window displaying these parameters opens. Click on ***OK*** to validate the modifications.

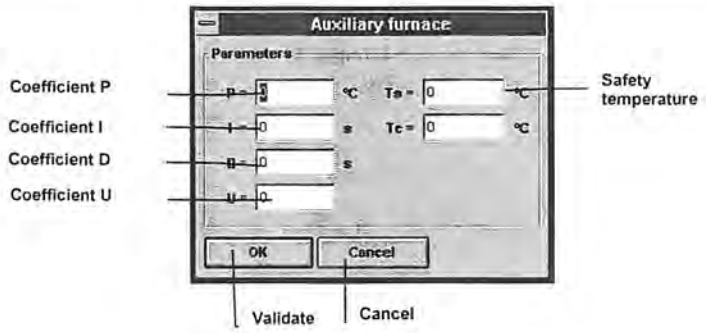


Figure 34 : The furnace parameters are modified

3. 4. Acquiring signals

Signals from the device are numerically displayed.

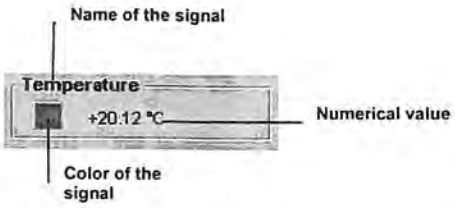


Figure 35 : Acquiring a signal

Remark The color of the signal is related to the graphic that is displayed in the real time drawing window.

3. 5. TG

Parameters related to the TG signal can be visualized via the TG display zone

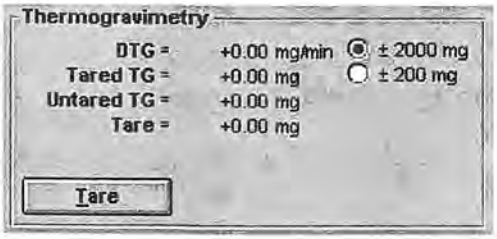


Figure 36: TG display area

The ***Tare*** button is used to make a tare of TG signal. Click on one of the two radio buttons available for this purpose to modify the measure range.

3. 6. TMA

Parameters related to the TMA signal can be visualized via the TMA display zone

Figure 37: TMA display area

The ***Tare*** button is used to make a tare of the TMA signal.

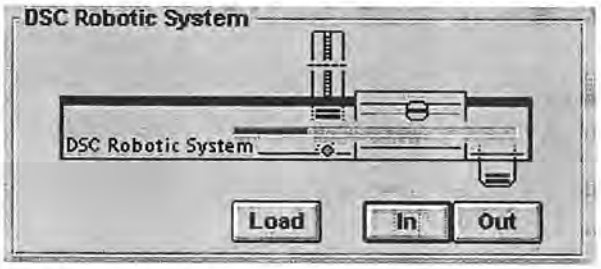
The up and down arrows are used to take the TMA probe up and down respectively. A deformation mode can be selected via one of the three radio buttons: Traction, Flexion and Compression.

Click on one of the two radio buttons available for this purpose to modify the measure range.

The ***Probe Weight*** button is used to start the procedure for determining the weight of the probe. A second click on the ***Probe Weight*** button will stop the procedure.

3. 7. Robotic system

From the ***Direct programming*** window the robotic system can be piloted via three buttons on the following screen:



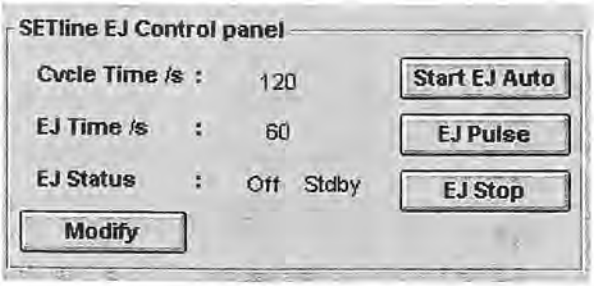
Controls of the robot

Three buttons are available:

- ***Load*** : loading the sample
- ***In*** : introducing the sample
- ***Out*** : extracting the sample

3. 8. SETline case

From the Direct Programming window, a Joule effect calibration can be controlled via the following screen:



Joule effect of the *SETline* apparatus

To understand the signification of the elements in the above-screen, refer to the ***«Commissioning-SETline Utilisation/Practical work »*** leaflet.

3. 9. Programme

3. 9. 1. Description

The display zone of the programme is used to visualize and modify these instanteneous values in the sequential programmer (see Figure 38).

The ***Modify*** button is used to modify the instanteneous values in the sequential programmer (see ***Manual Programming***, page 36).

Click on ***Start*** to start the manual programming (and not an experiment, otherwise see ***Defining and programming an experiment***, page 12).

Click on ***Stop*** to stop an experiment or manual programming. The experiment can be stopped via the ***Pause*** or ***Stop*** button.

The ***Pause/Continue*** button is used to fix the sequence in process or to re-start the sequence formerly stopped.

3. 9. 2. Manual programming

Sequences run by the controller are programmed on request via the manual programming mode. This mode is often used before running an experiment so as the controller is regulated to a given temperature.

Remark This mode is not available if an experiment is still in process.

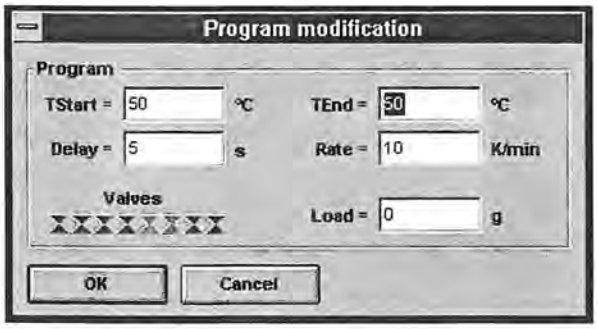


Figure 38 : Modification of the sequential programmer instantaneous values

- **Temperature at the beginning of the program**

  To define the initial temperature of the sequence. If the temperature of the sequence is modified, the instantaneous temperature is re-programmed.

- **Temperature at the end of the program**

  To define the temperature at the end of the sequence.

- **Delay**

  To define the time passed at the beginning of the sequence. If modified, the instantaneous delay is re-programmed.

- **Scanning rate**

  To defines the variation scanning rate of the temperature program. If modified, the instantaneous scanning rate is re-programmed.

CHAPTER 3 - DATA PROCESSING

1. Loading an experiment

1. 1. Method

Double click on the processing application icon.

Select the ***Experiment / Open an experiment*** menu. Then a window opens and the experiment to be processed can be selected (see *Figure 39*).

Once the experiment is selected, a window opens and the part to be processed and signals can be chosen (see Figure 40).

Once the choice is made a window displaying plotting curves and a palette appear on the screen.(see Figure 41 and Figure 44).

1. 2. Selecting an experiment

Click on ***Experiment / Open an experiment*** to open the experiment selection window:

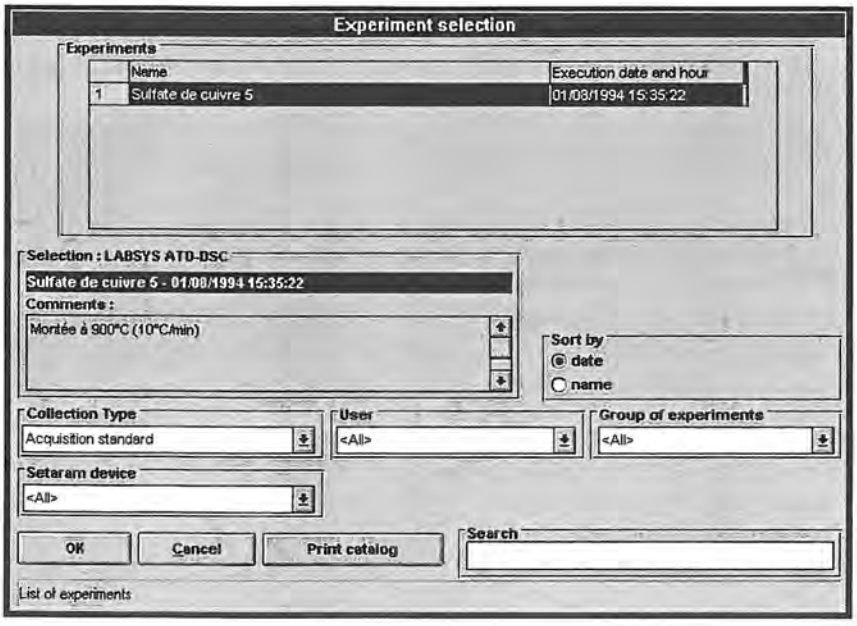


Figure 39 : Experiment selection window

The experiment to be processed can be selected via this window as various possibilities are available:

- Click on an experiment to preview the comment related to it.
- Experiments can be filtered by types of acquisition and device, the user's name or the family of experiment.
- Experiments can be filtered by alphabetical order or performance date.
- Experiments can be sorted by keywords (***Search*** zone, activated on experiment names and comments - no selection if the zone is empty).

Two possibilities are available to validate the experiment:

- Select an experiment and click on ***OK***.
- Double click on the name of the experiment.

Remark The name of the last four experiments are found in the ***Experiment*** menu. Select the experiment to be processed via this menu instead of going to the window shown on Figure 39).

1. 3. Selecting sequences and signals

Once the experiment is selected, the signals and sequence selection window opens:

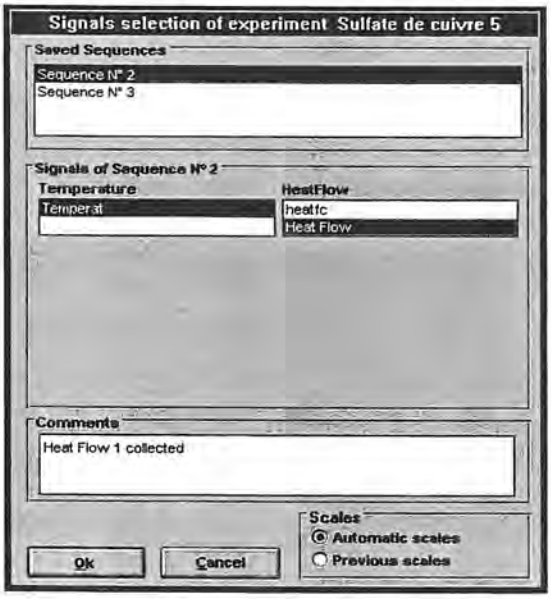


Figure 40 : Sequences and signals selection window

Three types of selection are available:

- Experiment to be processed.
- Signals to be processed.

- Scales.

1. 3. 1. Selecting the part of the experiment to be processed

The experiment might have been saved in separate sequences. The ***Saved sequences*** frame recalls the saved parts of the experiment, and the sequence to be processed can be selected. When loading the experiment, the selected sequence only is loaded.

1. 3. 2. Selecting the signals to be processed

A saved sequence is associated to a few signals (acquired signals and possibly signals from processing - e.g. acquired temperature, constant temperature, etc.). These signals are gathered by types (temperature, heat flow, thermogravimetry, etc., depending on the device). The user can only select one signal for each type. The ***comments*** zone provides him with a comment associated to the last signal clicked.

1. 3. 3. Selecting scales

The user can choose to load the experiment either with automatic scales or with scales defined when the latest application was processed. Such a choice is very interesting when successive and almost identical experiments are processed. The scale displayed is that selected when the window was closed for the last time.

Once the type of experiment, signals and scales are selected, click on ***OK*** to validate.

2. Unloading an experiment

Unloading an experiment is a key step as a few parameters (such as make up, colors, etc.) can be saved. Various possibilities are available:

- Select the plotting window related to the experiment or select the name of the experiment in the palette and go to the ***Experiment / Close an experiment*** menu.
- Close the plotting window related to the experiment.

Remark When quitting the software via the ***Experiment / Quit*** menu or the ***Close*** system of the application, the experiments are automatically unloaded.

3. Loaded experiment

3. 1. Description

Once the part of the experiment and signal to be processed are selected, two windows automatically open:

- A window displaying the plotting of signals (see *Figure 47*).
- A palette displaying listing experiments and signals (see *Figure 41*).

Among these signals are displayed the ones selected in the window shown on Figure 39 plus derivative signals and time. The characteristics of the experiment and of each signal can be selected from the palette (see Figure 42). Go to the palette and double click on the item related to the piece of information required.

3. 2. Content of the palette

The palette is basically made up of two parts:

- A list of experiments.
- A list of signals.

Figure 41 : Palette

3. 2. 1. Listing experiments

This listing provides for the name of the loaded experiment and possibly other experiments loaded before.

When an experiment is selected among the list, the plotting window related to the experiment is activated (and becomes the first listed).

Conversely, if several plotting windows are open, when one of them is activated, the experiment related to the plotting is selected in the palette. Up to a certain point in the list, the plotting windows are as numerous as the experiments.

Remark Four experiments can be opened simultaneously.

Remark The same experiment can be opened several times.

Remark An experiment can be processed while in acquisition. To visualize the last acquired points at a certain moment, close **ALL** the plotting or experiment windows where the experiment is loaded and then re-open the experiment.

3. 2. 2. Listing signals

This list corresponds to the signals linked to the experiment selected in the previous paragraph. Derived signals are found among the list. The filter value (one per signal type) used during the last processing application is used to calculate the derived signals. This value might be automatically modified if much higher or lower than the signal duration.

3. 3. Characteristics of the experiment

Double click on the name of the experiment displayed in the palette to open the experiment window:

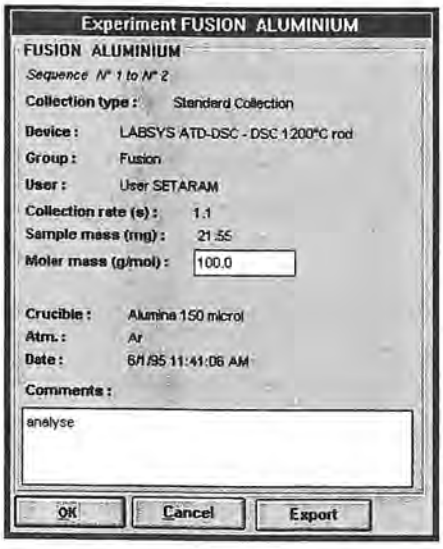


Figure 42 : Characteristics of the experiment

This window displays the experiment characteristics:

- Type of acquisition.
- Name of the device (and sometimes of the rod) used to perform the experiment.
- Group of experiments of the performance.
- User's name.
- Acquisition period of this part of the experiment.
- Mass of the sample (this field might not appear for a few devices).

- Length of the sample (this field might not appear for a few devices).
- Molar mass of the sample (can be modified).
- Type of vessel, crucible, atmosphere or probe, depending on the instruments.
- Date and time of the performance.
- Comments about the experiment (can be modified).

Click on ***OK*** and ***Cancel*** to close the window and save or delete the possible modifications in the window.

The numeric values of the experiment signals can be printed via the ***Export*** button.

This window allows to select the signal to print, the limits and the pitch.

3. 4. Exporting signals

When clicking on the ***Export*** button (see the former paragraph), the following window appears:

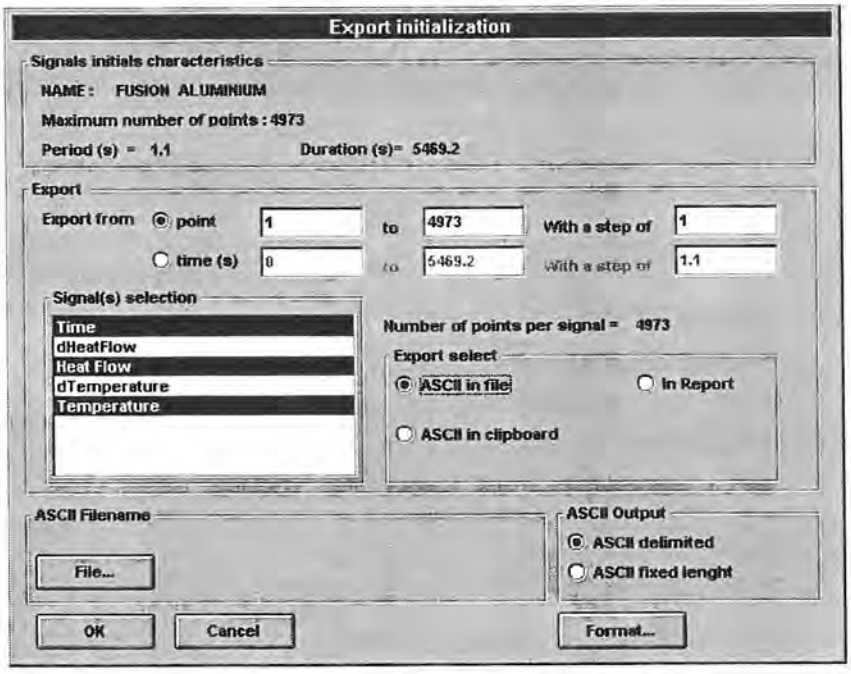


Figure 43: Selecting the export parameters

This window allows to select:

- the signal(s) to be exported
- the limits and the export step, in point or time
- where to be exported:
  - ♦ in ASCII in a file
  - ♦ in ASCII in the clipboard
  - ♦ in a report printed on paper

- exporting in a file: a frame allowing to select the name of the file is displayed
- exporting in ASCII (in a file or in the clipboard): the values are either exported via a data delimiter and/or field separator, or exported with a fixed length. According to the selection the delimiters or the field length must be entered.

Click on the ***Format*** button to enter additional data. The following window appears:

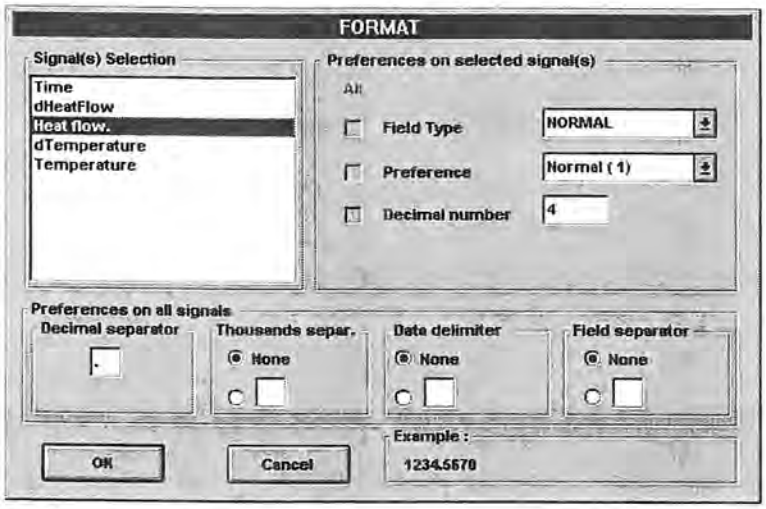


Figure 44: Selecting the format of the signals to be exported

The window allows to choose for the selected signal(s):

- the display type (normal or mathematical)
- if the + sign is to be displayed or not in front of the value
- the number of decimals

The user may also enter or modify for all the signals (selected or not):

- the decimal separator
- the separator for thousands (if wanted)
- the data delimiter (if exported in ASCII)
- the data separator (if exported in ASCII)

In the ***Example*** frame, the reprentation of a number corresponding to the selected parameters for the first signal (Time above) is displayed whether it is selected or not.

Click on ***OK*** from the window of Figure 43 to run the export operation.

3. 5. Characteristics of a signal

Double click on any signal displayed in the palette to open a window displaying its characteristics:

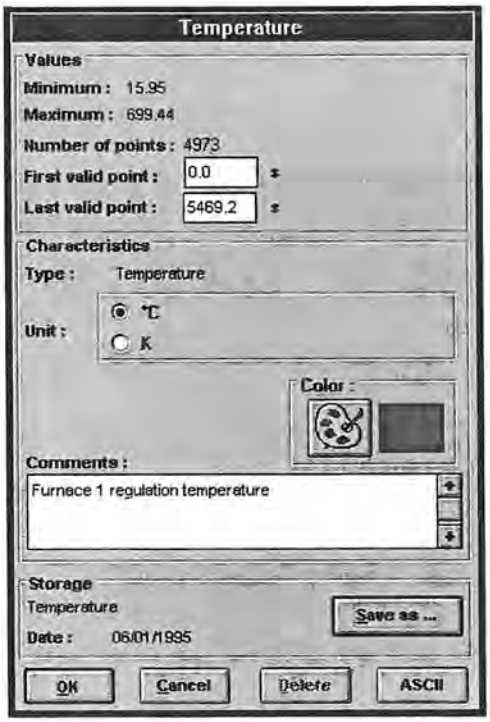


Figure 45 : Characteristics of a signal

This window displays the characteristics of the selected signal. The content of the window generally varies with the types of signal and is made up of:

- A ***values*** frame related to the points used to form a signal contains minimum and maximum values of this signal, the total number of points, and the first and last valid points. The last two values can be modified if a part of the signal is to be ignored. The minimum and maximum are calculated between the first and the last valid point.
- A ***characteristics*** frame describes the signal. This frame provides for information about the type, the unit (can be modified), the color and a comment of the signal (the last two items can be modified). If the signal is derived, the frame also provides for the filter value (can be modified) used to calculate the derivative.
- A ***storage*** frame only appears when signals are or could be saved (this frame is not available when signals are derived). The signal can be saved if not saved until then or saved under another name (displayed in the window shown in Figure 39. The frame also indicates when the signal was generated (date of acquisition or calculation if the signal was generated by processing).

Remark The unit can be changed in the above mentioned window (mn or h for time signal, % for the TG signal, etc.).

Remark However, some operations occurring on signals can modify the user's choice (for instance subtracting 2 temperature signals is done in °C).

This window includes an ASCII button to export the signal under an ASCII form. The user has to choose :

- the decimal separator
- the number of decimals
- the type of separator between the values
- if all the points or onely one point is to be exported on n
- the name of the file

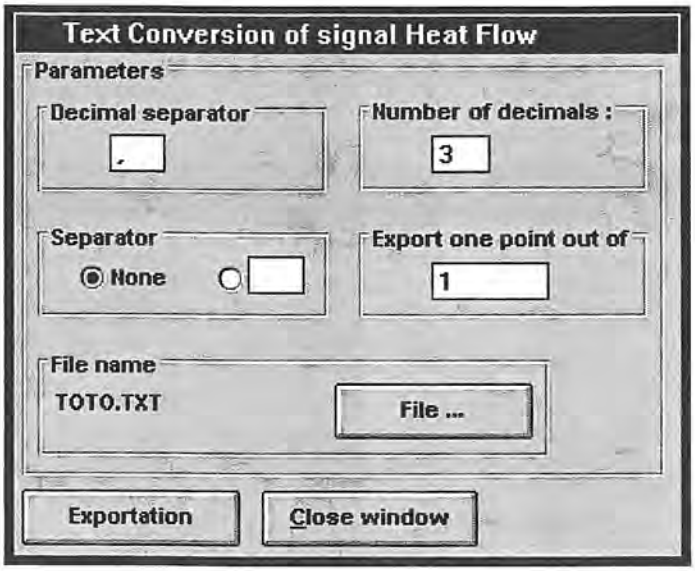


Figure 46 : ASCII export

4. Experiment make up

4. 1. Locating a signal on an axis

The window where signals are plotted is made of an X axis and can have up to six Y axes (Y1...Y6).

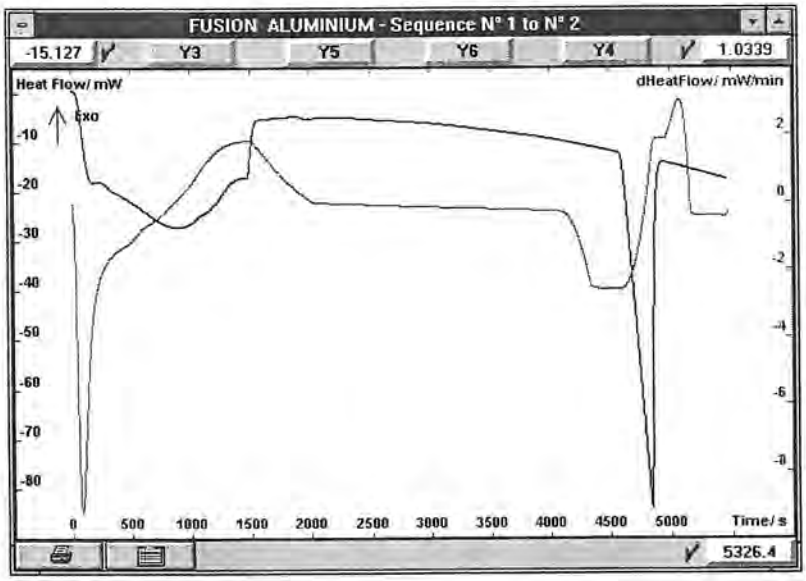


Figure 47 : Plotting window

Buttons related to Y axes where the signals are plotted are identical to the plot backcolor, while the others are gray.

If an axis is occupied, its button gives the current location of the cursor, otherwise the name of the axis is displayed (Y1...Y6). The X axis is of course always occupied.

When a plotting window opens, the make up remains the way it was when the latest experiment was closed (same signals on the same axis with the same colors).

Moreover, on the palette (see *Figure 41*), signals are plotted with the color of the corresponding plotting window, while the non plotted signals are gray.

A signal can be added on an axis: click on the signal on the palette and keep the mouse left button pressed and move it on the button related to the axis. Any signal already located on this axis is deleted. Any signal already displayed on another axis is removed from the former axis. If this axis is the X axis, it is replaced by time. If a signal is located on an occupied axis, the former signal is automatically removed (indeed, only one signal is available per axis).

Double click on the button related to the axis to remove a signal from the axis. Then, double click on ***Remove from axis*** in the window that just opened (see *Figure 49).*

4. 2. Characteristics of the plotting window

The plotting window (Figure 48) is made up of a backcolor, seven axes, and a button to print the plotting in process. Double click on the backcolor window to obtain their properties.

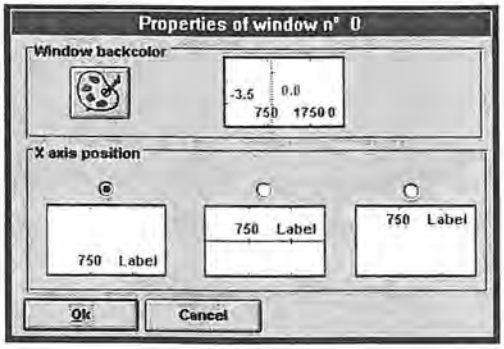


Figure 48 : Properties of the plotting window

The drawing backcolor and the X axis location can be modified. Double click on the button related to the axis properties to have them on the screen and then a window opens:

Figure 49 : Properties of an axis window.

Remark The window only opens if a signal is affected to the axis. The color of the axis can be modified as well as scales (the color of the affected signal is also modified). (see *Axis scales page 49*).

Remark A box ***Hide axis*** -to be ticked- also allows the plotting of the axis.

An axis is selected when the button related to this axis is ticked, otherwise the selection is removed. Selection will be a key notion when the signal is made up.

The print button located on bottom left in the plotting window is used to print the curve via the printer selected in the ***Experiment / Printer setup*** menu.

The button right to the print button is used to export the plotting in vectorial form in the clip board.

For example, to export the figure into Microsoft Word 6.0. follow the instructions hereafter:

- Export the plotting into the clipboard,
- Run Microsoft Word 6.0.,
- Create a new document and activate the ***Edit/Paste*** menu,
- Double click on the new object.

The plotting appears on the screen and it is possible to modify the color of a signal, the title of a curve...

To go back into the document, click on the ***Close Image*** button.

4. 3. Axis scales

When an experiment is closed, scales of each type of signal are saved.

When an experiment is open, signals can be plotted using the scales saved during the previous experiment or automatic scales (see Figure 40).

4. 3. 1. Automatic scales

The software can plot a signal on an axis using automatic scales. The minimum and the maximum of the signal between the first and the last valid point are searched and the axis scale is defined by:

- A minimum value that is slightly inferior to the minimum value of the signal.
- A maximum value that is slightly superior to the maximum value of the signal.
- A graduation interval providing for enough graduations on the screen.

One plotting signal only can have automatic scales, and two possibilities are available:

- Double click on the button corresponding to the axis where the signal is plotted, then the window shown on figure 8 opens, and finally, click on ***Automatic*** and ***OK*** respectively.
- Select the axis required (press the corresponding button and depress the others) and activate the ***Display / Automatic scales*** menu (or click on the corresponding icon located on the tool bar).

The latter possibility provides for automatic scales simultaneously calculated for several signals when the corresponding axes are selected before.

4. 3. 2. Manual scales

Double click on the axis button corresponding to the axis to define manual scales. A window opens and minimum, interval and final scales can be entered (see *Figure 49*).

Remark The value of the interval entered by the user may not be respected. Indeed, as wording never overlaps, some of them may not be displayed on the screen. That is the reason why the result displayed on the screen may be different from the printed one.

4. 3. 3. Zoom

First, select the axes to be zoomed.

Then select the ***Display / Zoom in*** menu or the corresponding icon located on the tool bar.

Press the mouse left button and select the upper left part of the screen and move to the lower right part to define the part of the plotting to be selected.

Several zooms can successively be done up to a maximum (a message appears on the screen).

If the X axis is selected, only this axis is zoomed, and the rectangle on the screen is as high as the plotting. Conversely, if the X axis is not selected, the rectangle is as large as the plotting window.

If axes having a signal are selected, the plotting after zooming is identical to the content of the rectangle selected on the plotting.

4. 3. 4. Former scales

When scales of an axis are modified, the software memorizes the scales formerly entered. Therefore, the last nine scales are memorized per axis.

Two possibilities are available to recall the former scales on the screen:

- Double click on the axis button where the signal is plotted, the window shown on Figure 49 opens, and then click on ***Previous*** and ***OK*** respectively.
- Select only the axis required (press the button and depress the others) and activate the ***Display / Previous scales*** menu (the icon can be clicked on the tool bar).

Advantage of the latter possibility: Automatic scales can be recalled for several signals when axes are selected before.

The nine scales formerly selected are deleted if the axis signal is removed. However, the last signal is memorized if the last make up is saved. That is why if a signal is replaced, the same scales are available but the ***Previous scales*** command is useless.

4. 4. Curve printing

Click on the button representing a printer, at the bottom left of the plotting window in order to print the information of this window. The printed document shows a header in addition to the plotting of curves.

it is recommended to use the landscape **presentation** before printing the document (the presentation can be modified with the ***Printer setup ...*** menu).

The document setup (margins) can be modified with the ***Experiment / Preview before printing...*** menu. Then a window opens :

Figure 50: Setup window

The setup window has a ***Header...*** button in order to modify the content of the header that is automatically created:

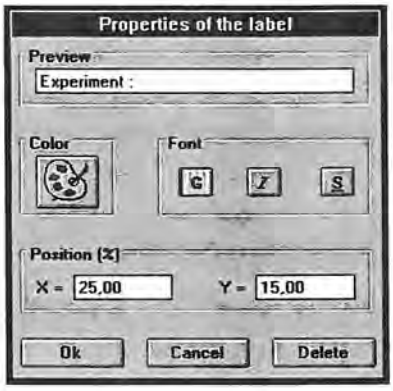


Figure 51: Header window

Double click on the header window to modify the various labels. A window opens:

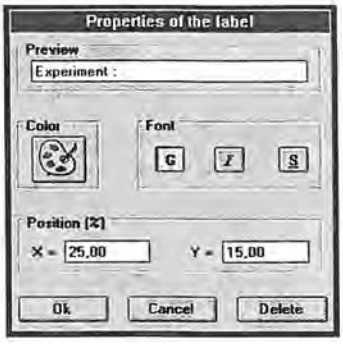


Figure 52: Properties of a label window

The content, the font, the color and the position of the label can be changed via this window.

4. 5. Writing comments on the plotting

Select the menu ***Display / Comments... / Write*** or the corresponding toolbar icon in order to write comments on the plotting. The usual speed of the mouse pointer changes. Then go to the plotting where the comment is to be inserted. Click once to open the comments window:

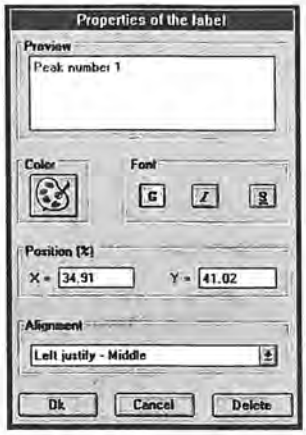


Figure 53: Comments window

Once the text is entered, click on ***OK*** and the comment is displayed on the plotting.

To modify the text, enter it as if it is a new text, but click on it.

Select the ***Display / Comments... / Move*** menu or the corresponding icon on the tool bar in order to move a comment. Then click on the text and move it while pressing the mouse left button.

4. 6. Superimposing experiments

Superimposing experiments requires their loading on the screen, setting up using the same scales and going to the window →superimposition menu.

Then a window displaying the superimposed signals appears. This window shows three buttons:

- a button to print the plot.
- a button to export the plot in the clipboard and integrating it in another software package (such as a word-processing package).
- a button to close the window.

Remark It is possible to superimpose up to four experiments.

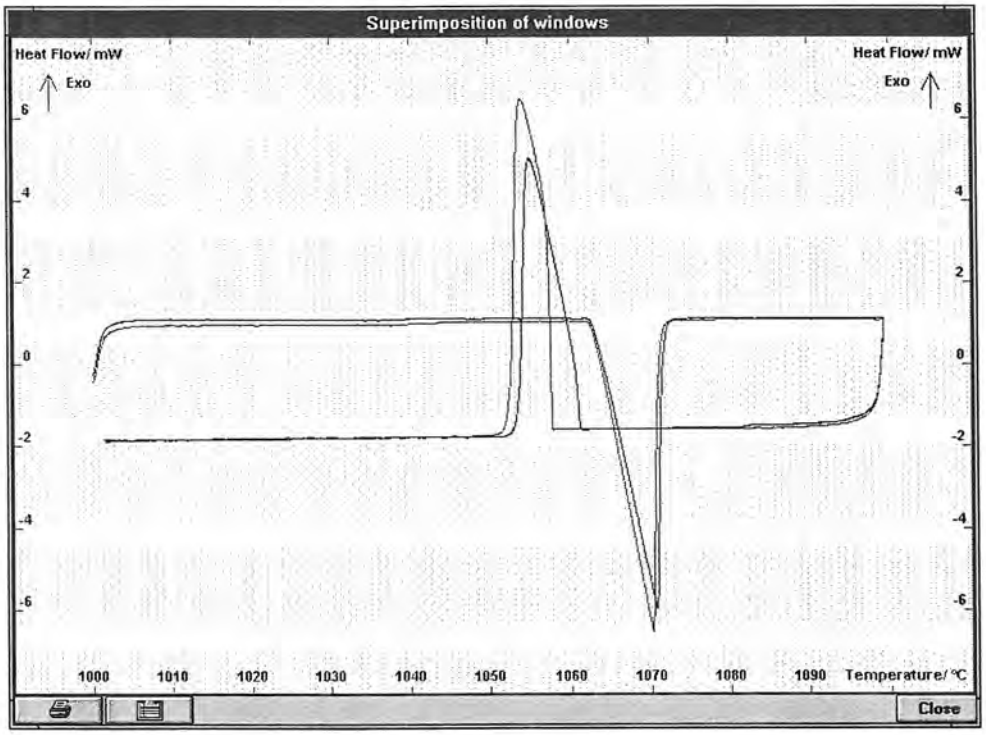


Figure 54: Superimposing two experiments

5. Subtracting a base line

5. 1. Running the correction

Subtracting a blank means subtracting signals of two experiments performed under the same conditions, but one with a sample (experiment to be corrected) and the other without (blank).

If the experiment is saved into sequences, the sequences must be corrected one after the other. Subtracting a blank generates new signals that are added to the experiment to be corrected.

Example :

Experiment carried out with a sample (experiment to be corrected) - sequences 1 to 3 :

1. Temperature signals:
   - Acquired temperature.
2. Heat flow signals:
   - Acquired Heat flow.

Experiment without sample (blank) - sequences 1 to 3 :

1. Temperature signals:
   - Acquired temperature.
   - Constant temperature
2. Heat flow signals:
   - Acquired Heat flow.
   - Constant Heat flow.

Load the experiment to be corrected (the one carried out with the sample) to subtract a blank. The above mentioned example is very simple because neither the part of the experiment, nor the signals to be corrected are to be chosen (only one part of the saved experiment and only one signal of each type).

Once loaded, select the ***Experiment / Subtract base row*** menu. A first window opens (shown on Figure 39) and the operation to be subtracted (blank) can be selected. Once the experiment is chosen, another window (shown on Figure 40) opens to chose:

- Possibly the part of the experiment to be subtracted if the « blank » experiment was saved into several sequences (no choice required in the above mentioned example).
- Signals to be subtracted in this part. The list of temperature signals is unactivated because temperature signals are not subtracted. But the user must

choose the Heat flow signal to be subtracted (acquired Heat flow or constant Heat flow of the blank).

Once selected, the corrected Heat flow is displayed on the screen. The signal is as long as the shortest of the two signals.

Remark Various signals are subtracted for the various instruments:
- the Heatflow signals
- the TG signals
- the Pressure signals

5. 2. The correction is done

Once corrected, the signal appears on the screen and is displayed in the palette, named ***Heat flow corrected***. Then the user has two Heat flow signals in the plotting window and therefore he cannot calculate integration or glass transition. He can choose:

- Either to delete the new signal.
- Or to save it.

Double click on the Heat flow signal that is corrected on the palette in order to do so. Then, the window shown on Figure 42 opens.

5. 2. 1. Deleting the new signal

Click on ***Delete*** to delete the signal from the palette.

5. 2. 2. Saving the new signal

Click on ***Save as...*** to save the corrected Heat flow signal. A window opens and the new signal can be named. For instance, the signal can be named ***Heat flow corrected***. Once this name is entered, click on ***OK*** in the window shown on Figure 42 to validate.

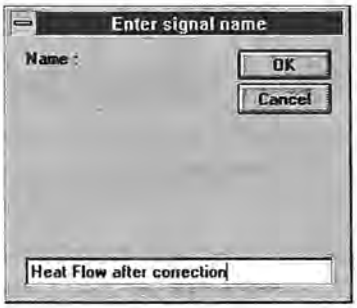


Figure 55 : Window used to enter the saved signal name

Then, the non corrected Heat flow signal and its derived signal are unloaded and the derivative of the Heat flow signal after the correction is automatically

generated. The new signal is called ***Heat flow*** instead of ***Heat flow corrected*** in the palette.

Let us take the previous example where the experiment after correction is made up of the following signals:

Experiment with sample (experiment after correction) - sequences 1 to 3 :

1. Temperature signals:
   - Acquired temperature.
2. Heat flow signals:
   - Acquired Heat flow.
   - Heat flow after correction.

Corrected signals can now be processed.

6. Selecting points

6. 1. Role

Before performing several processing operations (such as integration, glass transition, etc.), select points on a curve (e.g. 2 or 3 points on the Heat flow curve for an integration, 2 points on the TG curve for a mass loss, 2 points on the Heat flow curve for a glass transition).

In order to perform it, make sure that the Heat flow is displayed on the plotting window and select the chosen processing operation in the menu or on the toolbar. Then, a window opens:

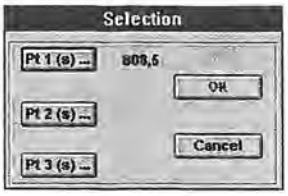


Figure 56 : Selection of points after one point is selected.

Two or three points can be selected on the curve. As soon enough points are selected, the ***OK*** button turns gray.

6. 2. Selecting a point

Click on one of the pt 1, pt 2 or pt 3 buttons to select a point. The selection window is displayed as follows:

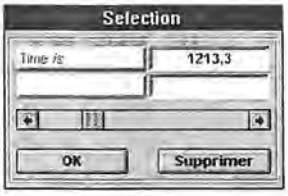


Figure 57 : Point selection window when a point is selected.

A vertical bar moves toward the middle point of the curve if no other point is selected before or on the selected point if any. Use the horizontal bar located on the bottom of the window to change the selection.

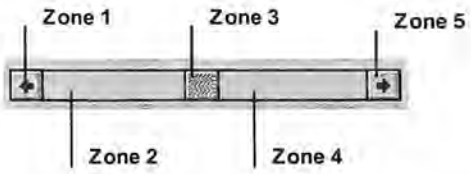


Figure 58 : Selection bar for a point

The square (zone 3) shows the location of the cursor (time) compared to the total deviation of the signal. The lift length shows the total duration of the experiment.

Several possibilities are available to move the cursor:

- Click on zone 3 and press the mouse until a new location is reached.
- Click on zones 1 and 5 arrows. The cursor moves toward a point when clicked. Press the mouse to move faster.
- Click on zones 2 and 4. The cursor moves toward 1% of the signal total length. Press the mouse to move faster.

Values such as current time and temperature at the location of the cursor are displayed.

Once the point is selected, click on ***OK*** to validate or on ***Delete*** to delete it. Then the window shown on Figure 56 is recalled on the screen.

On the plotting a point in the selection process is symbolized by a vertical bar as high as the plotting; a point that is already selected is symbolized by a small vertical mark.

If the same point is selected twice, one of them is automatically deleted. Once selected, points are rearranged as followed: Pt1 < Pt2 < Pt3 (values given in time). When an additional point is selected, its location is that of the previous point.

Remark The selection bar of a point may not be displayed if the point is selected outside the visible signal or if the signal where the selection is made is not plotted.

7. Signal Integration

7. 1. Running an integration

Before treating the integration, plot the signal to be integrated and activate the plotting window with the signal.

This software can integrate two types of signals: Heat flow and dTG signals.

Then select either the ***Processing/Integration/ on Signal Heat flow*** menu or ***Processing/Integration/on Signal dTG*** menu. The icon corresponding to the first menu is also on the tool bar.

The window used to select points opens and the integration delimiters (two points and a possible intermediary point if a double peak occurs). Once the points are selected, the integration window opens:

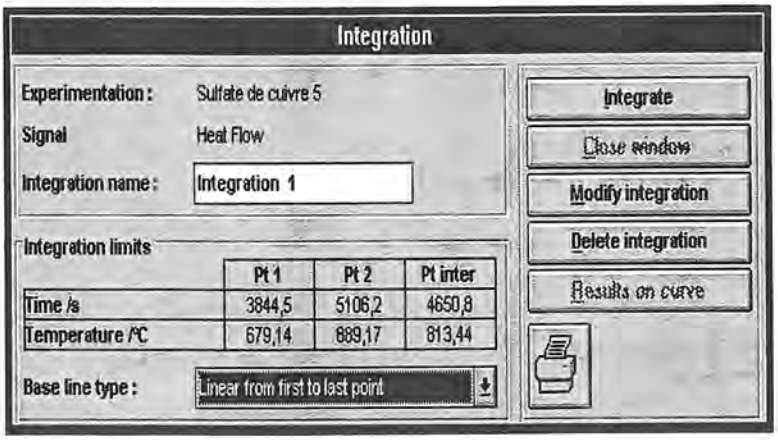


Figure 59 : Integration window before a base line is selected.

The window displays :

- The name of the experiment.
- The name of the signal (saved name).
- A name automatically generated but which can be modified to mark out the integration. (***Integration 1***).

- Selected points (values in time and temperature).

Several buttons are available:

- To print the window.
- ***Modify integration*** to modify the integration (back to the window shown on Figure 56 to modify the selected points).
- ***Delete integration*** to delete the integration that is currently processed.
- ***Integrate*** to start the calculation of the integration.
- ***Results on curve*** to print some results of the integration on the plotting.

The base line to be used for the integration can be selected via the integration window. Various types of line are available:

- ***Linear from first to last point*** : the base line is a straight line joining the two extreme points selected on the curve.

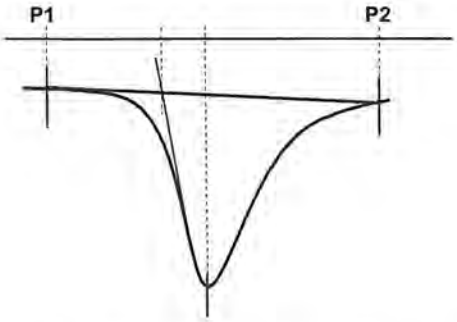


Figure 60 : «Linear from first to last point» base line type

- ***Horizontal drawn from first point*** : integration in relation to a horizontal line passing through the first selected point.

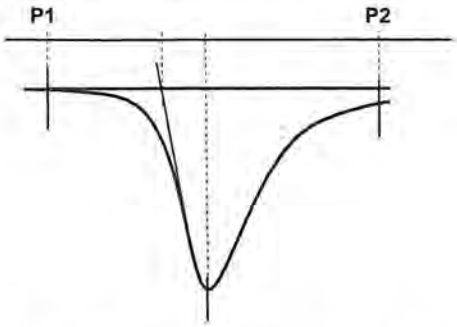


Figure 61 : «Drawn from first point» horizontal base line type

- ***Horizontal drawn from last point*** : integration in relation to a horizontal passing through the last selected point.

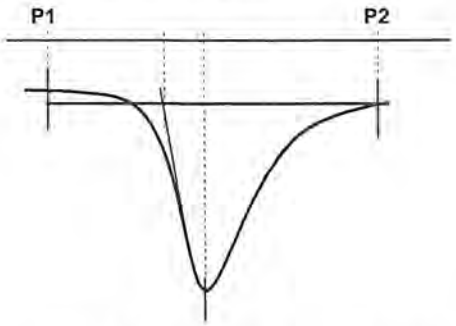


Figure 62 : «Drawn from last point» horizontal base line type

- ***Equal to zero*** : integration in relation to the original base line (signal = 0).

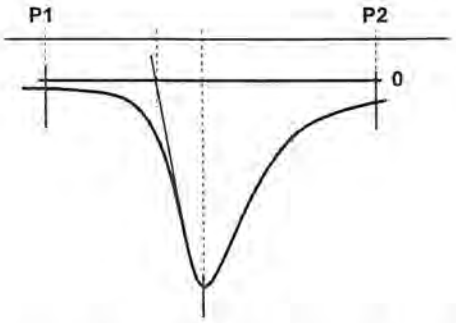


Figure 63 : «Equal to zero» base line

- ***Curve base line*** : curvilinear integration taking account of the variation in specific heat before and after transformation.

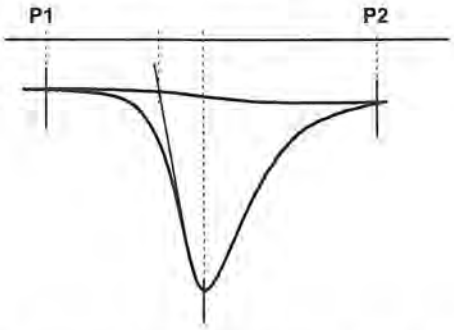


Figure 64 : «Curve base line» base line

7. 2. Calculating the integration

Click on the ***Integrate*** button to calculate the integration. A message informing that the selected points are modified may appear if the points selected are too close or close to the signal extremity for certain base line types.

Once the integration is calculated, the window shown on Figure 65 is enlarged to show the results of the integration.

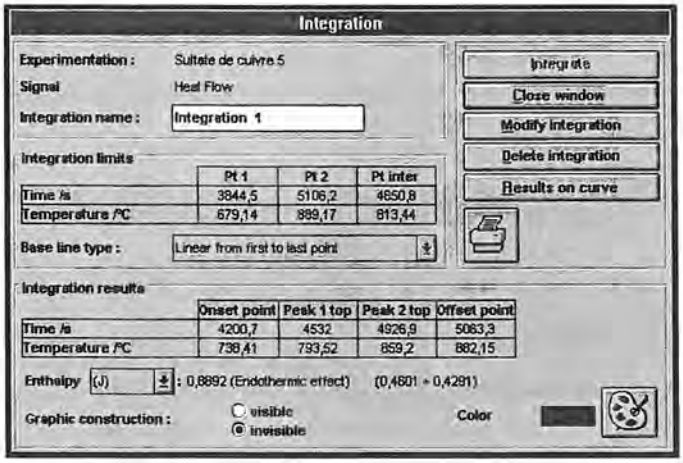


Figure 65 : Integration window once the integration is calculated

Simultaneously, a graphic is shown on the curve and may be found behind the window. Click on ***Close window*** to close the window. The integration is then displayed on the palette.

7. 3. The integration is calculated

A graphic is plotted to preview:

- The selected points.
- The base line plotting.
- One (or more) peak's top.

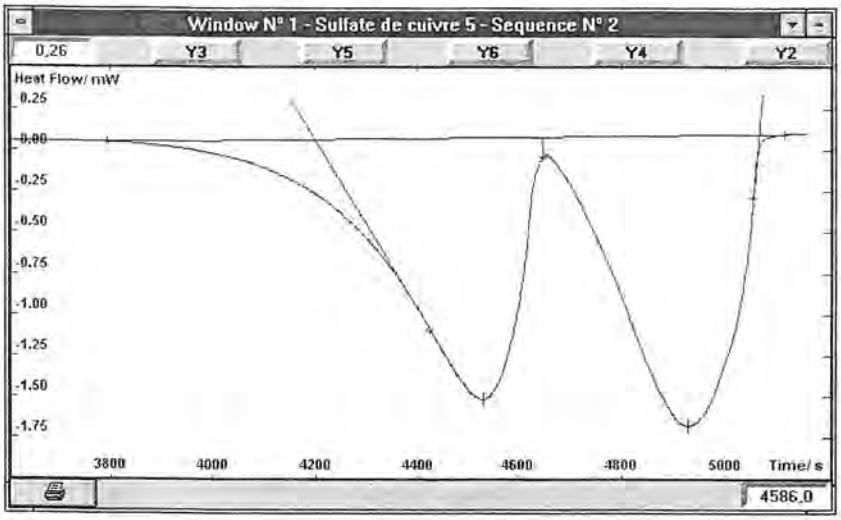


Figure 66 : Integration plot

The user can display Figure 65 at any time: double click on the integration name on the palette. Several possibilities are available from this window:

- Click on the palette to change the color of the graphic.
- The plotting of the graphic may be invisible.
- Preview the value of enthalpy in the various units.
- Double click on the ***Modify integration*** button to modify the integration conditions (selected points, base line type).
- Click on the ***Delete integration*** button to delete the integration.

Remark ***Delete integration*** definitely deletes the integration (results are lost), while the ***Close window*** button simply closes the window.

7. 4. Running another integration

The user can simultaneously calculate several integrations on the same signal. The various integrations calculated can be listed on the palette and each integration can be named.

Using the first integration, the user may:

- Modify it if not satisfactory: click on ***Modify integration*** shown on Figure 59 and the former integration is then lost.
- To create a second integration in order to compare it with the first one: click on the first integration displayed in the palette to select it (click once only) and go to the ***Integration*** menu to start with the points selected in the first integration.

Remark The selection of an integration in the palette displays the word ***Integration*** in the selected color.

8. Glass transition

8. 1. Calculating a glass transition

Before performing a glass transition, plot the Heat flow signal and activate the window showing this signal. Then select the ***Processing / Glass transition*** menu or click its icon on the tool bar. The point selection window opens and the glass transition delimiters can be chosen (two points). Once the points are selected, the calculation of the glass transition can be calculated and the glass transition window opens:

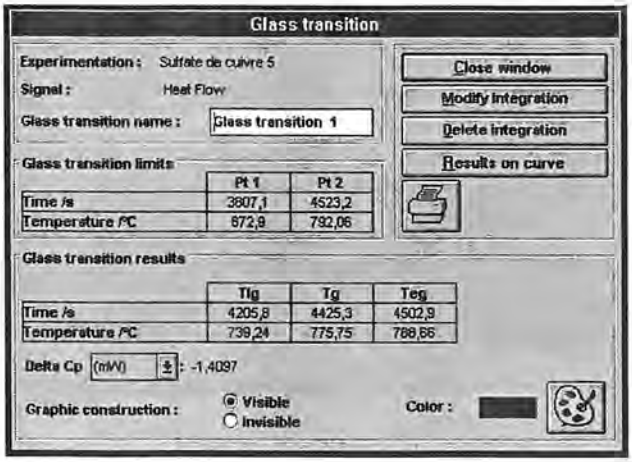


Figure 67 : Glass transition window

The window shows:

- The name of the experiment.
- The name of the signal (the saved one).
- A name is automatically given -and can be modified- to track the glass transition (***Glass transition 1***).
- The points selected (values in time and temperature).

and displays the results of the glass transition:

- ***Tig***, ***Tg*** and ***Teg*** points.
- The ***Delta Cp*** values in the various units.

8. 2. The glass transition is performed

Several buttons are available on the window:

- To print the window.
- ***Modify glass transition*** to modify the glass transition (go back to the window shown on *Figure 55* to modify the selected points).

- ***Delete glass transition*** to delete the glass transition in process.
- The color of the graphic structure can be modified via a button and can be visible or invisible via another one.
- ***Close window*** to close the window and preview the graphic structure of the plotting window.
- ***Results on curve*** to print some of the results of the glass transition on the plotting.

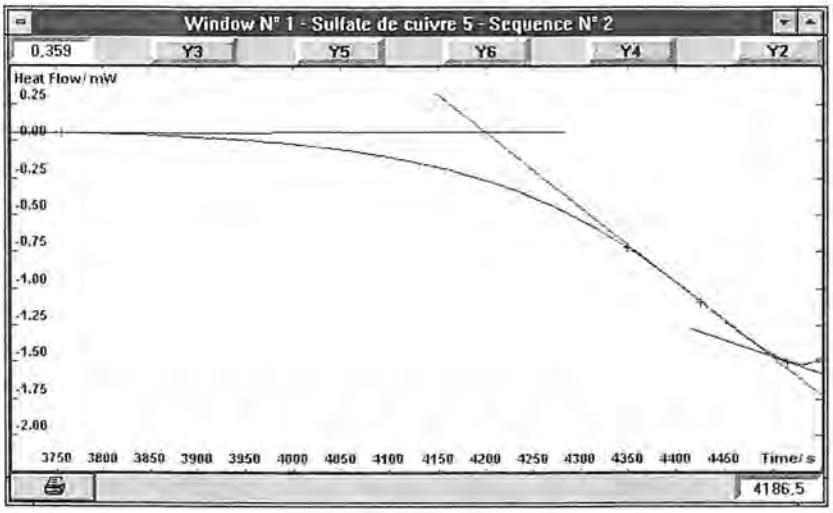


Figure 68 : Glass transition plotting.

The glass transition is therefore displayed in the palette; double click on its name to recall Figure 67.

Like the integration, the user can perform a second glass transition that is quite similar to the first one: click on the palette to select it and go to the ***Glass transition*** menu. The points used in the first transition are displayed.

9. Mass Variation

9. 1. Running a mass variation

Before calculating a mass variation plot the TG signal and activate the window containing this signal. Then select the ***Processing / Mass variation*** menu or click on the corresponding icon on the tool bar. The selection of points window opens and the limits of the mass variation can be selected (2 points). Once these points are selected the mass window opens:

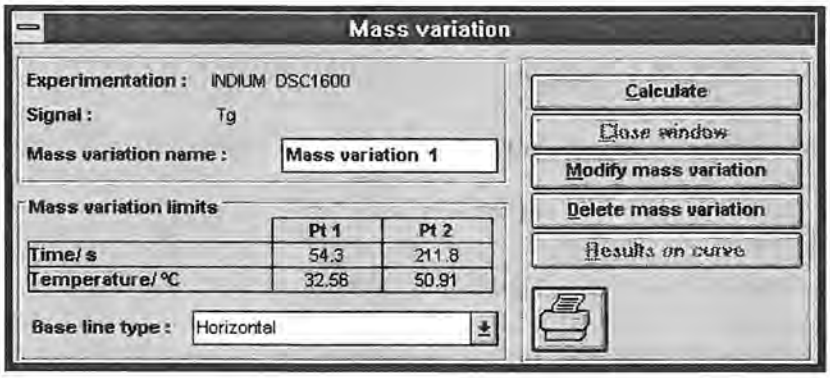


Figure 69 : Mass variation window before a base line is selected

The window displays:

- The name of the experiment,
- The name of the signal,
- A name is automatically generated but that can be modified to mark out the mass variation (***Mass Variation 1***),
- Selected points (values in time and temperature).

Several buttons are available:

- To print the window,
- ***Modify mass variation*** to modify the mass variation (go back to the window shown on Figure 56 to modify the selected points),
- ***Delete mass variation*** to delete the mass variation that is being processed,
- ***Calculate*** to start the calculation of the mass variation;
- ***Results on curve*** to print some results of the mass variation on the plotting.

The base line to be used for the mass variation can be selected via the mass variation window. Two types of line are available:

- ***Horizontal***

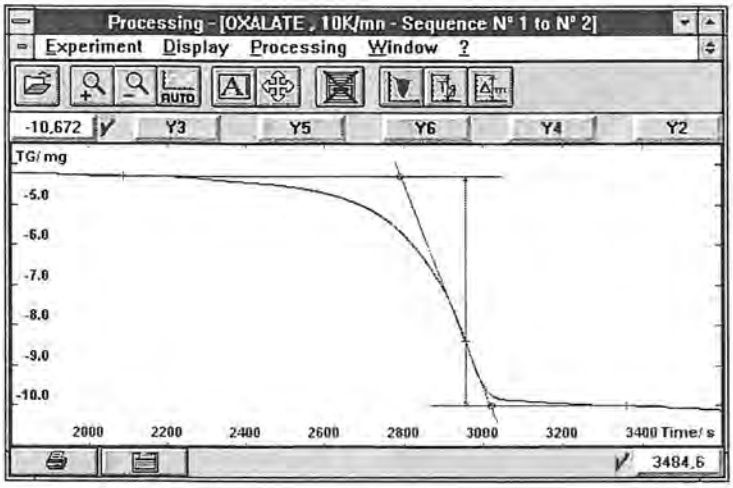


Figure 70: Horizontal base line

- ***Tangent***

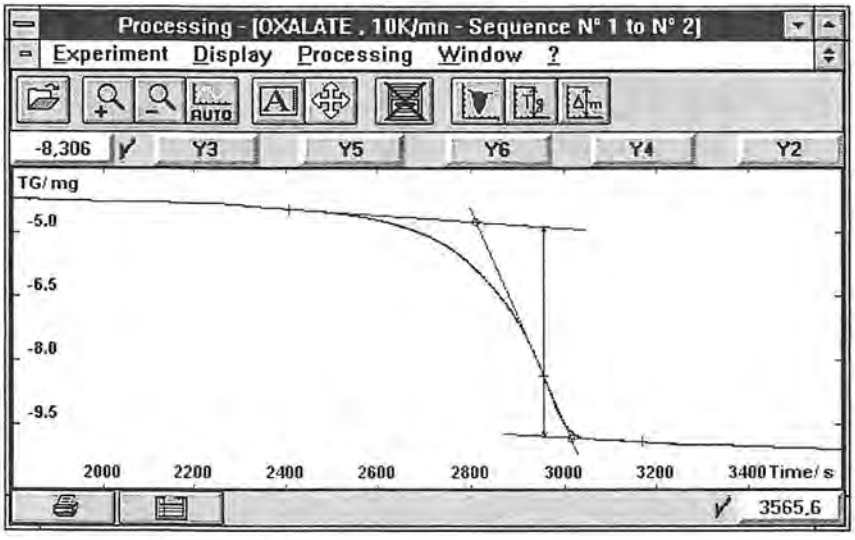


Figure 71: Tangent base line

9. 2. Calculating the mass variation

Click on the ***Calculate*** button in order to calculate the mass variation.

Once the mass variation is calculated, the window shown on Figure 69 is enlarged to show the results of the mass variation.

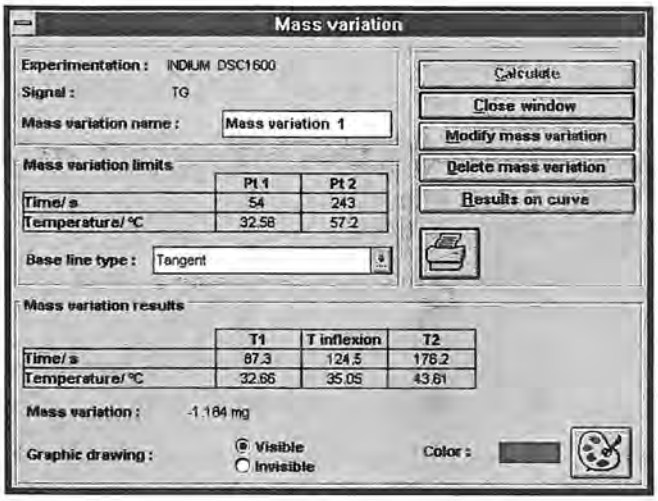


Figure 72: Mass variation window

A graphic is simultaneously shown on the curve and is to be found behind the window. Click on ***Close window*** to close the window. The mass variation is then displayed on the palette and the window shown on Figure 72 can be called again when double clicking on the name.

A second mass variation -which is almost similar to the first one- can be carried out as follows: Select the mass variation in the palette (click once) and go to the ***Mass variation*** menu. The points that were previously selected during the first mass variation process are displayed.

10. Temperature correction

10. 1. Principle

The temperature read on teh thermogramme corresponds with the temperature of the measurement thermocouple which is located close to the sample. To take the response time into account, a first temperature correction, which mostly depends on the scanning rate must be applied and is :

$dt=b0+b1.T+b2.V+b3.V^2$

where T: temperature in °C

V: temperature scanning rate in $K.min^{-1}$

Teh coefficients b0, b1,b2 and b3 must be entered in the ***Parameters window*** (window #4) before running the experiment.

These coefficients are determined by the base processing software ***(Processing/temperature correction determination*** menu).

10. 2. Utilisation

Select the ***Processing/temperature correction determination*** menu, then a window appears:

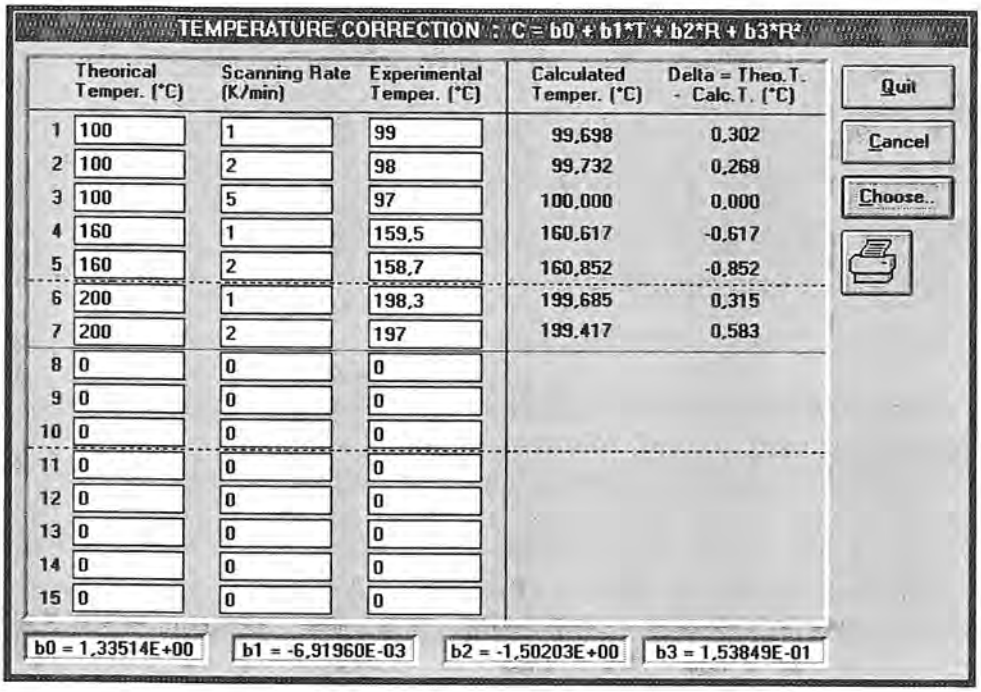


Figure 73: Determination of the temperature correction coefficients

Every thing is done simultaneously on this spread sheet: coefficients are entered and calculated.

First, a minimum of 4 triplets representing 2 different temperatures and 3 different scanning rates must be entered and then, a coefficient calculation is displayed. A maximum of 15 triplets is available. The zero value in the scanning rate is considered as a stop test. Therefore, only the triplets entered before this value are taken into the calculation.

Various buttons are available:

- ***Quit***: saves the entered values before quitting the window
- ***Cancel***: does not save the values when quitting the window
- ***Choose***: to modify the degree of the calculated polynom

The degree of the polynomial is chosen via the following window:

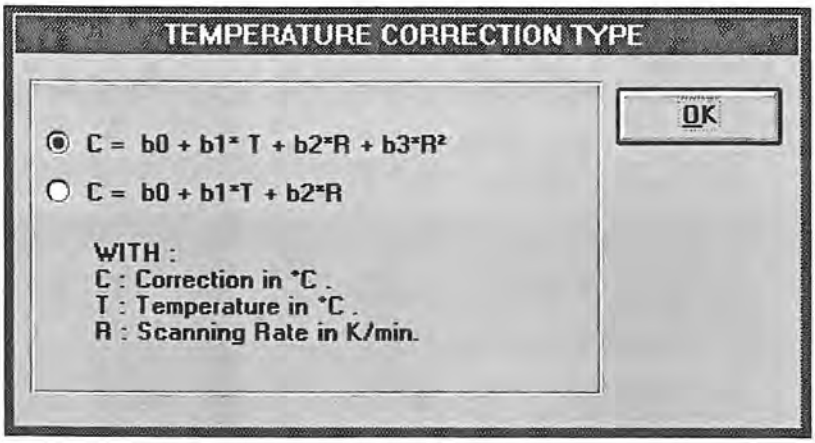


Figure 74: Choosing the degree of the correction polynomial

11. Regression

11. 1. General

An y=f(x) type monovariable modelisation under different formats from -3 degreee up to +5 degree can be performed using this option.

11. 2. Utilisation

When selecting the ***Processing / Regression*** menu a window is displayed :

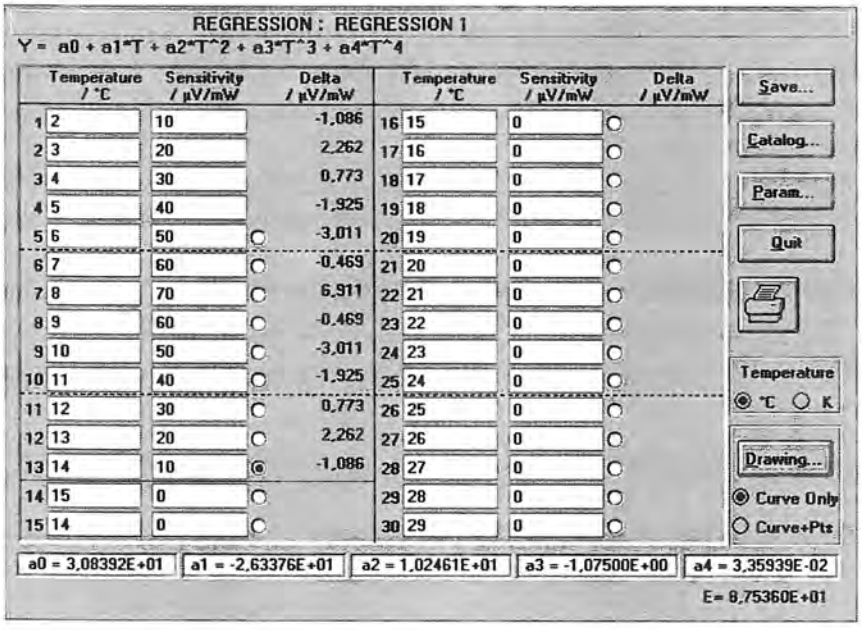


Figure 75: Regression

This spreadsheet provides for entering the points (x,y) as well as the coefficient calculation simultaneously.

In the case of regression, 6 points at least (Temperature, Sensitivity) representing 6 different temperatures must be entered in order to determine the sensitivity curve.

The radio button on the right of a point (x,y) gives the number of points taken into account for the calculation. A red line located below the latest selected point (x,y) shows where the user wants to stop the calculation.

A maximum of 30 points (x,y) can be entered.

Temperatures can be switched from °C to K when selecting the corresponding radio button.

Plotting can be performed via the ***Drawing*** button. But before, the user must select if the regression curve alone will be plotted (select ***Curve only***) or the curve plus the experimental points.

Various buttons are displayed:

- ***Save...*** : to save the current regression
- ***Catalog...*** : to reload a regression previously stored
- ***Param...*** : to change the regression parameters
- ***Quit*** : to quit the processing of the regression. ***Warning*** : remember to save the regression ***before*** if supposed to be kept.

The type of regression as well as the label of the Y axis can be selected via the following window:

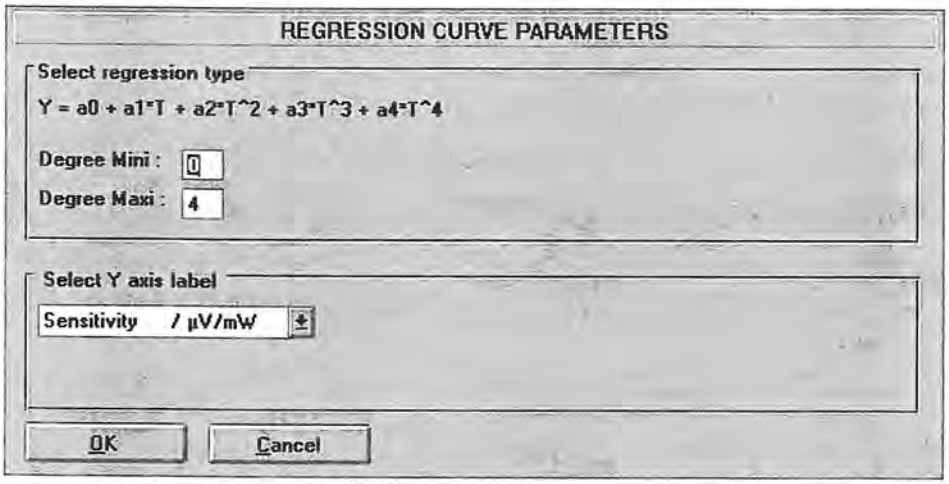


Figure 76 : Regression parameters of the curve

- Select the minimum degree and the maximum degree. For instance, a minimum degree of 0 and a maximum of 4 allow to compute a curve with a sensitivity of the following form : $Y = a_0 + a_1 . T + a_2 . T^2 + a_3 . T^3 + a_4 . T^4$. This is possible between the limits of the degrees -3 and +5.
- A predetermined label can be selected for the Y axis (ex. Cp/J/g . K) or a user label can be defined. In this case select ***User...*** and then enter the name of the Y axis as well as its unit.
- Click on the ***Ok*** button to save the modifications and go back to the previous window.

The following window allows to select a regression previously stored (***Load regression***) or to save the current regression (***Save regression***):

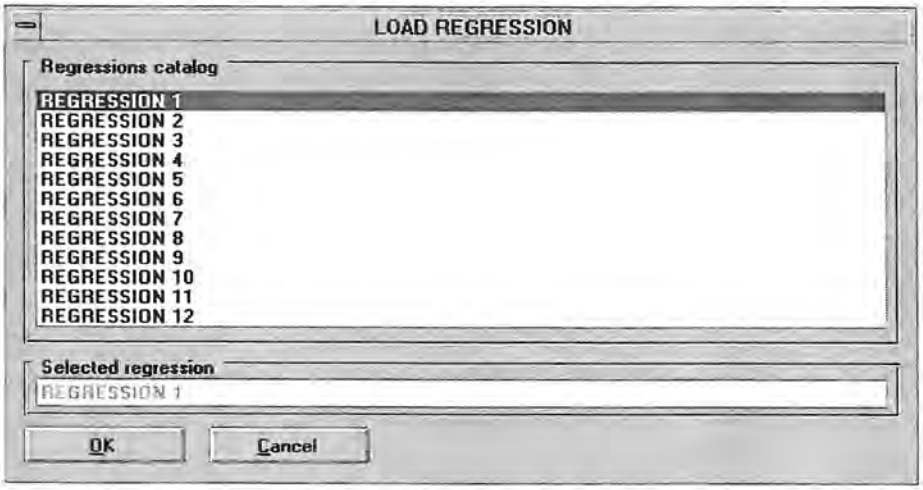


Figure 77 : Selecting a stored regression

- Click on the ***Ok*** button to select the regression.

12. Annexes

12. 1. Commands of the menu

12. 1. 1. Experiment menu

❑ **Open an experiment**

(see *Loading an experiment page 38*).

❑ **Close an experiment**

(see *Unloading an experiment page 40*).

❑ **Print current procedure**

To print the heating procedure of the loaded experiment.

- **Change signal**

  A signal can be modified once the experiment is loaded (e.g., the acquired Heat flow can be replaced by the corrected Heat flow signal).

- **Subtract base line**

  (see *Subtracting a base page 54*).

- **Preview before printing**

  To modify the setup (see *Curve printing page 51*)

- **Printer setup...**

  The printer can be setup via this menu (e.g., when the printer is changed).

- **Quit**

  To close the processing application.

- **At the end of experiment menu**

  The last 4 experiments are listed.

12. 1. 2. Display menu

- **Zoom in**

  To zoom a screen (see *Zoom page 50*).

- **Previous scales**

  To display the previous scales (see *Former scales page 50*).

- **Automatic scales**

  Automatic scales are defined (seeAutomati *page 49*).

- **Preferences / Tool bar**

  To display or remove the toolbar.

- **Preferences / palette**

  To display or remove the palette.

- **Comments... / Write**

  To write comments on the plotting (see *Writing comments on the plotting page 52*).

- **Comments... / Move**

  To move comments on the plotting.

12. 1. 3. Processing menu

- **Integration**

  To treat an integration (see *Processing/Integration/ on Signal Heat flow* page *32*).

- **Glass transition**

  To perform a glass transition (voir *Glass transition page 63*).

- **Mass variation**

  To perform a mass variation (see *Mass page 64*)

- **Temperature correction determination**

  To calculate the temperature correction coefficients (see *Temperature correction page 67*)

- **Regression / Cp Regression**

- **Regression / Sensitivity Regression**

12. 1. 4. Window menu

- **Cascade**

  To rearrange the plotting windows in cascade mode.

- **Tile**

  To rearrange the plotting windows in title mode.

- **Arrange icons**

  To rearrange the icons in the plotting windows.

- **Superimposition**

  To superimpose the open plotting windows (this menu is displayed when 2 experiments at least are loaded).

- **At the end of Window menu**

  To list the open plotting windows.

12. 2. Commands on the toolbar

Each icon displayed on the toolbar refers to a command in the menu, such as:

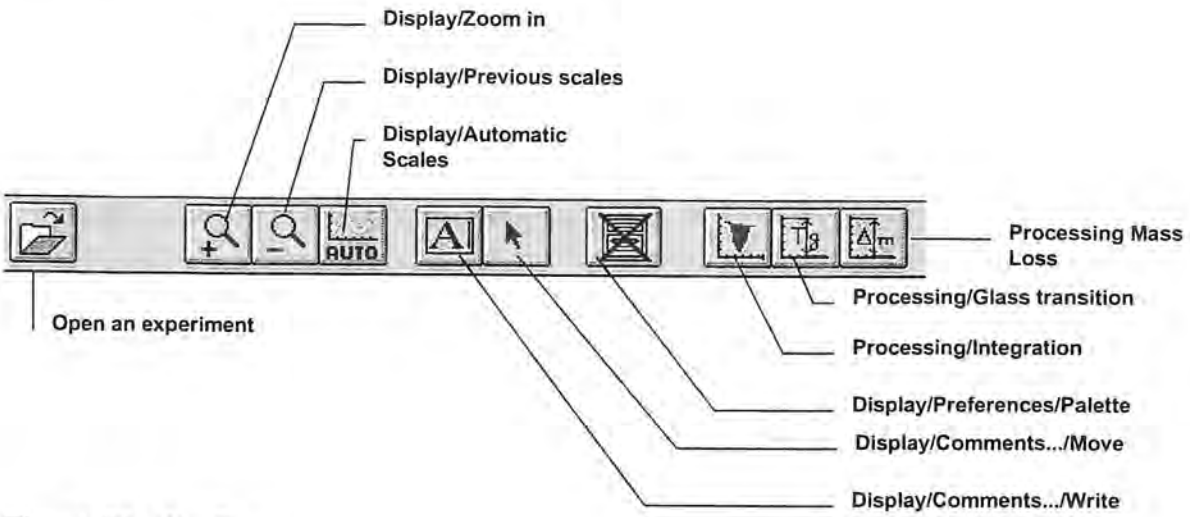


Figure 78 : Toolbar

13. Application

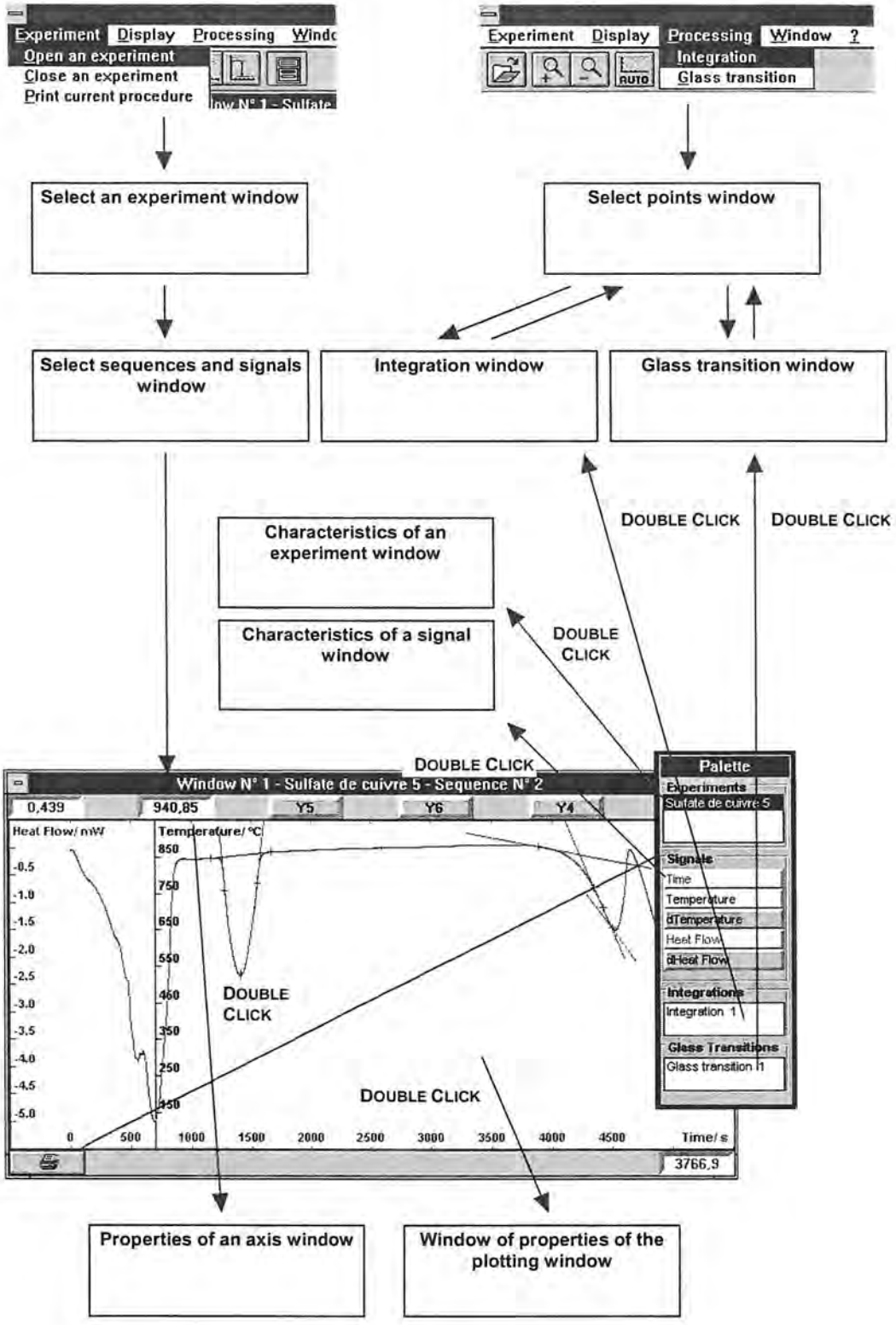


Figure 79 : Processing module

CHAPTER 4 - DATA MANAGEMENT

Double click on the ***Database Tools*** application icon in order to run the software.

1. Printing an experiment

Select the ***Experiment/print*** menu. Then a window opens and the experiment to be printed can be selected (see Figure 80) . For more information on the selection window see ***Selecting an experiment*** in Chapter 3, paragraph 1. 2..

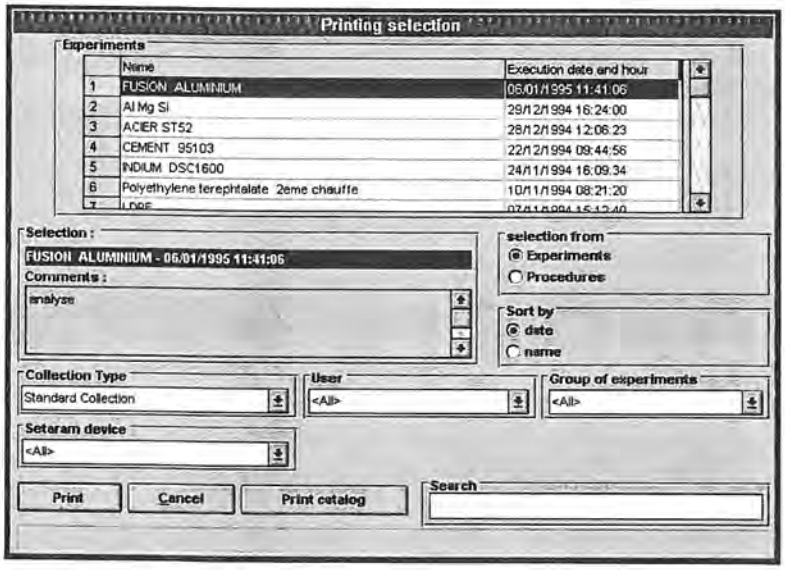


Figure 80: Experiment selection window

Two possibilities are available to validate the experiment:

- Select the experiment and click on **Print**
- Double click on the name of the experiment

A window opens (see Figure 81) and sums up the conditions of the experiment. For more information see Chapter 2 - Data Collection, Paragraph 1. 10. 1. ***Printing the current experiment conditions***.

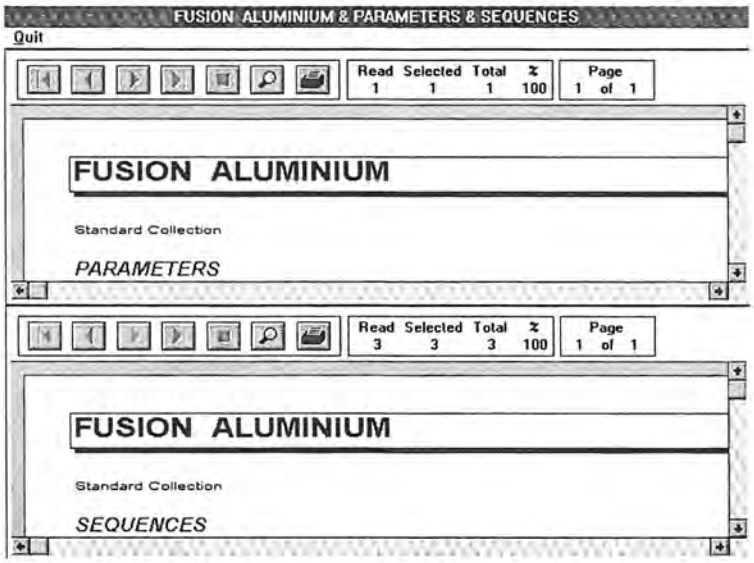


Figure 81: Experimental conditions printing window

Then click either on  to print one of the two zones of the window or on ***Quit*** to close the window.

2. Deleting an experiment

Select the ***Experiment/Delete*** menu to delete an experiment or a procedure, the following window opens:

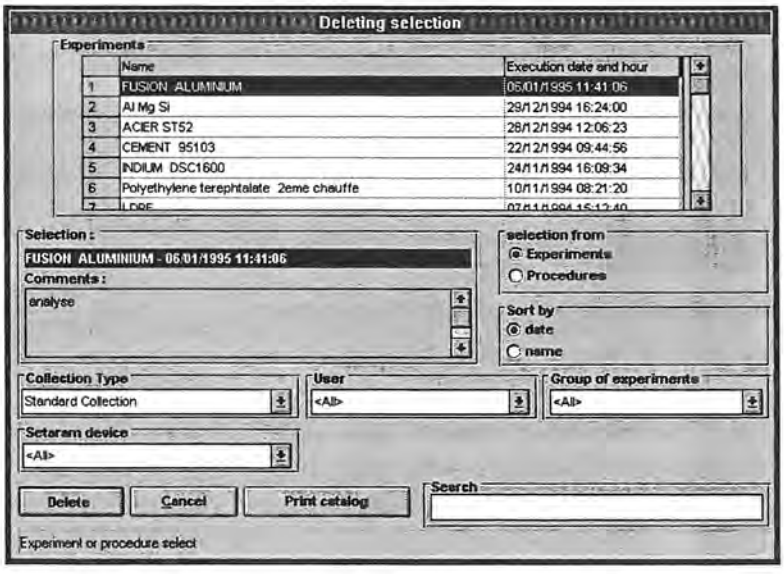


Figure 82: Select procedure/experiment window

The contents of this window is similar to that of Figure 80. Click on ***Delete*** to delete the selected experiment (or procedure).

WARNING When an experiment is deleted, its experimental conditions as well as the points stored during the experiment are deleted.

3. Modifying an experiment

Select the ***Experiment/Modify*** menu and the experiment selection window appears (see Figure 83)

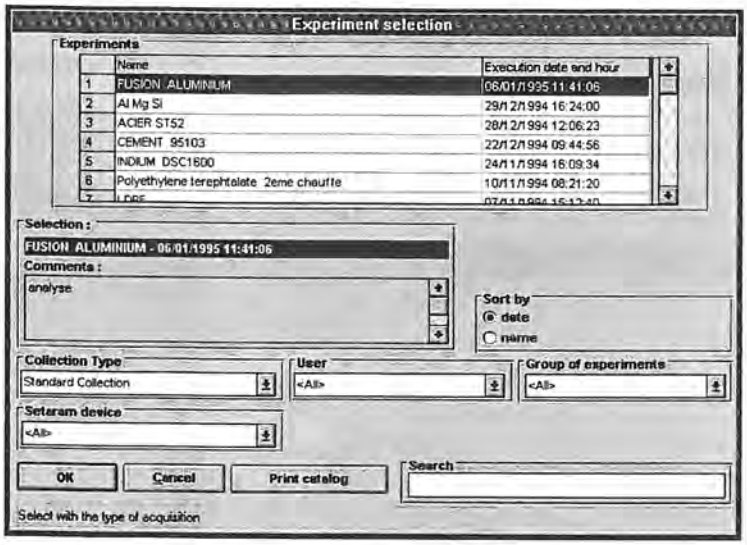


Figure 83: Experiment selection window

Select an experiment and click on ***OK***.

The open window allows to modify (see Figure 84):

- Name of the experiment
- Comments on the experiment
- Name of the procedure used with the experiment
- User's name
- Group of experiment
- Atmosphere, probe or crucible (according to the instrument)
- Mass, length or section (according to the instrument)

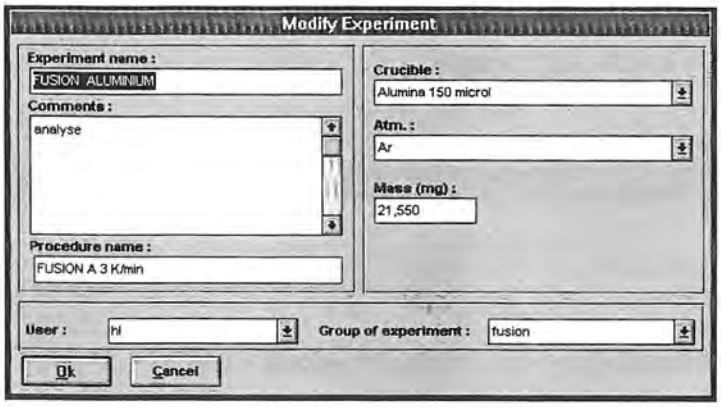


Figure 84: Modify an experiment

4. Archiving an experiment

Select the ***Experiment/Store*** menu. The following window appears:

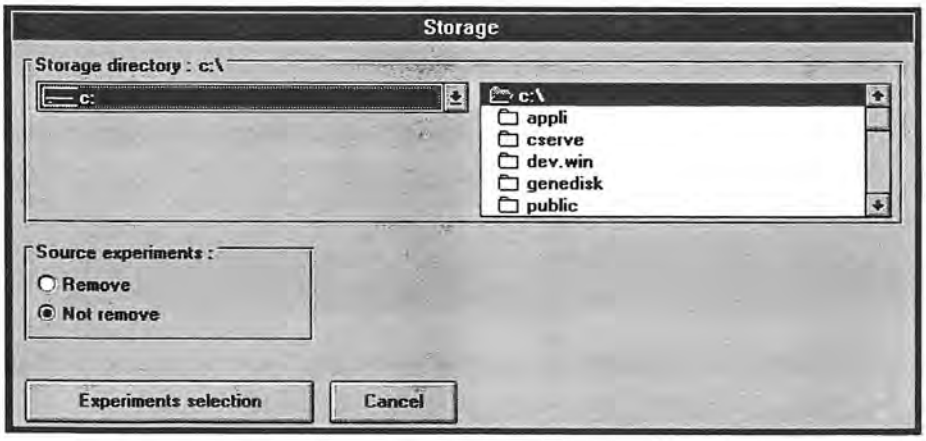


Figure 85: Storage of an experiment

This window allows to select:

- the archiving drive (disquette, computer hard disk or network drive)
- the directory where the experiments will be stored (to be created via the file manager if it does not exist)
- the archiving method (deleting or keeping experiments that were exported)

If the directory selected already contains experiments, the window content is slightly different:

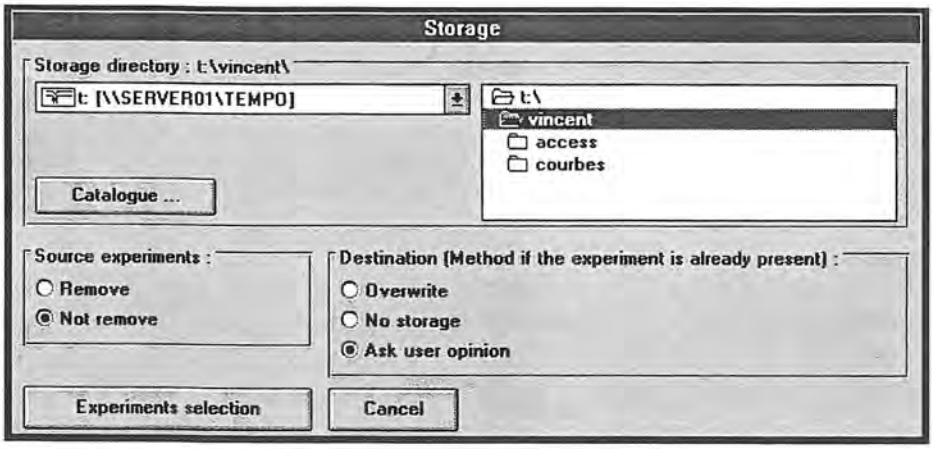


Figure 86: Storage in a directory containing experiments

In the ***Storage directory*** a ***Catalogue*** button used to display the content of the saving directory (and even to delete experiments) appears.

Another frame ***Destination*** also appears and gives teh instructions to follow if the experiment which is being exported is already in the saving directory: the software overwrites the former version or does not perform the archival storage or ask the user.

Then click on the ***Experiments selection*** button to choose the experiments to archive in the catalogue.

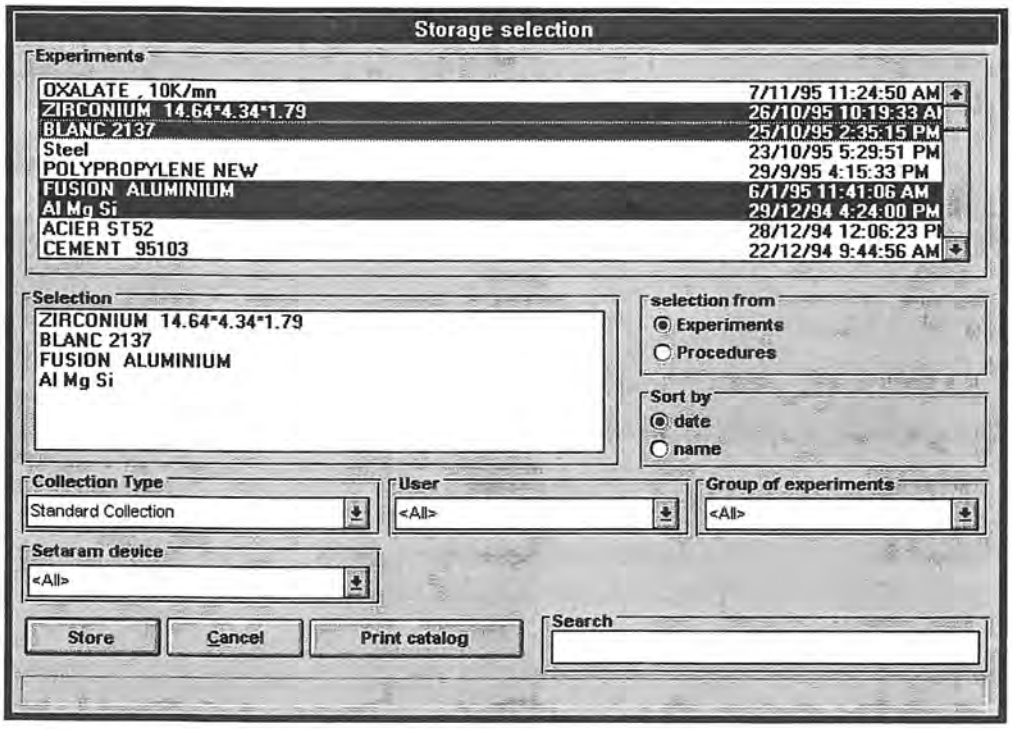


Figure 87: Catalogue of experiments

The ***Store*** button allows to run the archival storage.

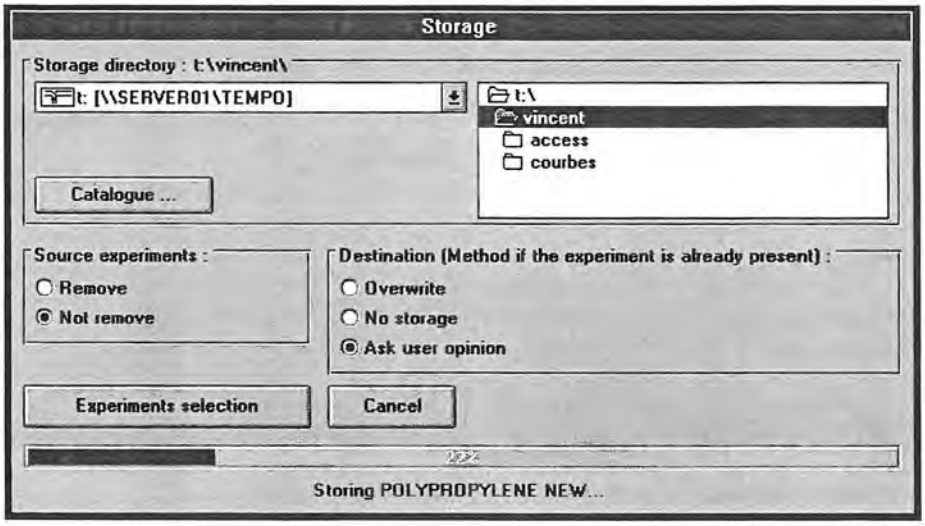


Figure 88: Running the storage

Note If there is not enough place in the destination directory, a window appears to inform the user, then the catalogue is displayed and the experiments that cannot be exported there are selected.

When archiving, the following message might appear: ***Time out, impossible to store the experiment*** if another computer is also archiving or restoring in the same directory. Re-run the storage.

Note During the storage, two sub-directories are created in the selected directory: one ***/curves*** directory and one ***/access*** directory.

5. Restoring an experiment

Select the ***Experiment/Store*** menu. The following window appears:

Figure 89: Restoring an experiment

This window allows to select the drive and the directory where the experiments are stored (disquette, computer hard disk ou network drive). When the selected directory contains experiments the ***Experiments selection*** is no longer in grey.

This window also allows to choose the restoring method if the experiment to restore is already there (same name, same time): the experiment is overwritten or not restored or the user is questioned about it.

Click on the ***Experiments selection*** button to select the experiments to restore and on the ***Restore*** button to run the restoring operation.

Note The directory to be selected is the one created during the storage. Do not select the ***/curves*** or ***/access*** sub-directories.

Note The saving directory must be in writing-reading access.

6. Restoring a DOS experiment

Select the ***Experiment/Restore DOS experiment*** menu. The following window appears:

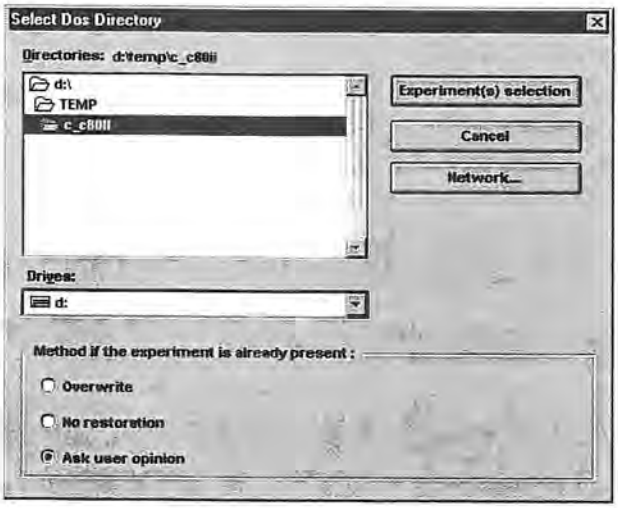


Figure 90 : Restoring a DOS experiment

This window allows to select the drive and the directory where the DOS experiments are stored (disquette, computer hard disk or network drive). When the selected directory contains experiments, the ***Experiment(s) selection*** button is no longer in grey.

This windows also allows to choose the restoring method if the experiment to restore is already there (same name, same time) : the experiment is overwritten or not restored or the user is questioned about it.

Click on the ***Experiment(s) selection*** button to select the DOS experiments to be restored.

The following window appears:

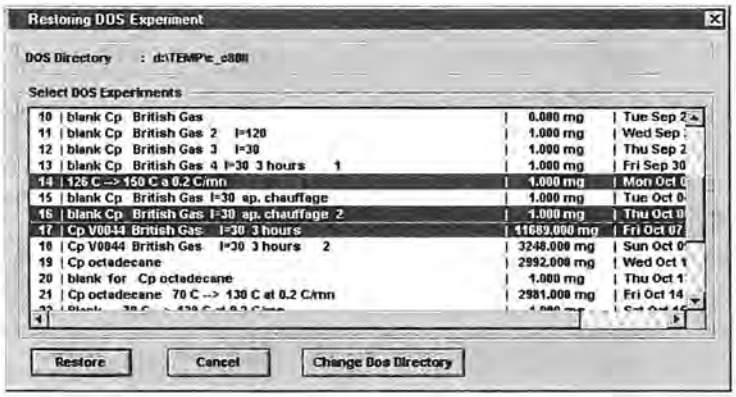


Figure 91 : Restoring a DOS experiment

This window allows selecting one or several DOS experiments :

- The first digital field gives the number of the DOS file (similar to the one found in the DOS software),
- The second field gives the name of the experiment,
- The third field gives the mass (in mg) of the sample for the DTA or DSC, TG type experiments or the length (in mm) for the DTA-type experiments,
- The fourth field gives the date and time of the DOS file saving (corresponding to the date of the experiment if the file has not been copied or modified) .

The user can select another DOS directory via the ***Change DOS Directory*** button.

Running the restoring process is possible via the ***Restore*** button. The restoring process will start.

A window gives the number of the DOS file in restoring process.

Note When restoring a DOS operation, the following message : ***Time out, impossible to store the experiment*** may appear when another computer is performing at the same time a storing or a restoring operation within the same directory. Then rerun the storing operation.

Note The full name of the DOS procedure is found -after the restoring procedure- in the complementary field. On the graph, only the first fifty characters of the DOS procedure name are displayed.

Note Some characters (particularly '' , ') found in the name of the DOS experiment (or the name of the DOS procedure) may be automatically replaced by the « blank » character to ensure compatibility with the Windows software.

7. Deleting a signal

Select the ***Signal/Delete*** menu and choose the experiment the signals of which are to be deleted. The signal selection window appears (see Figure 92).

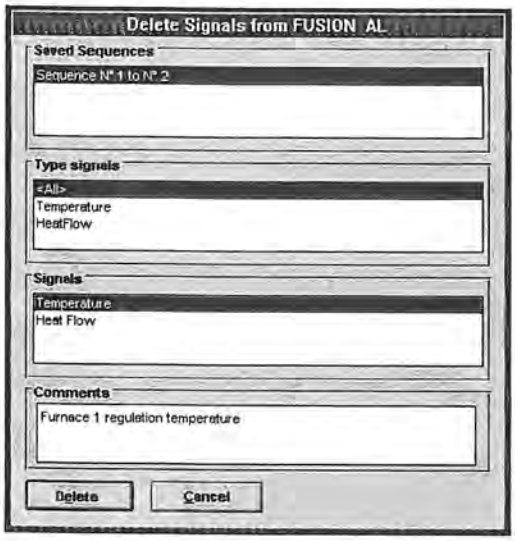


Figure 92: Select signal(s)

This window is made up of four parts :

- The upper part sums up all the sequences saved for the experiment
- The middle part displays the signal type used
- The next part contains all the signals according to the selected sequence and signal type selected
- The lower part displays the comments of the last selected signal

To delete signals, first select a sequence, then the signal type to be deleted (or all the type) and finally the signals to be deleted.

Then click on the ***Delete*** button.

Remark

- if you delete all the signals in a sequence, all the sequences will be deleted
- if at least there is no sequence, all the experiments will be deleted

8. Importing the signal under ASCII form

This menu allows a signal to be added to the existing experiment.

Via this function the user can for instance :

- export the signal of an experiment under ASCII form,
- processing it with a processing software,
- then re-importing it in the SETARAM software for reprocessing (such as integrating it for instance).

Select the ***Signal/Import signal under ASCII form*** menu and then choose the experiment in which the signal must be added. The following window appears :

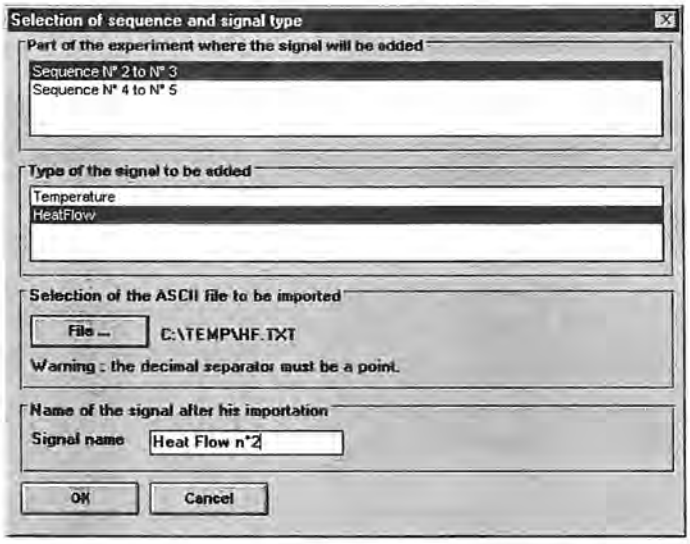


Figure 93 : Selecting the sequence and the type of signal

This window allows to select :

- the part of the experiment in which the signal must be added,
- the type of the signal to be added (Temperature, Heat Flow...),
- the ASCII file containing the signal to be imported,
- the name to be given to the signal in the adding process (name by which it will be found in the SETARAM software).

Remark the period of the added signal must be similar to the period of the experiment.

Remark the decimal separator for the ASCII file must be a full stop (.).

9. Changing the signal

Select the ***Signal/Change*** menu and select the experiment containing the signal to be changed. The signal selection window opens.

This window is similar to the one in the previous paragraph, but in this window, one signal **only** can be selected (see Figure 94).

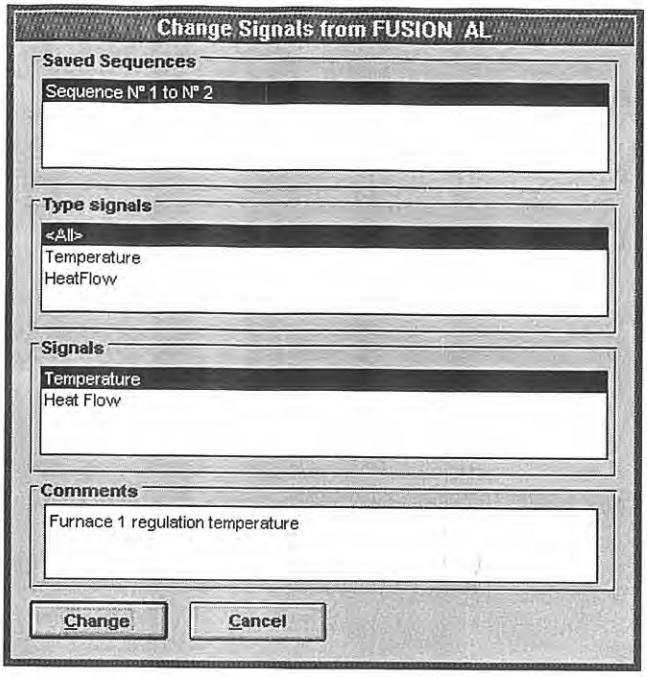


Figure 94: Select the signal to be modified

After selecting the signal, the name and the comments of this signal can be modified (Figure 95).

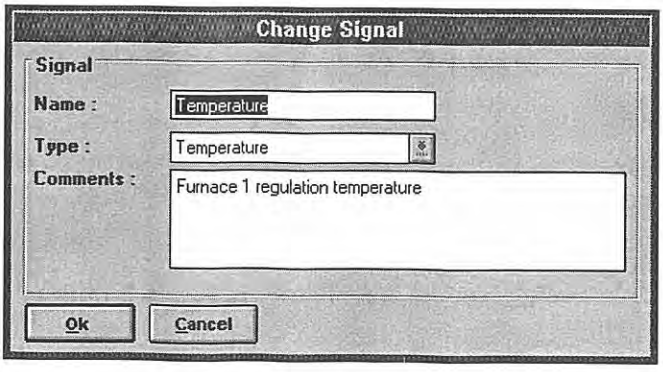


Figure 95: Modify the signal

10. Configuration

Select the ***Utilities/Add/Remove Item*** menu to open the configuration window:

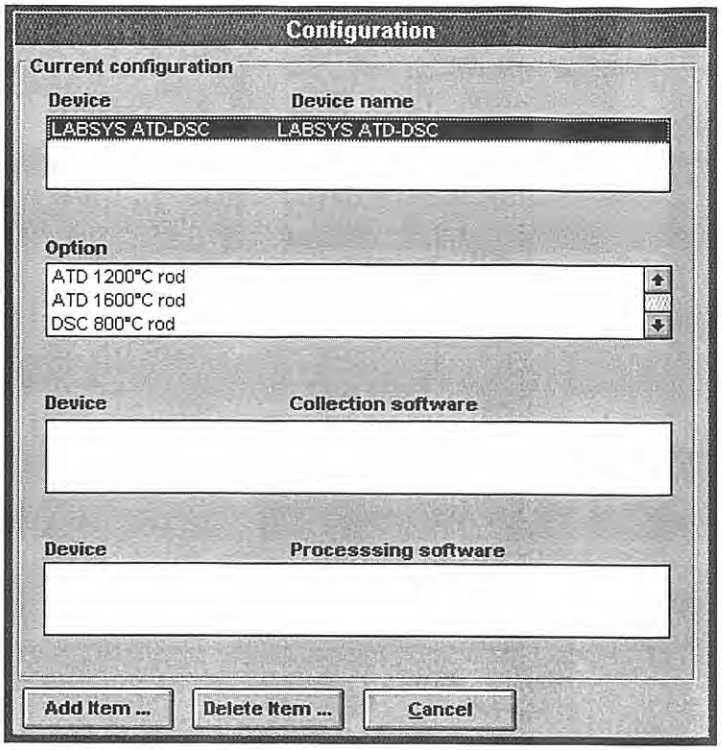


Figure 96: Configuration

The window is divided in four parts :

- The list of the apparatus already installed
- The list of the options installed, according to the selected device
- The list of the collection software installed
- The list of treatments software

Remark Each software collection or treatments refers to **one** apparatus.

Three buttons are available:

- ***Add Item*** to install new collection, treatments or apparatus softwares
- ***Delete Item*** to desinstall collection, treatments or apparatus softwares
- ***Cancel*** to close the window

11. Installing new software collection, processing or instrument

Open the configuration window (see Paragraph 10.) and click on the ***Add Item*** button and choose the drive where the file option is located (see Figure 97).

Figure 97: Default drive A:

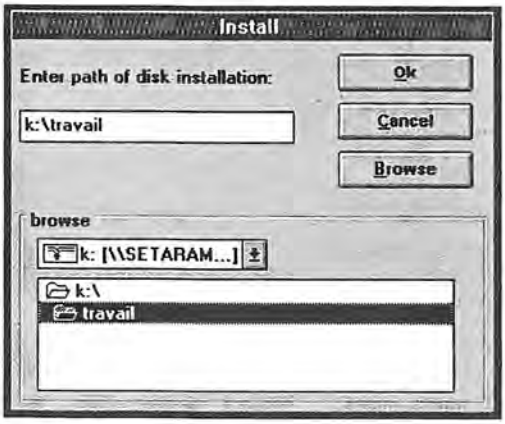


Figure 98: Select drive (click on "Browse")

The window containing the item to be installed appears, this window is similar to the configuration window (see Figure 99).

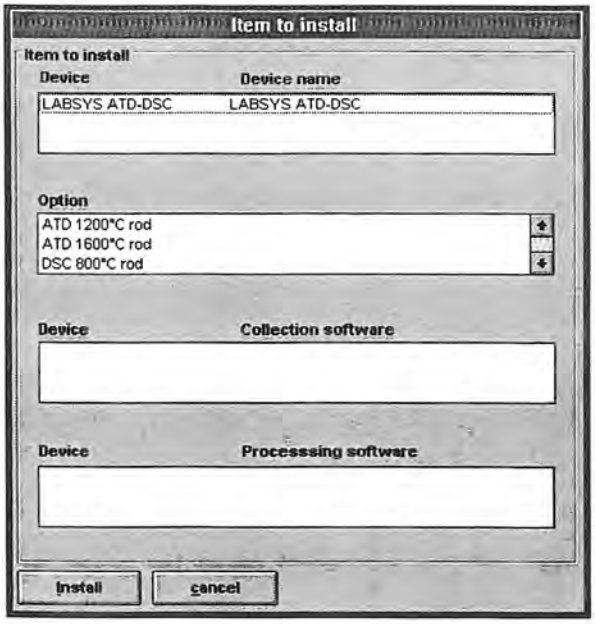


Figure 99: Select the item to be installed

The list sums up the item you can install, two buttons are available :

- ***Install*** : the new item selected will be installed
- ***Cancel*** : return to the configuration window

Select the item to be installed and then click on the ***Install*** button. The window will be closed and the new item will appear in the configuration window.

Now the new item can be used in the collection sofware and processing software.

Remark If a new apparatus is installed you have to enter a name to identify it (see Figure 100).

Figure 100: Enter the name of the new device

APPENDIX - SENDING AND RECEIVING AN EXPERIMENT BY E-MAIL

1. Foreword

The present appendix aims at explaining how to send and receive by e-mail one or several thermal analysis experiment(s) carried out by the ***Setsoft*** software package.

WARNING Procedures described hereafter only apply from the ***Setsoft***'s 1.30 version.

---

2. Sending one or several Setsoft/Windows-acquired experiment(s) by e-mail:

- Create a temporary directory on the hard disk (for instance the C:\TEMPO directory).
- Run the ***Setsoft***'s ***Database Tools*** software.
- Select ***Experiment / Store*** to export the experiment(s).
- In ***Storage directory*** point on C:\ TEMPO (for the present example).
- Click on ***Experiments selection*** .
- Select the experiment(s).
- Click on the ***Store*** button to run the archiving process.
- The experiment(s) is (are) now available and the ***Database Tools*** software is no longer needed.
- Copy all the files from the C:\ TEMPO\ACCESS to the E-mail.
  - For a standard experiment:
    There are 2 files: « STANDARD.MDB » and « STANDARD.LDB ».
  - For a Cp measurement experiment:
    There are 2 files: « DET_CP.MDB » and « DET_CP.LDB »
- Copy all the files available from the C:\TEMPO\COURBES directory to the e-mail.
  - For a standard experiment:
    The files are of a « Sxxxxxxx.xxx » type.

- For a measurement Cp experiment:
  The files are of a « Cxxxxxxx.xxx » and possibly of a « Dxxxxxxx.xxx » type.

3. Retrieving a Windows experiment received by e-mail

- Create a temporary directory on the hard disk for instance the C:\TEMPO directory).
- Create two subdirectories from the temporary directory:
  ACCESS
  COURBES

WARNING the spelling of the names of these two directories must absolutely be respected.

For this example the following tree structure is given:

C:
  |__TEMPO
    |__ACCESS
    |__COURBES

- From the e-mail click on ***File \ Save as*** for each enclosed file.
  - For a standard experiment
    - Save the two files « STANDARD.MDB » and « STANDARD.LDB » in the ACCESS directory.
    - Save all the « Sxxxxxxx.xxx » files in the COURBES directory.
  - For a Cp measurement experiment
    - Save the 2 files « DET_CP.MDB » and « DET_CP.LDB » in the ACCESS directory.
    - Save all the « Cxxxxxxx.xxx » files and possibly the « Dxxxxxxx.xxx » files in the COURBES directory.

WARNING Pay attention to the file names: they will not contain any path such as C:\ACCESS\STANDARD.MDB to ensure their saving.

WARNING Make sure to use the ***Save as*** Procedure. Indeed, if not done this way files will then saved as Scrap() and cannot be used by the ***Setsoft*** software package.

Once they are copied the new tree structure is:

C:
|__TEMPO
|__ACCESS
| |__DET_CP.MDB
| |__DET_CP.LDB
|
|__COURBES
|__C2000002.002
|__C2000003.002
|__D2000002.002
|__D2000003.002
|__.....
|__.....

- Once the files are all saved, run the ***Setsoft***'s ***Database Tools*** software package.
- Select ***Experiment / Restore*** to import the experiment.
- Point on C:\TEMPO (for the present example).
- Click on ***Experiments selection*** .
- Select the experiment(s).
- Click on the ***Restore*** button to run the restore procedure.
- The experiment is now available and can be processed by the ***Setsoft*** software.

SETARAM : excellence in thermal analysis

LABSYS™ : low cost series of multi-module thermal analyzers

- DSC131 : -150 to 700°C (heat flux sensor)
- DTA, TG/DTA : ambient to 1600°C
- DSC, TG/DSC : ambient to 1600°C
- TMA : ambient to 1000°C

SETSYS : top of range in thermal analyzers

- DSC141 : -150 to 600°C (power compensation)
- DTA, TG/DTA : -150 to 2400°C
- DSC, TG/DSC : -150 to 1600°C
- TMA, DLTMA : -150 to 2400°C

micro DSC : high sensitivity DSC and calorimetry

- micro DSCIII : -20 to 120°C ("batch and flow")
- micro DSCVII : -45 to 120°C ("batch")

CALVET PRINCIPLE DSC

- DSC 121 : -120 to 830°C
- DSC Robotic Sytem : -120 to 830°C

CALVET CALORIMETERS

- BT 2.15 : low temperature calorimeter from -196 to 200°C
- MS 80 : standard calorimeter from ambient to 200°C
- HT 1000 : high temperature calorimeter from ambient to 1000°C
- C 80 : mixing and reaction calorimeter from ambient to 300°C
- Tytris : titration calorimeter from ambient to 75°C
- calorimeters based on your analysis needs

96 LINE : high temperature and large volume thermal analyzers

- MULTI-HTC 96 : DSC and calorimetry
  calorimetric detectors up to 1500°C
  DSC detectors up to 1600°C
- TG 96 : thermogravimetry
  ambient to 1750°C
- DHT 96 : dilatometry
  1750°C and 2100°C versions

SYMMETRICAL THERMOGRAVIMETRY LINE

- TAG 24 : a line of symmetrical thermoanalyzers
  -150 to 2400°C
- TG-DSC 111 : the unique TG-DSC coupling
  -120 to 830°

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GROUPE KEP INSTRUMENTATION • REGULATION
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http:\\www.setaram.com

4

A/ETALA

CALIBRATION KITS

Low Temperature : In, Sn, Pb, Zn, Al
High Temperature : Ag, Au, Ni, Pd, Al_2O_3

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GROUPE KEP

CONTENTS

CHAPTER 1 - INTRODUCTION

SETARAM's calibration kits provide for the enthapy and temperature calibration of DSC and DTA instruments.

They are composed of reference materials with a purity of 99.99%. Two additional kits are also available, adapted to the temperature range to be reached.

The Low Temperature version is made of:

Indium	(In)
Tin	(Sn)
Lead	(Pb)
Zinc	(Zn)
Aluminium	(Al)

for calibration with a temperature range from 157°C to 660°C.

The High Temperature version is made of 4 metals and 1 oxyde:

Silver	(Ag)
Gold	(Au)
Nickel	(Ni)
Palladium	(Pd)
Sapphire	(Al_2O_3)

for calibration with a temperature range from 962°C to 2052°C.

CHAPTER 2 - MAKING USE OF THE TEST

Two types of transformation are revealed in this chapter :

1. Endothermic transformation of the type fusion
2. Exothermic transformation of the type crystallisation

The methods used for determining the transformation temperatures (or times) comply with the international ***ISO*** standards in force or in draft.

1. Endothermic transformation

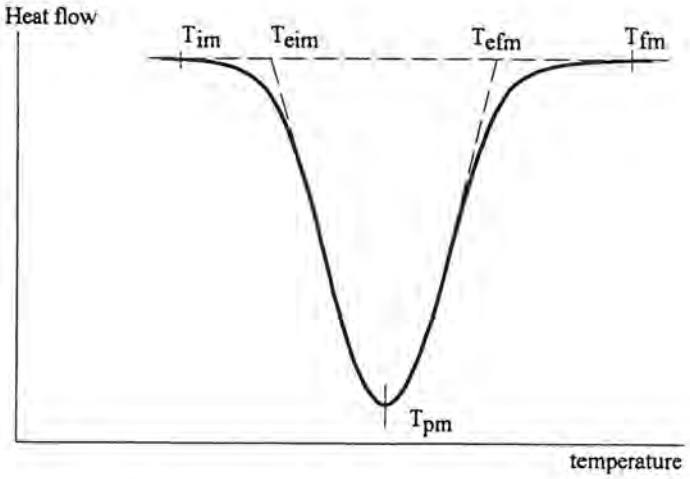


Figure 1: Endothermic transformation thermogramme

The accepted practice is to determine the following temperatures (or times) :

- Temperature T_{im} (or time t_{im}) at the peak start corresponding with the peak's take-off in relation to the base-line plotted between the start and the end of the peak
- Temperature T_{eim} (or time t_{eim}) corresponding with the ***onset*** temperature, i.e. the intersection between the base-line and the tangent at the peak's inflexion point in the increasing phase
- Temperature T_{pm} (or time t_{pm}) corresponding with the top of the peak.

- Temperature T_{efm} (or time t_{efm}) corresponding with the ***endset*** temperature, i.e. the intersection between the base-line and the tangent at the peak's inflexion point in the decreasing phase.
- Temperature T_{fm} (or time t_{fm}) at the peak end corresponding with the peak returning to the base-line.

In the special case of a pure, crystalline substance the fusion temperature is measured at the ***onset*** temperature T_{eim}.

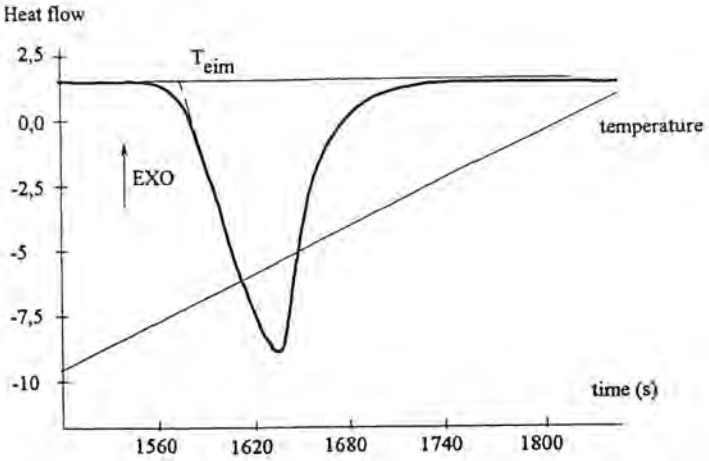


Figure 2: Thermogramme of the fusion of a pure substance

Remark For semi-crystalline substances, like numerous polymers, the fusion temperature is measured at the T_{pm} temperature on the peak top.

2. Exothermic transformation

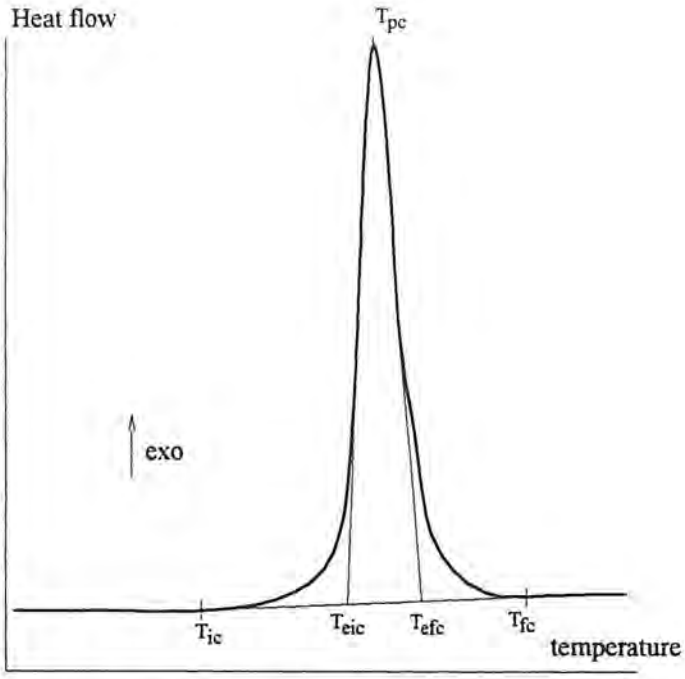


Figure 3: Thermogramme of an exothermic transformation

The accepted practice is to determine the following temperatures (or times) :

- Temperature T_{ic} (or time t_{ic}) at the peak start corresponding with the peak's take-off in relation to the base-line plotted between the start and the end of the peak.
- Temperature T_{eic} (or time t_{eic}) corresponding with the ***onset*** temperature, i.e. the intersection between the base-line and the tangent at the peak's inflexion point in the increasing phase
- Temperature T_{pc} (or time t_{pc}) corresponding with the the top of the peak
- Temperature T_{efc} (or time t_{efc}) corresponding with the ***endset*** temperature, i.e. the intersection between the base-line and the tangent at the peak's inflexion point in the decreasing phase
- Temperature T_{fc} (or time t_{fc}) at the peak end corresponding with the peak returning to the base line

Remark In the same way as for fusion the crystallisation temperature in a pure, crystalline substance is measured at the ***onset*** temperature T_{eic} .

Remark For a semi-crystalline substance it is measured at the T_{pc} temperature on the peak top.

CHAPTER 3 - TEMPERATURE CORRECTION

1. Measuring the fusion temperature of a pure substance

To explain measurement let us take the example of fusion (figure below). Various temperatures need to be considered :

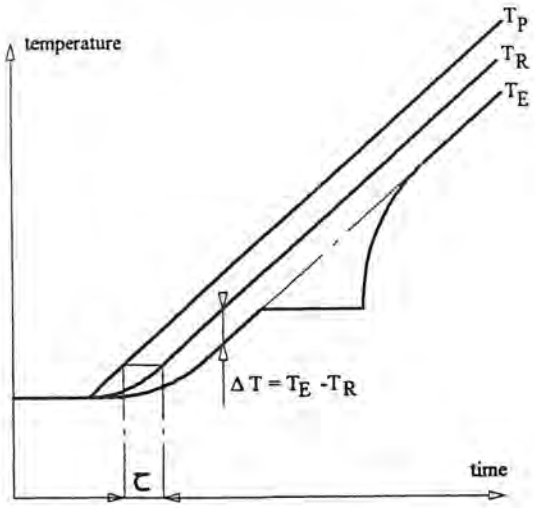


Figure 4 : Principle for heat measurement

T_p : scanning temperature in the calorimetric block

T_R : reference temperature

T_E : sample's temperature

During temperature scanning the sample's temperature lags behind the scanning temperature. When the sample undergoes fusion, as transformation is invariant, the sample's temperature stays constant throughout the transformation. When the last crystal has melted this temperature attempts to catch up the other temperatures and to follow the same progression.

If the temperature difference T_E - T_R, is represented the characteristic peak for the sample's fusion is produced (see figure hereafter).

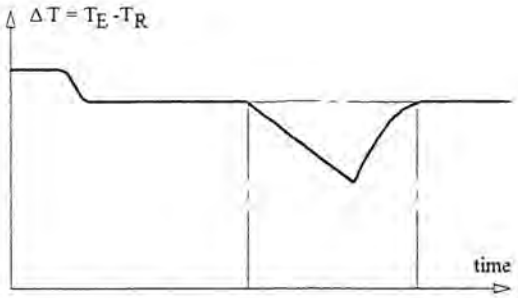


Figure 5: Principle for heat measurement

The sample's fusion temperature must be measured at the start of the peak; in practice the point taken is the extrapolated temperature, called the onset temperature.

With indium (T_{fusion} = 156,6°C), the scanning temperature measured on the curve gives (figure below):

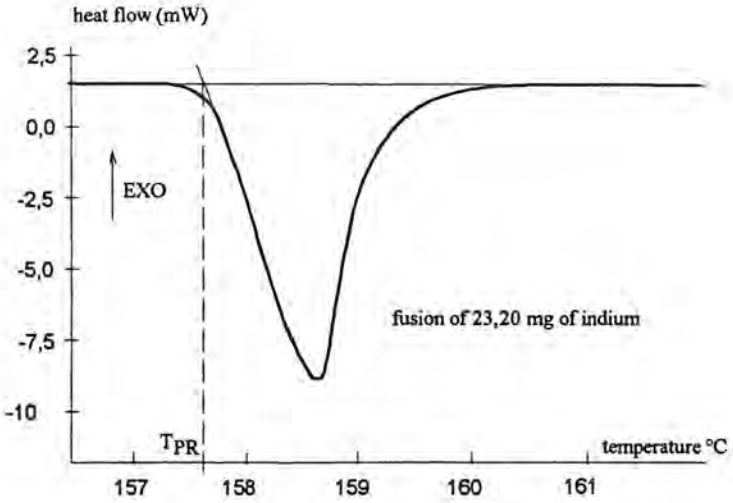


Figure 6: Curve of the fusion of indium

T_{pr} = 157,6°C

The temperature correction to be applied equals :

ΔT = 157,6 - 156,6°C that is 1,0°C.

This correction only applies to indium, and for the experimental conditions used (such as scanning rate, gas, crucible).

In practice, although this measurement is done near the sample a small difference may be noted with the sample's real temperature due to the thermal gradient and the time for the heat.

In fact, this temperature correction will vary with :

- Temperature
- The scanning rate used.
- The type of crucible involved.
- The type and rate of sweeping gas.

Standard materials with known fusion or transformation points are required to carry out this temperature correction.

Remark To ascertain if temperature correction is needed to:

- Bring about the fusion of a known standard within the temperature range of the transformation being studied.
- Compare the value measured with the one given in the literature.

Should the difference be equal or lower than the degree, the correction is not compulsory.

2. Standard materials used

Metals are prepared for determining temperature calibration:

METAL	MELTING POINT (°C)
Indium (In)	157
Tin (Sn)	232
Lead (Pb)	327.5
Zinc (Zn)	419.6
Aluminium (Al)	660
Silver (Ag)	962
Gold (Au)	1064
Nickel (Ni)	1455
Palladium (Pd)	1554
Sapphire (Al_2O_3)	2052

WARNING Only indium (NIST RM 758) and tin (NIST RM 758) are recognized as official standards for the DTA method. For the other metals choose a 4N purity (99,99%) or better 5N (99,999%).

WARNING If the platinum crucible is used (or any other metal crucible) it first needs to be partly filled with alumina before arranging the sample so as to prevent any contact between the molten sample and the crucible (alloys may be be formed).

WARNING The samples must be melted in an inert gas atmosphere, especially for a nickel sample (it may otherwise attack the alumina crucible).

WARNING When using these substances special attention must be paid to exhibiting high vapour pressures.

WARNING In contrast, certain substances can break down if they are heated beyond their transition or fusion temperature.

Remark It is thus VITAL to remain within the temperature measurement corresponding with the transformation given in the table.

3. Experimenting

Choose at least three standard materials including the temperature zone to be used for analyzing the samples.

Set the experimental conditions to be used for analyzing the samples especially :

- Type of crucible.
- Properties and flow-rate of the sweeping gas.
- Temperature scanning rate.

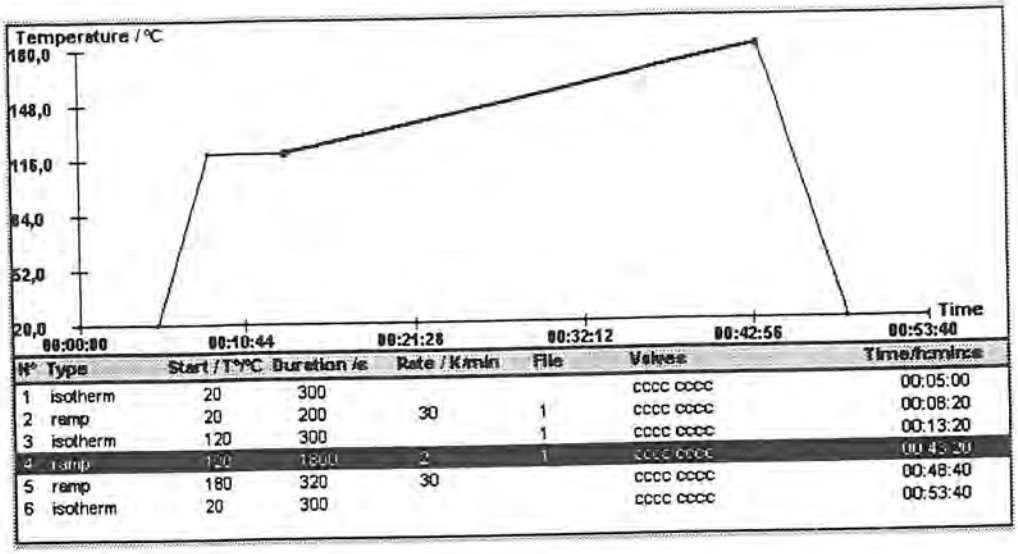
For each standard material:

- Weigh the substance placed into a crucible.
- Arrange the crucible on the ***sample*** side of the DTA transducer. Arrange an identical, empty, crucible on the ***reference*** side.
- Close the furnace and switch on the gas sweeping (if used) and wait for a few minutes.
- Prepare the scanning cycle so as to get the substance molten.

Remark In practice scan the furnace's temperature rapidly up to above 30°C before fusion. After an isothermal, stabilising level record the fusion at the chosen rate (5 to 15 min).

- Finally, scan the furnace cooling.
- Record the corresponding thermogramme and re-plot the part corresponding with the standard's fusion as a function of temperature.

- Repeat the operation for each material, each time adapting the temperature range for measuring fusion.



N°	Type	Start / T°C	Duration /s	Rate / K/min	File	Valves	Time/h:mn:s
1	isotherm	20	300			cccc cccc	00:05:00
2	ramp	20	200	30	1	cccc cccc	00:08:20
3	isotherm	120	300		1	cccc cccc	00:13:20
4	ramp	120	1800	2	1	cccc cccc	00:48:20
5	ramp	180	320	30		cccc cccc	00:48:40
6	isotherm	20	300			cccc cccc	00:53:40

Figure 7: Example of the scanning cycle

WARNING Expand the temperature range for analyzing fusion when the scanning rate increases.

WARNING A second fusion of the sample is recommended after cooling and this second thermogramme provides useful information.

Remark The first fusion does, in fact, often provide a compact shape to the sample, which is more helpful for the heat exchange with the transducer.

4. Temperature correction for a fixed scanning rate.

For each fusion peak determine the ***onset*** temperature T_{eim} as defined in *Chapter 2- 1* :

Given:

- T_{eim}, the measured ***onset*** temperature.
- T_{fi} , the sample i's real melting point.
- $dT_i = T_{eim} - T_{fi}$, the temperature correction.

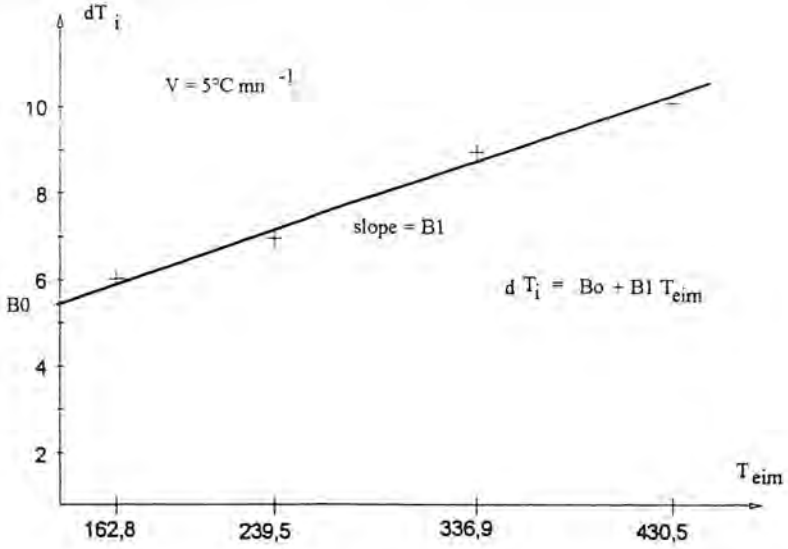


Figure 8: Temperature correction for a fixed scanning rate

Draw up a table (T_{eim} , T_{fi} , dT_i) and plot the variation $dT_i = f(T_{eim})$.

Express this variation in the form of a straight line: $dT_i = B_0 + B_1 \cdot T_{eim}$

Determine B_0 and B_1 by using a regression programme.

Enter the values B_0 and B_1 on to the software's ***Parameters*** page for temperature correction.

Reset the values B_2 and B_3.

WARNING This relationship provides for correcting any temperature for the analysis interval considered and by always using the same scanning rate.

5. Temperature correction for various scanning rates

If analyzing the sample has to be done at various temperature-scanning rates the fusion of the standard materials needs to be studied at various scanning rates V_i .

In practice carry out experiments for each standard at a minimum of three different rates whose values encompass the values of the rates to be used for the sample.

- Draw up a table (T_{eim} , T_{fi} , V_i , dT_i)
- Using the method of the least squares or a regression programme determine the coefficients B_0, B_1 and B_2 for the correcting relation: $dT_i = B_0 + B_1 \cdot T_{eim} + B_2 \cdot V_i$

In practice, if N is the number of tests carried out, calculate the following sums:

A	ΣT_{eim}
B	ΣV_i
C	ΣdT_i
D	ΣT_{eim}^2
E	$\Sigma T_{eim} \cdot V_i$
F	$\Sigma T_{eim} \cdot dT_i$
G	ΣV_i^2
H	$\Sigma V_i \cdot dT_i$

Here the coefficients are produced by the relations :

$B_o = (J/W)$

$B_1 = (K/W)$

$B_2 = (L/W)$

where :

$W = N (DG - E^2) - A^2G + 2ABE - DB^2$

$J = C (DG - E^2) - F (AG - EB) + H (AE - DB)$

$K = N (FG - HE) - A (CG - BH) + B (CE - FB)$

$L = N (DH - EF) - A (AH - EC) + B (AH - DC)$

The temperature correction thus determined applies for any temperature and scanning rate for the range under study.

Enter the values B_o , B_1 and B_2 on to the software's ***Parameters*** page for temperature correction.

WARNING During the experiments for determining temperature correction check or initially re-set the values B_o, B_1 , B_2 and B_3

CHAPTER 4 - ENERGY CALIBRATION

Although the DTA technique is above all a qualitative method, there is a facility, by use of the standards, for calibrating the DTA transducer as well as the DSC transducer, so as to transform the electrical signal S (in microvolts) into thermal power P (in milliwatts). The coefficient of calibration K is then determined, such as :

$S = K . P$

This coefficient of calibration K varies with various parameters :

- The sample shape and mass.
- The properties of the transducer.
- The experimenting temperature.
- The properties of the crucible.
- The properties and flow-rate of the sweeping gas.

1. Measuring the heat of fusion for a pure substance

The thermogramme corresponding with the fusion of a pure substance is represented in the diagram below:

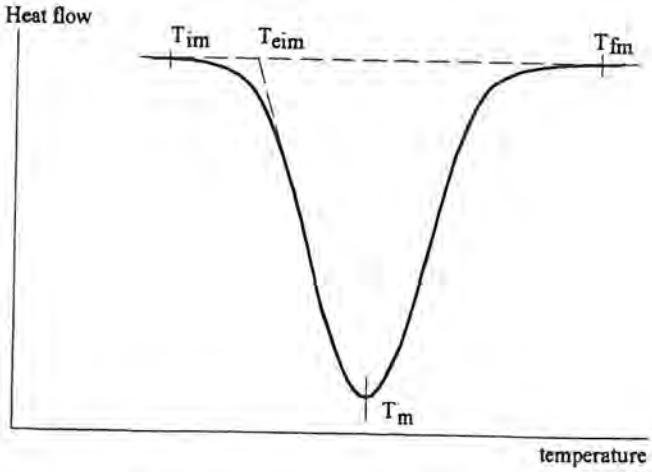


Figure 9: Thermogramme of the fusion of a pure substance

The heat of fusion for the sample analyzed is produced by integrating the area under the peak between the peak's start T_{im} and end T_{fm} temperatures without initial calibration, and the ordinate being expressed in µV and the abscissa in

seconds, the peak's area is expressed in µV.s. Integrating the peak is done via the ***Integration*** function on the base software after choosing the type of base-line. For a fusion peak a straight base-line is used between the temperatures T_{im} and T_{fm}.

2. Standard materials used

Chapter 3- 2 provides a table of metal standards for determining temperature correction.

The same standards may be used for energy calibration as they are thermally stable and offer the facility of providing numerous, successive tests without modifying their specifications.

Their fusion heat contents are used for energy calibration.

SUBSTANCE	FUSION HEAT CONTENT (J/g)	MELTING POINT (°C)
Indium	28.4	157
Tin	60.2	232
Lead	24.7	327.5
Zinc	107.4	419.6
Aluminium	395	660
Silver	104.5	962
Gold	64	1064
Nickel	299	1455
Palladium	162	1554
Sapphire	1090	2052

Based on the sample's transformation temperature the standard chosen for energy calibration will be the one with a melting point closest to the sample's transformation temperature.

WARNING Only tin (NIST SRM 2220) and zinc (NIST SRM 2221a) are recognized as standards certified for energy calibration. For the other substances the values given are taken from the literature.

Remark It should be noted that, for the same substance, significant differences may be observed over the value of the fusion heat content in the literature.

3. Experimenting

Choose one or several standards based on the transformation temperature range under study.

The experimental conditions are identical to those described in *Chapter 3 - 3*.

Plot the fusion curve as a function of time or temperature.

WARNING When performing a determination of energy calibration, check that the values of coefficients are reset in the software, otherwise the user must reset these values.

Remark In practice temperature and energy calibrations are carried out with the same experiment, on the same fusion peak of the metal standard.

4. Calibration with a single standard

If the transformation takes place within a limited temperature range a single coefficient of calibration can be used by choosing the standard closest to the melting point.

Let H be the fusion heat content of the metal standard chosen (in J / g).

Let m be the mass of standard analyzed (in g).

Let S be the area of the fusion peak (in $\mu V \cdot s$).

Then the coefficient of calibration at the standard's melting point is given by:

$K = (S/H) * (1/m)$ in microvolt per watt. K is better expressed in $\mu V/mW$.

For any peak area A (in $\mu V \cdot s$) , combined with the corresponding transformation Q (in Joules) the formula is :

$Q = A/K$

5. Calibration with various standards

In practice calibration with a single standard is not very accurate as the coefficient of calibration varies with temperature.

Various metal standards are recommended so as to plot a variation curve of the coefficient of calibration as a function of temperature.

The substances given in *Chapter 3 - 2* can be used.

Choose at least five standards to produce correct determining.

Let H be the fusion heat content of the standard i (in J / g), let m_i be the mass of standard analyzed (in grammes), let S_i be the area of the fusion peak (in μV . s), then the coefficient of calibration K_i at the standard's melting point T_{eim} is given by:

$K_i = (S_i/H_i) * (1/m)$ in $\mu V/W$.

A table (T_{eim}, K_i) can be done and the variation $K = f(T_{eim})$ can be plotted.

This calibration curve reveals the instrument's coefficient of calibration at any temperature.

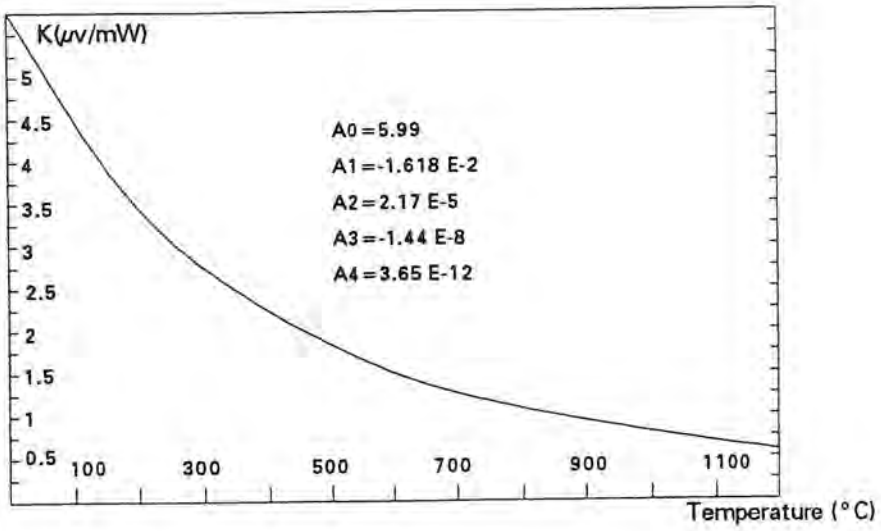


Figure 10: 1200°C argon gas Labsys DSC rod

This variation is best put in the form of a polynomial function of the fourth degree:

$$K = A_o + A_1 \cdot T_{eim} + A_2 \cdot T_{eim}^2 + A_3 \cdot T_{eim}^3 + A_4 \cdot T_{eim}^4$$

A regression software is needed for this work. At least 5 calibrating operations are required before performing a correct regression. If not enough standard is available, each measuring point can be doubled by another test.

The coefficients A_o, A_1, A_2, A_3 and A_4 thus determined are entered on to the software's ***Parameters*** page for automatically transforming the signal.

Therefore, integration of peaks directly gives the transformation heat in Joule.

The Windows(software performs the polynomial regressions of the four degree (see the beginning of the present section).

WARNING Using the calibration curve does not guarantee the accuracy of the results. This is linked to the performance of the transducer used as well as the standards chosen for calibration.

WARNING As a general rule, for a DTA transducer which is not designed for quantitative measurements, the accuracy for heat measurement is of the order of 10%.

WARNING For quantitative measurements the DSC-type transducers are recommended.

CHAPTER 5 - BIBLIOGRAPHY

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Draft on 11357-3 ISO norm "Plastics - DSC - Temperatures and enthalpies of melting and crystallization".

SETARAM : excellence in thermal analysis

LABSYS™ : low cost series of multi-module thermal analyzers

- DSC131 : -150 to 700°C (heat flux sensor)
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- micro DSCIII : -20 to 120°C ("batch and flow")
- micro DSCVII : -45 to 120°C ("batch")

CALVET PRINCIPLE DSC

- DSC 121 : -120 to 830°C
- DSC Robotic Sytem : -120 to 830°C

CALVET CALORIMETERS

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SETSOFT

KINETICS ON DTG

INSTALLATION - UTILISATION

SETARAM

GROUPE KEP INSTRUMENTATION • REGULATION

CONTENTS

CHAPTER 1 - INSTALLATION

1. Foreword

This booklet is designed for people who are already familiar with the base version of the SETARAM's ***Setsoft*** booklet. Indeed, most notions that are refered to in this booklet are detailed in the ***Setsoft*** booklet.

2. Installation

2.1. Preparation

2.1.1. Verification of software mapping

Installing the Controlled DTG software package first of all requires installing the base software on the hard disk. Refer to the base version booklet for the installation procedure (*Chapter 1 - Installation*).

2.1.2. Backup copies

Before the program is installed, backup copies of the SETARAM software package must be made with one of the following commands:

- ***Disk / Copy Disk*** in the Microsoft Windows™ manager file.
- The MS-DOS™ ***DiskCopy***.

2.2. Installing the software package

Refer to the base version of ***Setsoft*** (*Data Management / Installing New Software Collection* Chapter)

CHAPTER 2 - INTRODUCTION TO THE SOFTWARE

The software allows to determine the kinetic parameters of a sample. It is made up of three parts:

1. Modification (or selection) of the correction of temperature coefficient as well as the corrected temperature of the top of the peak
2. Determination of the kinetic parameters according to the OZAWA or the KISSINGER method.
3. Determination of the kinetic parameters according to the FREEMAN-CARROLL method including the Isothermal Simulation.

CHAPTER 3 - CORRECTION OF TEMPERATURE

The two methods : OZAWA and KISSINGER or FREEMAN-CARROLL require a precise knowledge of the sample temperature.

1. Principle

An accurate determination of the temperature T_S needs different corrections.

a) The temperature read on the thermogramme is the temperature of the measurement thermocouple set close to the sample. To take into account the temperature gradient a first temperature correction depending mainly on the scanning rate is carried as follow:

$dt = b_0 + b_1 T + b_2 V + b_3 V^2$

where T : temperature in °C

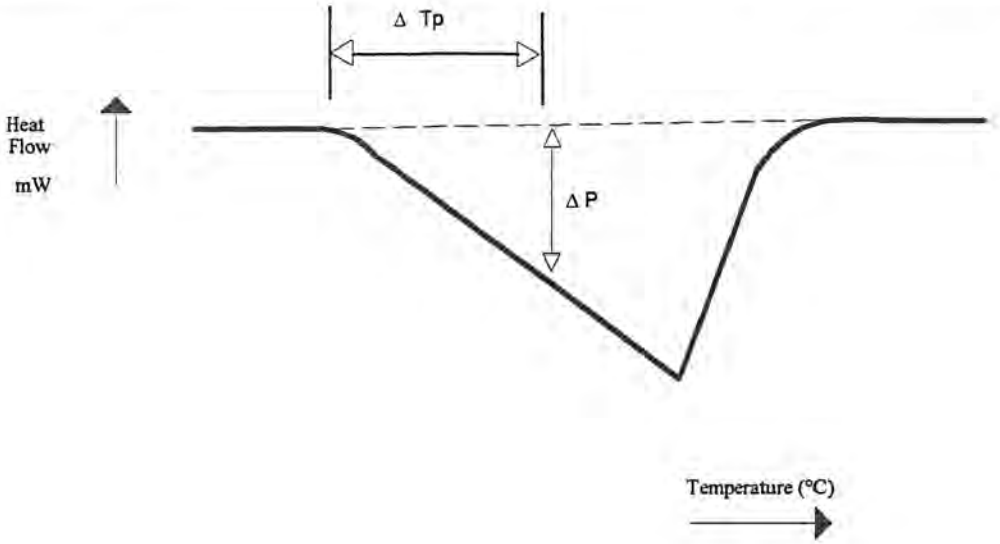
V : scanning rate in K. min^{-1}

To determine the parameters with a TG alone, the fall in the melting curve of metal standards is studied.

To determine the parameters with a TG DTA or DSC the fusion peaks of metal standards are studied.

b) With a sensitivity calibrated TG DTA or DSC the temperature Ts of the sample can be precisely determined and account must be take of the exchanged heat flux which causes a temperature rise (in the case of an exothermic process) compared to the temperature regulation.

To determine this temperature difference, the melting curve of a pure substance is studied. The melting process being invariant, the sample temperature at the beginning and at the top of the peak must be identical.



A correction factor K is determined, this factor takes into account the heat flow ΔP for an apparent temperature variation ΔT_P

$K = \Delta P/\Delta T_p$ en $mW.K^{-1}$

For a whatever transformation, the temperature correction to apply to the temperature read on the thermogramme will be :

$\Delta T = b_0 + b_1 T_p + b_2 V + b_3 V^2 . \Delta P/K$ $\quad K = c_0 + c_1 V + c_2 V^2$

According to the convention used, ΔP is positive for an exothermic reaction and negative for an endothermic reaction.

In order to calculate the coefficients of the K variation with the temperature scanning rate, it is necessary to carry out the study of the indium melting at various scanning rates and to determine the coefficient K for each experiment (for this measurement, the same type of crucible as the one used for the decomposition study must be used).

Deduct the second degree equation K = f(v)

2. Utilisation

2.1. Calculating the corrected temperature

Click on ***Calculate*** (see Figure 1) to go to the temperature correction after an integration on DTG.

Note Select ***Processing / Integration / on Signal DTG*** to perform this integration

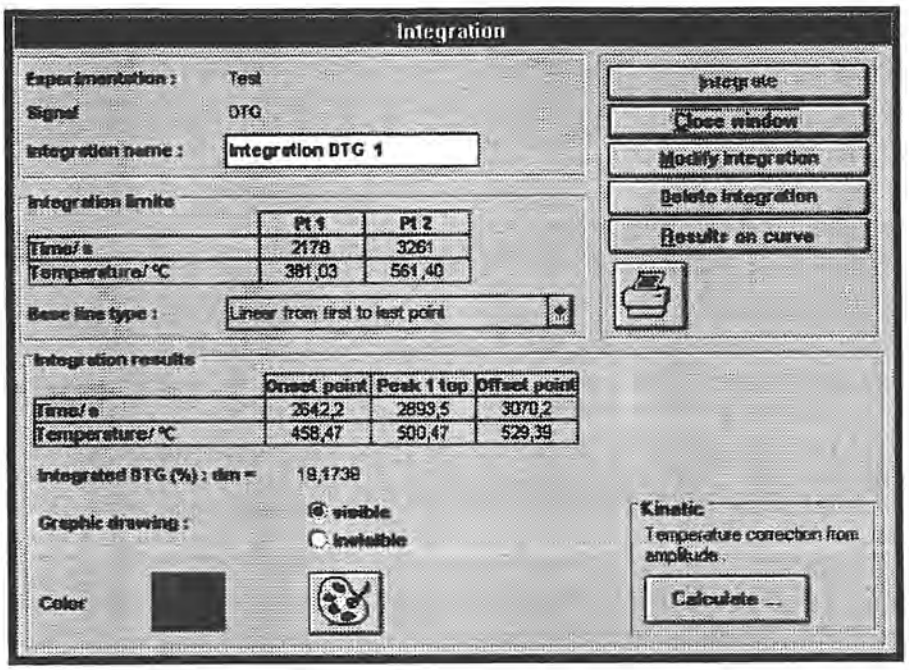


Figure 1

Then a window appears :

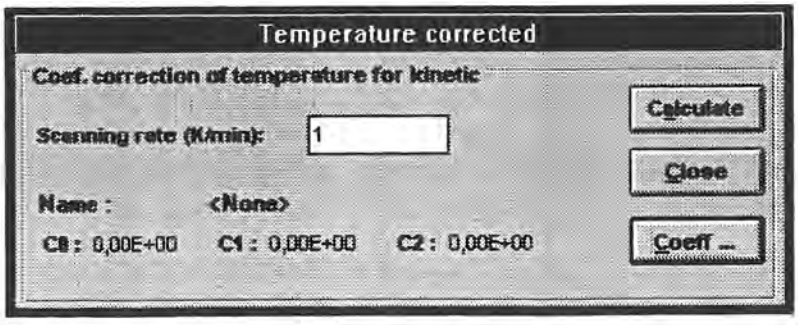


Figure 2

Then select the experiment scanning rate and check that the correction coefficients are correct. If they are not correct, click on ***Coeff*** to modify them.

If they are correct, click on ***Calculate*** to obtain the corrected temperature (see hereafter).

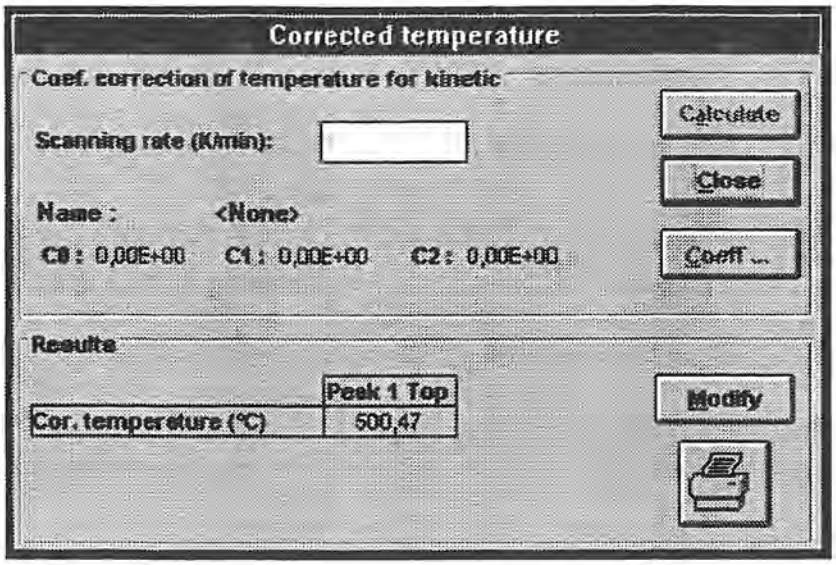


Figure 3

2.2. Selecting and modifying the correction coefficients

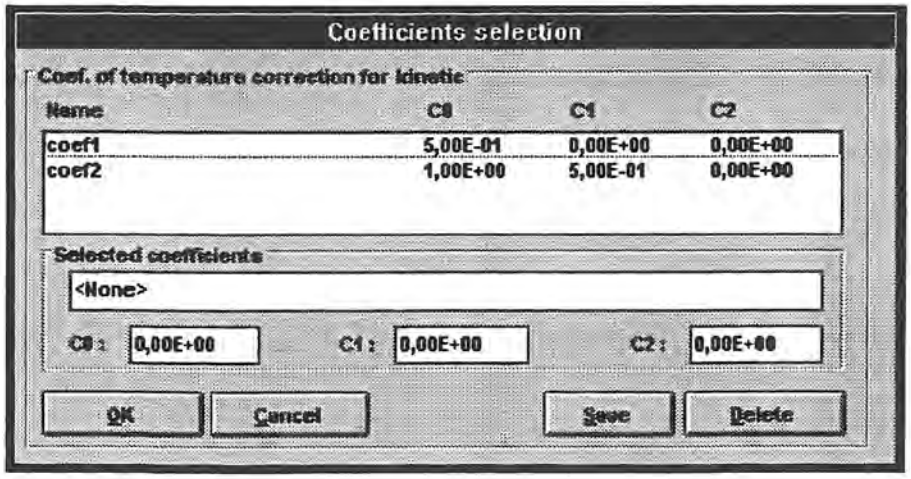


Figure 4

Select a series of coefficients that are already saved or enter a new series of coefficients. In that case click on ***Save*** to save them.

This window also allows to delete a series of coefficients : click on ***Delete***.

Click on ***OK*** to validate the selected coefficients, otherwise click on ***Cancel***.

CHAPTER 4 - DETERMINATION OF KINETIC PARAMETERS: OZAWA AND KISSINGER METHOD

The determination of kinetic parameters with the OZAWA or with the KISSINGER method is based on the exploitation of the decomposition peaks of material and, in particular, on temperature measurement at the top of the peak. The decomposition of the compound must be studied at different scanning rates of temperature.

1. Principle

The general kinetic relation is the Arrhenius law:

where $k = k_0 \exp(-E/RT)$ (1) with k : rate constant

k_0 : rate constant at 0 K

E : activation energy (cal. mol^{-1})

T : temperature (K)

R : perfect gases constant (1,987 cal. mol^{-1} K^{-1})

The TG signal derivative is generally interpreted in terms of instantaneous rates dm/dt :

$$\frac{dm}{dt} = K.f(c) \qquad (2)$$ with c : reactive concentration

If α is the reacted fraction and n the reaction order,we can write for a thermal decomposition:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \qquad (3)$$

or :

$$\frac{d\alpha}{dt} = k_0 \exp\left(-\frac{E}{RT}\right) x (1-\alpha)^n \qquad (4)$$

The two methods assume that the maximum of the reaction rate corresponds practically to the top of the DTG peak.

$$\frac{d}{dt}\left(\frac{d\alpha}{dt}\right)\max = 0 \qquad (5)$$

On derivating (4) the result is :

$$\frac{d}{dt}\left(\frac{d\alpha}{dt}\right) = -\frac{K_0 E}{R}\cdot\frac{1}{T^2}\exp\left(-\frac{E}{RT}\right) x\,(1-\alpha)^n \frac{dt}{dt} - K_0\, n \exp\left(-\frac{E}{RT}\right) x\,(1-\alpha)^n \frac{d\alpha}{dt}$$

(6)

At the top of the peak, T = Tm

$$-\frac{E}{R}\cdot\frac{1}{T_m^{\,2}}\cdot\frac{dT}{dt} = n\frac{1}{1-\alpha}\frac{d\alpha}{dt}$$

$$= n\frac{1}{1-\alpha}\cdot K_0 \exp(-E/RT_m)\, x\,(1-\alpha)^n$$

$$= K_0\, n\,(1-\alpha)^{n-1}\exp(-E/RT_m)$$

and (dT/dt = a) where a is the scanning rate.

$$Log\left(\frac{a}{T_m^{\,2}}\right) = Log\frac{K_0 R_n}{E} + (n-1)\,Log(1-\alpha) - \frac{E}{RT_m} \qquad (7)$$

1.1. OZAWA method

OZAWA proposed an approximative method to determine the activation energy from the temperature at the maximum of the peak and the corrresponding scanning rate (refer to T. OZAWA, *Journal of Thermal Analysis*, Vol 2 (1970) 301-324). This method is generally applied to solid samples.

OZAWA proposes the following relation:

$$\log a = -0.4567\,\frac{E}{RT_m} - 2.315 + \log k_0 \times \frac{E}{R} - \log G(x_m)$$

The relation is differenciated as function of $\frac{1}{T_m}$, and it gives :

$$\frac{d\log a}{d\left(1/T_m\right)} = -0.4567\,\frac{E}{R}$$

The slope of the line log a as function of $\frac{1}{T_m}$ enables to calculate the activation energy E. It requires then to study the decomposition powder at different scanning rates.

1.2. KISSINGER method

The KISSINGER method can also be used (voir *Anal. Chem.* 29, 1702, (1957)).

The relation (7) gives :

$$\frac{d\,Log\left(\frac{a}{T_{m^2}}\right)}{d\left(\frac{1}{T_m}\right)} = -\frac{E}{R}$$

The slope of the line $Log\left(\frac{a}{T_{m^2}}\right)$ as function of $\frac{1}{T_m}$ enables to calculate the activation eneregy E. It then requires to study the decomposition at different scanning rate.

2. Utilisation

Before using the ***Kinetic on DTG*** software, it is necessary on using the base software to carry out various decomposition tests at variable scanning rate.

2.1. Memorizing decomposition tests

Use the SETARAM base software to carry out the various decomposition tests successively (refer to the ***Setsoft*** booklet).

- Set a small quantity of sample in a Platinum or an Alumina crucible. It is recommended to use only 1 or 2 mg of sample to limit the quantity of vapour released during the decomposition.
- ***Procedure*** : seeing that only the scanning rate varies, memorizing a procedure for this type of measurement will be an advantage.
- ***Heating Procedure*** : for low scanning rates, it is interesting to plan a first sequence enabling the passage from the ambiant temperature to a temperature of about 20°C lower than the starting temperature of decomposition. In the second sequence, go from this temperature to a temperature higher than the temperature of decomposition ending.
- The decomposition temperature rises when the scanning rate increases. Take it into account when selecting the initial and final temperature in sequences. Then return to the starting temperature.
- Start the experiment.

- Remove the crucible and introduce a new crucible containing a similar quantity of the same sample. Start the experiment again. For a right utilisation of the OZAWA or KISSINGER method, carry out at least three tests, at different scanning rates (1, 5, 10°C/mn for instance), but it is recommended to achieve more than three tests for a better precision of the method.
- After ending the last experiment, go to ***Processing***.

2.2. Determining kinetic parameters

After collecting the various decomposition curves (refer to paragraph *2.1*), carry out an integration on the various DTG curves to determine the corrected temperature for the top of the peak (refer to *Chapter 3*).

Note Select ***Processing / Integration / on Signal DTG*** to perform this integration

---

The determination of kinetic parameters can be started.

- Select ***Processing/Kinetic/OzawaKissinger*** to go to the selection window.

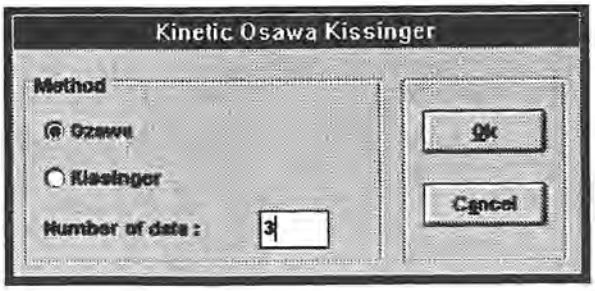


Figure 5

- Select the method : ***OZAWA*** or ***KISSINGER***.
- Enter the number of decomposition curves to use for computing.
- Click on ***OK*** to continue (or ***CANCEL*** to stop the determination of kinetic parameters).
- A window appears:

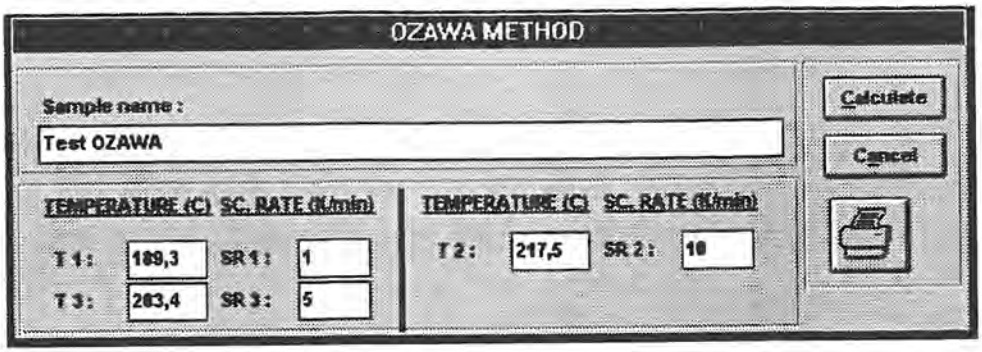


Figure 6

- A name may be given to the determination.
- Enter the different corrected temperatures of the top of the peak as well as the scanning rate related to each temperature.
- Click on the printer icon to print the window.
- Click on ***Cancel*** to finish the processing.
- Click on ***Calculate*** to continue the computing.

Then a screen appears:

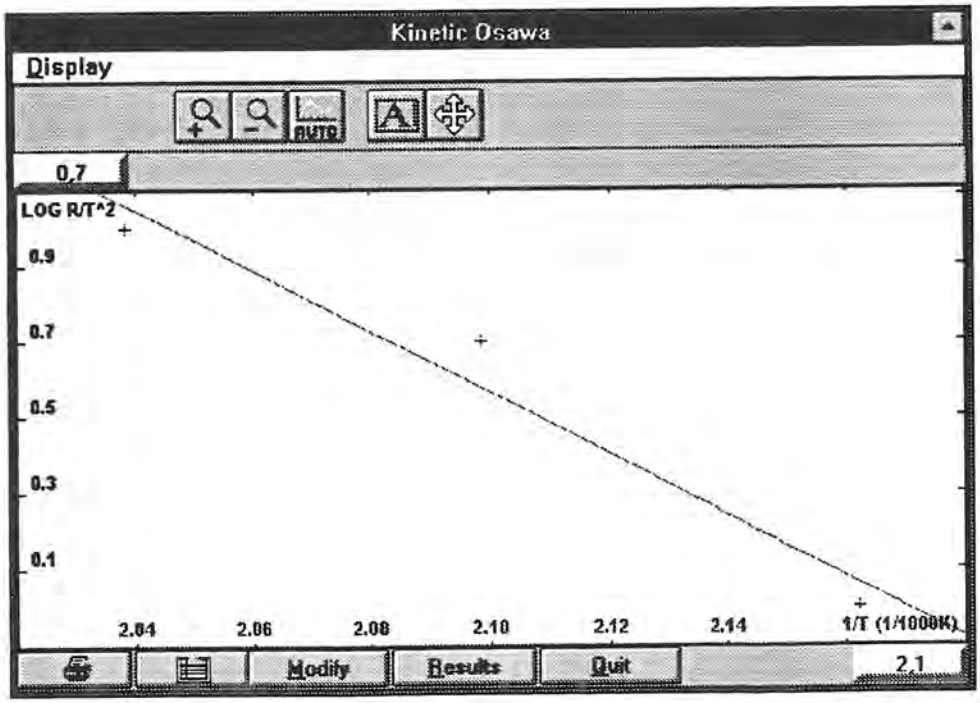


Figure 7

This screen displays the different possibilities available in the base software: ***Zoom***, ***Write a label***, ***Print***, ***Go to the Clip board***, ... (refer to the ***Setsoft*** booklet)

Click on ***Modify*** to modify all or some of the parameters entered for the determination of kinetic parameters.

Click on ***Results*** to display the results of the computing which are in fact the activation energy and the correlation coefficient of the method used.

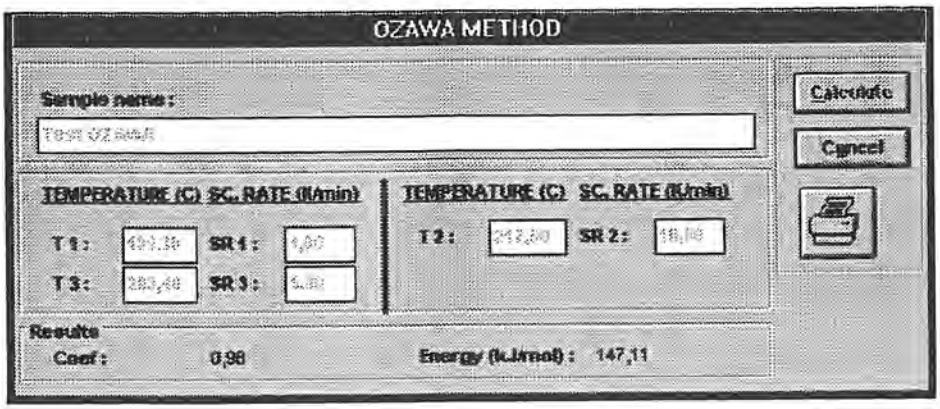


Figure 8

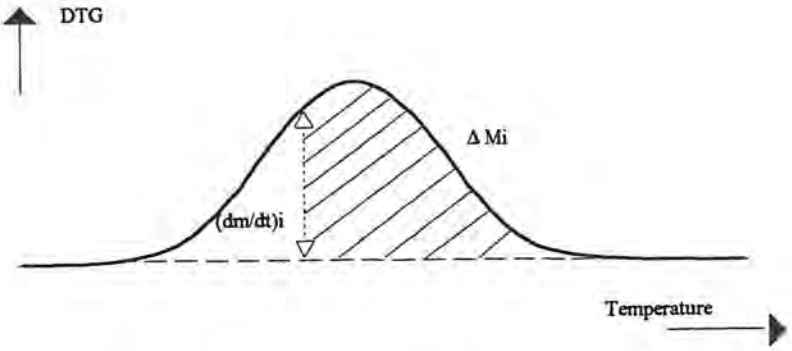
CHAPTER 5 - DETERMINATION OF KINETIC PARAMETERS: FREEMAN-CARROLL METHOD

Freeman-Carroll method enables, from the exploitation of only one DTG peak, to determine the order, the rate constant and the activation energy of reaction.

1. Principle

In scanning mode, the reaction rate may be written as follow:

$$\frac{dm}{dt} = k\,c^x = k_0 \exp\frac{E}{RT_i}\,c^x$$

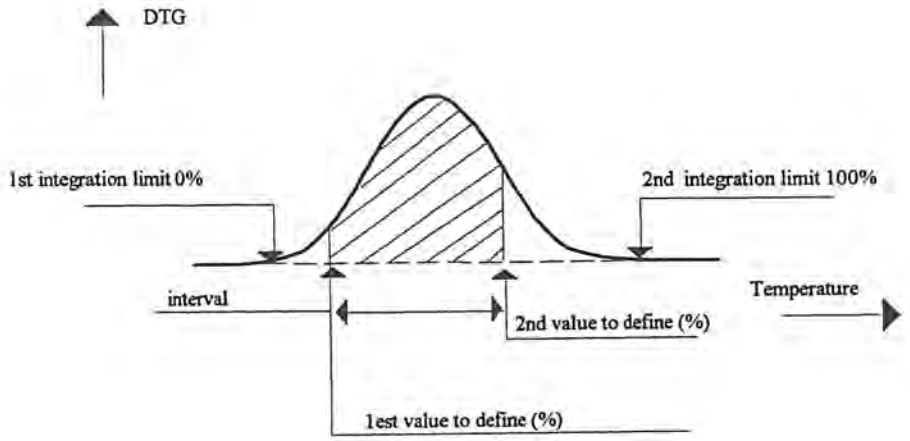


1.1. Calculating the order of the reaction

By means of three experimental points of the curve, we obtain three relations which allow the determination of the order x:

$$x = \frac{\dfrac{Log\dfrac{(dm/dt)_3}{(dm/dt)_1}}{1/T_1 - 1/T_3} - \dfrac{Log\dfrac{(dm/dt)_2}{(dm/dt)_1}}{1/T_1 - 1/T_2}}{\dfrac{Log\dfrac{\Delta M_1}{\Delta M_2}}{1/T_1 - 1/T_2} - \dfrac{Log\dfrac{\Delta M_1}{\Delta M_3}}{1/T_1 - 1/T_3}}$$

Practically, you just have to select two values (in %) which define the interval in which the calculation will be carried out. The third value is defined -by the software- between the two selected values.



1.2. Calculating E and k_0

If x = 1, the rate constant k_i is equal to:

$k_i = (dm/dt)_i / \Delta M_i$

The slope of the line Log k_i as function of $1/T_i$ determines the activation energy E and the ordinate at the origin gives k_0.

1.3. Isothermal simulation

From the calculated kinetic data, it is possible to calculate the variation of conversion rate of the reaction as function of time at a fixed temperature.

Use the following kinetic relations:

$$\frac{d\alpha}{dt} = K\,(1-\alpha)^x$$

α :conversion rate

K : constant rate

x : order of the reaction

$$K = K_0 \exp\left(-\frac{E}{RT}\right)$$ avec E: activation energy

The fixed temperature T is determined:

$\alpha = 1 - (1+(x-1)\,Kt)^{1/(1-x)}$

The α variation can be plotted versus time.

2. Using the software

Before using the ***Kinetic on DTG*** software the experiment corresponding to the reaction of the compound must be previously carried out on the base software.

2.1. Performing the experiment

Use the SETARAM base software to perform the experiment on the compound and to save the reaction (refer to the ***Setsoft*** booklet).

Introduce the sample in the crucible and the crucible in the instrument.

- ***Procedure*** : seeing that only the scanning rate varies, memorizing a procedure for this type of measurement will be an advantage.
- ***Heating Procedure***: choose the temperature range among which the sample is to react.

Choose a temperature scanning rate of about 5K.mn^{-1}. Be careful not to choose a temperature that is too high so as to avoid a temperature gradient too high for the sample.

- Then return to the starting temperature.
- Start the experiment and then at the end of the experiment start processing the data.

2.2. Determination of kinetic parameters

After acquiring a test for the reaction of a compound, perform an integration of the DTG signal (see the ***software*** booklet).

Note Select ***Processing / Integration / on Signal DTG*** to perform this integration

Note First of all select an integration in the palette to calculate the determination of kinetic parameters. Click on the name of the integration to be calculated. For instance, the palette in Figure 9 displays the selected integration named ***Integration DTG1***.

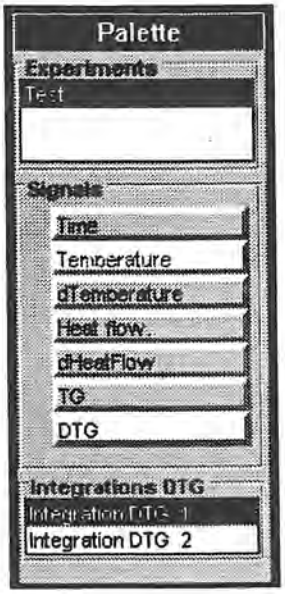


Figure 9

Choose ***Processing/Kinetic/Freeman-Carroll/Ozawa Kissinger/On Signal DTG*** to go to the following window:

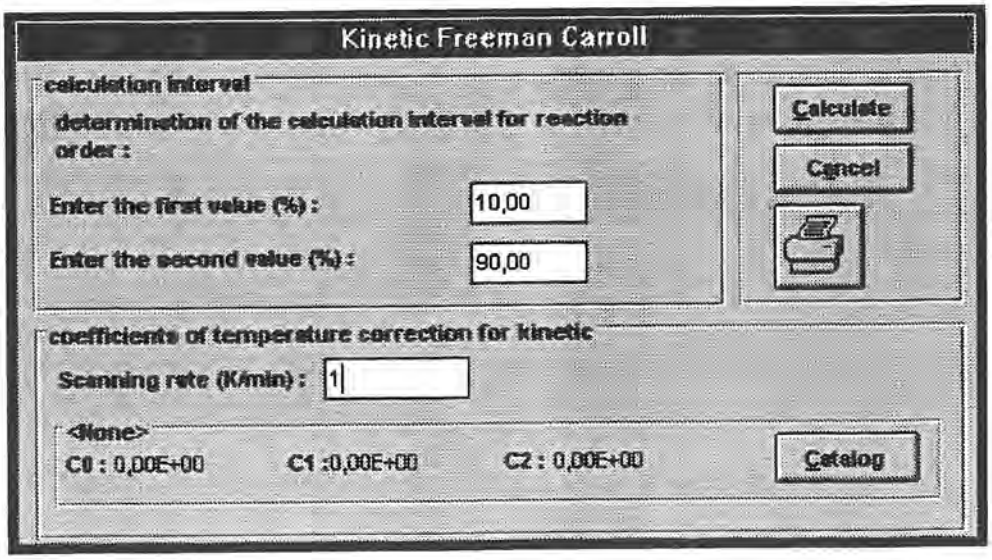


Figure 10

- Define the calculation interval to calculate the order of the reaction and enter the maximum and minimum limits. Avoid extreme values (see ***Principle***) that is to say use limits comprised between 10% and 90%.
- The scanning rate may be entered for temperature correction. Click on ***Catalog*** to modify the correction coefficients; then another series of coefficients can be modified or selected (see chapter 0, Chapter 3 - Correction of Temperature).
- Click on ***Calculate*** to start the calculation, then a screen appears:

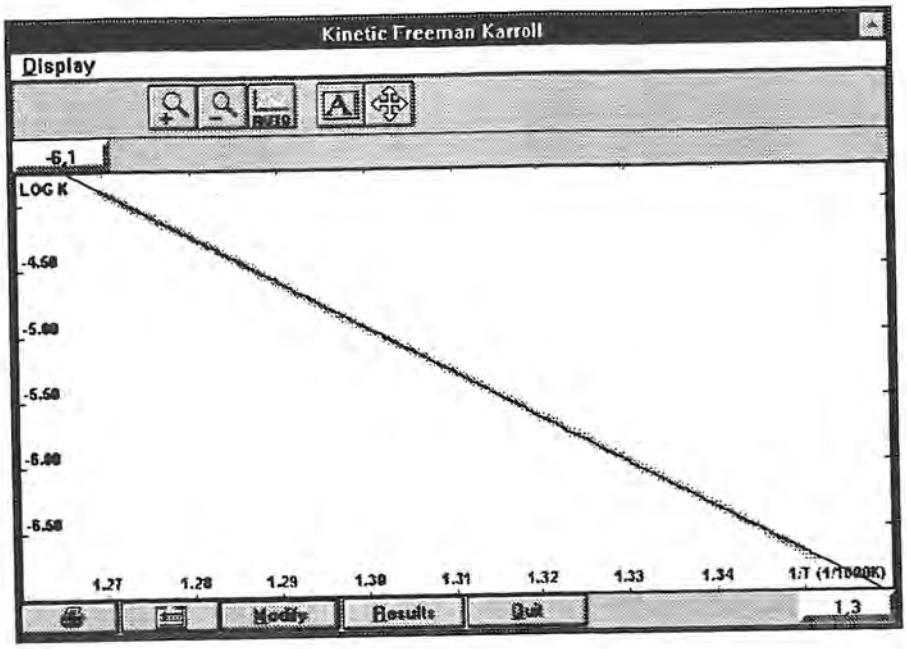


Figure 11

This screen displays the different possibilities available in the base software: ***Zoom***, ***Write a label***, ***Print***, ***Go to the Clip board***, ... (refer to the ***Setsoft*** booklet)

Click on ***Modify*** to re-calculate the different limits.

Click on ***Results*** to display the results:

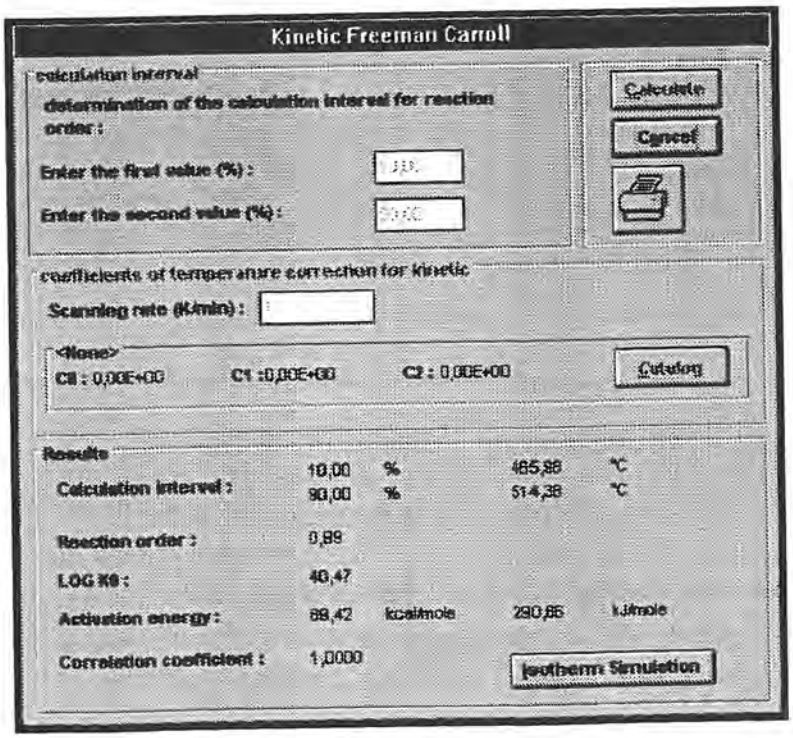


Figure 12

2.3. Isothermal simulation

After determining parameters using the FREEMAN-CARROLL method, reaction rate at a given temperature can be calculated. Click on the ***Isotherm Simulation*** on the results window (see Figure 12).

A window appears:

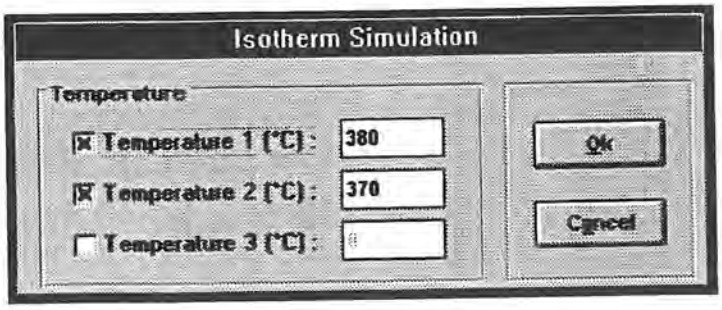


Figure 13

- Enter the simulation temperature(s) needed. Three different simulation temperatures can be entered.
- Click on ***OK*** to start the calculation, then a window appears:

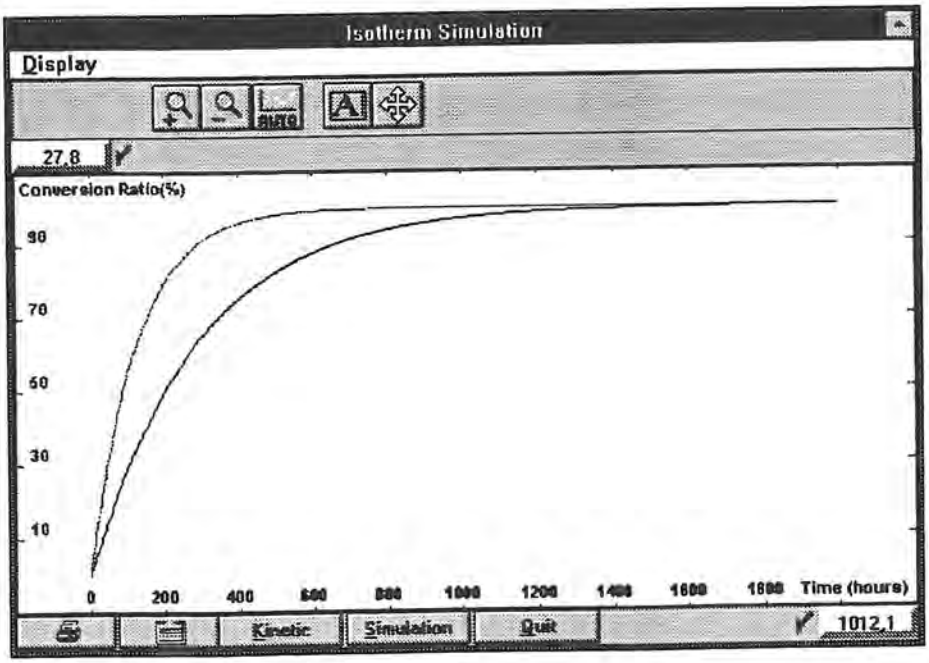


Figure 14

- This screen displays the different possibilities available in the base software: ***Zoom***, ***Writing a label***, ***Print***, ***Go to the Clip board***, ... (refer to the ***Setsoft*** booklet)

Note The colour of the different curves can be changed when double clicking on the background of the window (as if to change the colour of the window background).

- The ***Kinetic*** button is used to re-start another calculation for parameters determination using FREEMAN-CARROLL method but with the same initial integration (to modify the calculation limits for).
- Click on ***Simulation*** to modify the simulation temperature(s).

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SETSOFT

ADDITIONAL OPERATIONS ON THE CURVES

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CONTENTS

CHAPTER 1 - INSTALLATION

1. Foreword

This booklet is designed for people who are already familiar with the base version of the SETARAM's ***Setsoft*** booklet. Indeed, most notions that are refered to in this booklet are detailed in the ***Setsoft*** booklet.

2. Installation

2.1. Preparation

2.1.1. Verification of software mapping

Installing the ***Additional operations on the curves*** software package first of all requires installing the base software on the hard disk. Refer to the base version booklet for the installation procedure (*Chapter 1 - Installation*).

2.1.2. Backup copies

Before the program is installed, backup copies of the SETARAM software package must be made with one of the following commands:

- ***Disk / Copy Disk*** in the Microsoft Windows™ manager file.
- The MS-DOS™ ***DiskCopy***.

2.2. Installing the software package

Refer to the ***Setsoft*** booklet (*Data Management/ Installing New Software Collection* chapter).

CHAPTER 2 - DESCRIPTION OF THE SOFTWARE

This software enables various operations to be carried out on previously recorded curves. These modified curves can themselves be saved for subsequent reprocessing.

The software offers various processing:

- Addition - Subtraction of curve(s)
- Smoothing by the SAVITZKY and GOLAY method
- Inverse filtering by derivation
- Slope correction
- Interpolation
- Naperian logarithm

CHAPTER 3 - UTILISATION

Additional operations on curve are generally composed of three main phases, which are described in the paragraphs below.

1. Additional operations on the curves

After loading the experiment, select a signal in the palette by clicking on its name.

Then, a mark appears on the left side of the name of the signal.

For instance, in the palette below, the Temperature signal is selected.

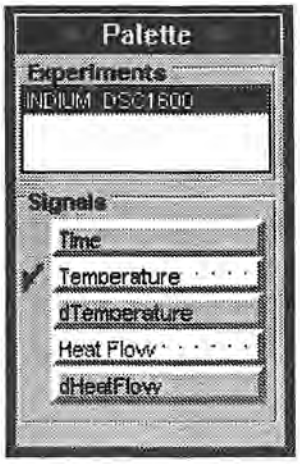

Figure 1: Palette

WARNING The signals saved on the disk only can be (***Température, Heat Flow, TG,*** ...); as in fact these signals are the only ones to be displayed in the selection of signals window.

WARNING Conversely, the derivated signals (for example, ***dHeat flow***, the ***Time*** signal...) cannot be selected.

2. Operations on curves

After selecting a signal (see above) in order to carry out for instance an interpolation, choose ***Processing/Interpolation***.

3. Saving a new signal (or resulting signal)

When the processing needed is performed a window appears:

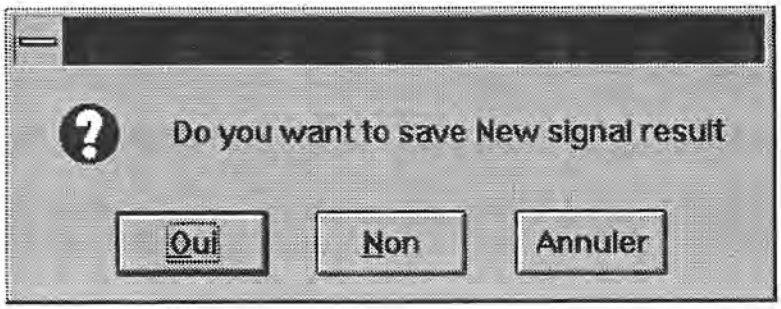

Figure 2 : Saving a new signal result

- ***Annuler*** returns to the processing.
- ***Non*** does not save the new signal.
- ***Oui*** goes to the next window(figure below):

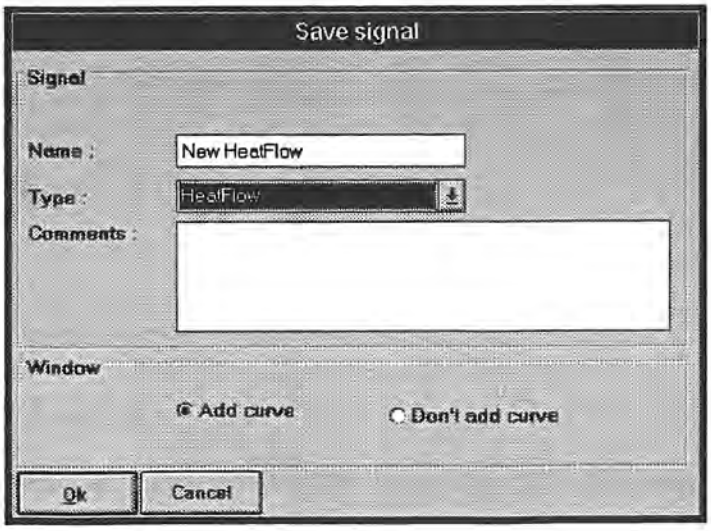

Figure 3: Saving a signal

- ***Cancel*** cancels the saving procedure for the signal.
- ***OK*** saves the new signal after different information are given:
  - Enter the name of the signal (compulsory).

- For an addition or a subtraction, the type of the new signal could be selected.
- Comments related to the new signal can be entered.
- ***Add Curve*** replaces the former signal by the new one in the display window. It is to be noticed that the former signal is not deleted and remains available for loading this experiment.
- ***Don't add curve*** saves the new signal but this signal does not immediately appears in the window.

CHAPTER 4 - ADDITION - SUBTRACTION

1. Principle

This option provides for:

- adding or subtracting two curves, produced by identical experimenting conditions.
- adding or subtracting a constant term to the resulting curve.
- and possibly, working on a single file (to do that, simply enter a null term as the value of C).

S (t) = A/B x Signal 1 + C/D x Signal 2 + E

with

S (t) :	value of the resulting signal at p point
Signal 1 :	selected in the palette
Signal 2 :	selected in a catalogue
A/B :	coefficient to be applied to Signal 1
C/D :	coefficient to be applied to Signal 2
E :	constant to be added to the resulting curve

For each file, enter the coefficient to be applied to the selected curve(s).

Example 1 : This option provides for calculating the curve produced with a mixture of 30% of A and 70% of B. To do this, enter: A = 30 ; B = 100 ; C = 70 ; D = 100 ; E = 0.

Example 2 : This option provides for calculating the curve of a sample of a given mass (e.g. 1 g). To do this, enter: A = 1 ; B = mass in grammes for A ; C = 0 ; E = 0.

Example 3 : This option provides for off setting curve A based on the ordinates. To do this, enter: A = 1 ; B = 1 ; C = 0 ; E = value of the off set required.

2. Utilisation

After selecting the first curve (Chapter 0), choose ***Processing/Addition/Subtraction***. A window appears:

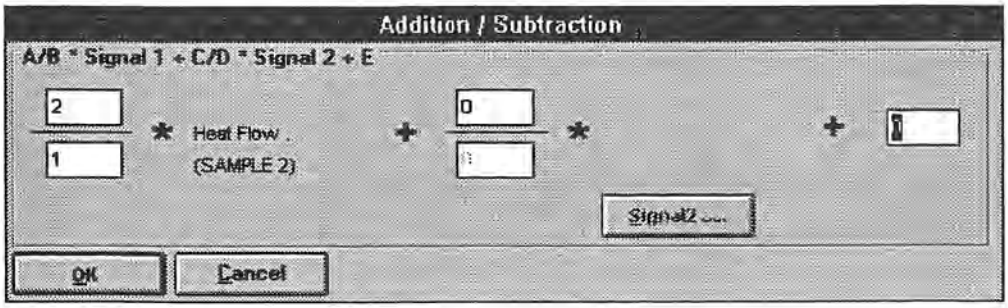

Figure 4: Addition/Subtraction

Enter the different coefficients to be applied to the signals 1 and 2.

If valid coefficients are entered for the signal 2, click on ***Signal 2*** to select this signal, ... then you have access to the signal selection (refer to the ***Setsoft*** booklet).

Click on ***OK*** to start the calculation, then a window appears :

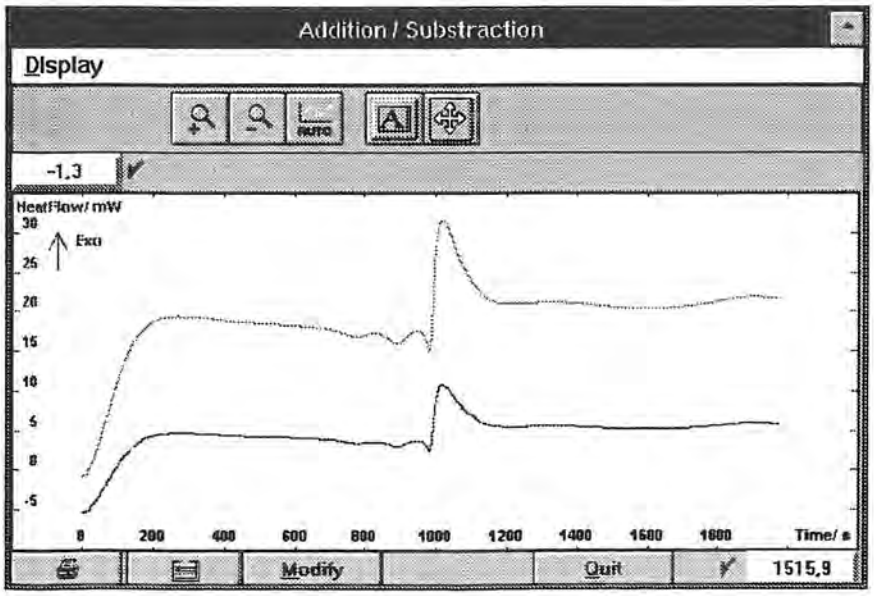

Figure 5 : Addition/Subtraction window

- This screen displays the different functions offered in the base software: ***Zoom, Write a label, Print, Go to the Clip board***, ...(refer to the ***Setsoft*** booklet). The initial signal(s) and the resulting signal are displayed.

Note The colour of the different curves can be changed: double click on the window background (as for changing the colour of the window background).

Click on ***Modify*** to change the calculation parameters.

Click on ***Quit***, and the window for saving a new signal appears (refer to *Saving a new signal (or resulting signal)*).

CHAPTER 5 - SMOOTHING

1. Principle

This option provides for smoothing an entire curve using the SAVITZKY and GOLAY method (3 degrees of filter available).

2. Utilisation

After selecting a curve in the palette (refer to *Chapter 3*), choose ***Processing / Smoothing***. A window appears:

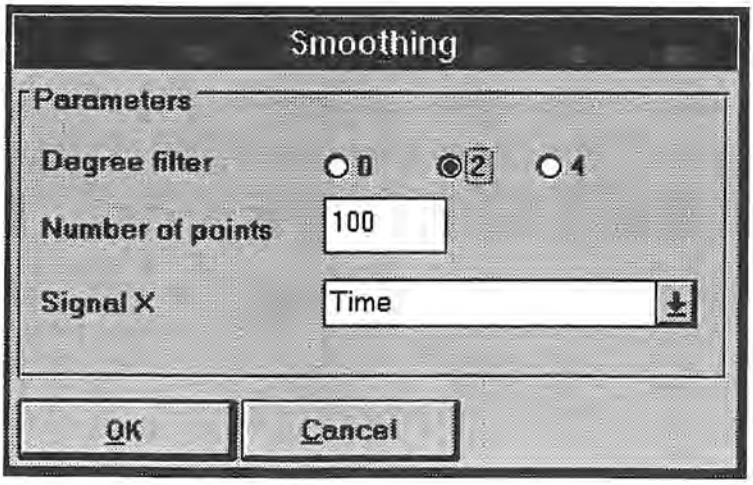

Figure 6 : Smoothing window

- Enter the degree of filter,
- The number of points,
- Select also the X axis to add the new signal on the graph.

Click on ***OK*** to start the calculation. A window appears:

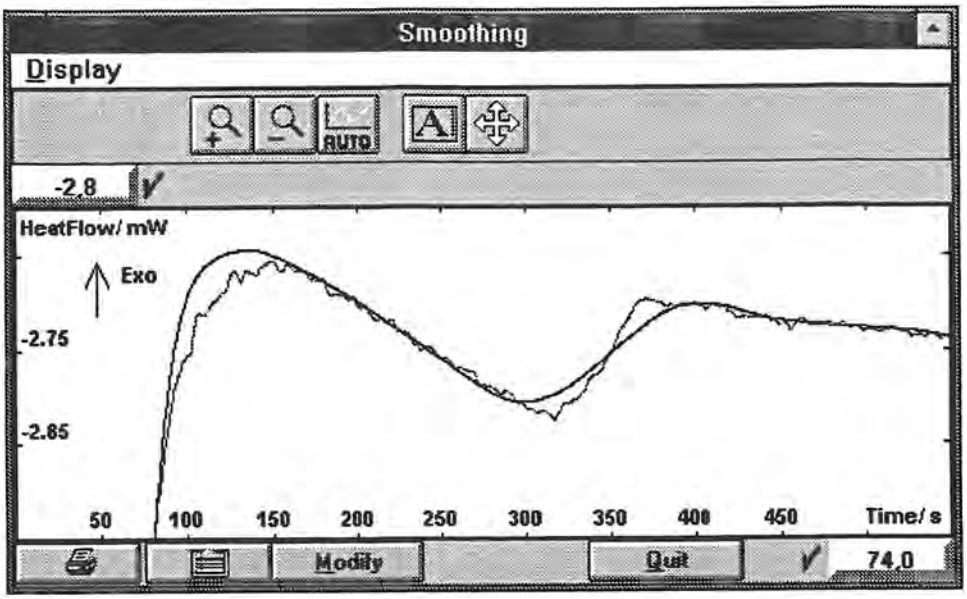

Figure 7: Smoothing window

- This screen displays the different functions offered in the base software: ***Zoom, Write a label, Print, Go to the Clip board***, ...(refer to the ***Setsoft*** booklet). The initial signal(s) and the resulting signal are displayed.

Note The colour of the different curves can be changed: double click on the window background (as for changing the colour of the window background).

Click on ***Modify*** to change the calculation parameters.

Click on ***Quit***, and the window for saving a new curve appears (refer to *Saving a new signal (or resulting signal)*).

CHAPTER 6 - INVERSER FILTERING

1. Principle

Inverse filtering of a curve supplied by an instrument enables work to be done without this instrument's time constant so as to reconstitute the true response from the sample analyzed. The method involves supposing that the instrument has an exponential response to an impulse. A transformation will thus be produced by derivation: the instrument's time constant will then be entered: this is how inverse filtering is carried out.

Inverse filtering by derivation

$S'(t) = S(t) + \tau \, dS(t) / dt$

with $S'(t)$: filtered signal

$S(t)$: initial signal

τ : the instrument's time constant (in seconds)

It can generally be considered that an instrument (calorimeter) has several decreasing time constants $\tau 1$, $\tau 2$, $\tau 3$ ... For inverse filtering based on various time constants, inverse filtering is first done on the largest time constant $\tau 1$, then on the resulting curve. This is followed by inverse filtering base on $\tau 2$, etc.

2. Utilisation

After selecting the curve in the palette (see chapter 0), choose : ***Processing / Inverse filtering***. A window appears:

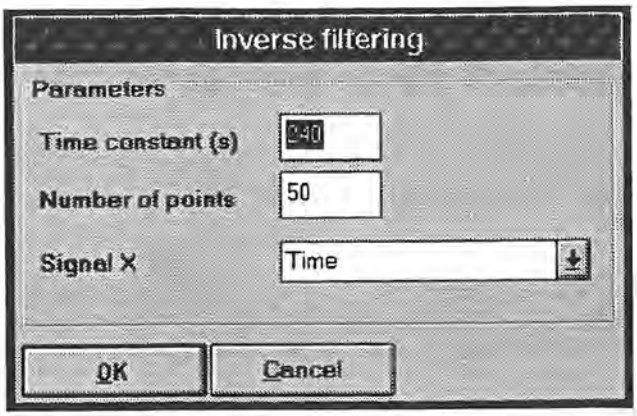

Figure 8 : Inverse filtering

- Enter the instrument's time constant in seconds,
- Enter the number of points N required for calculating,
- Select also the X axis to add the new signal on the graph.

Click on ***OK*** to start the calculation. A window appears:

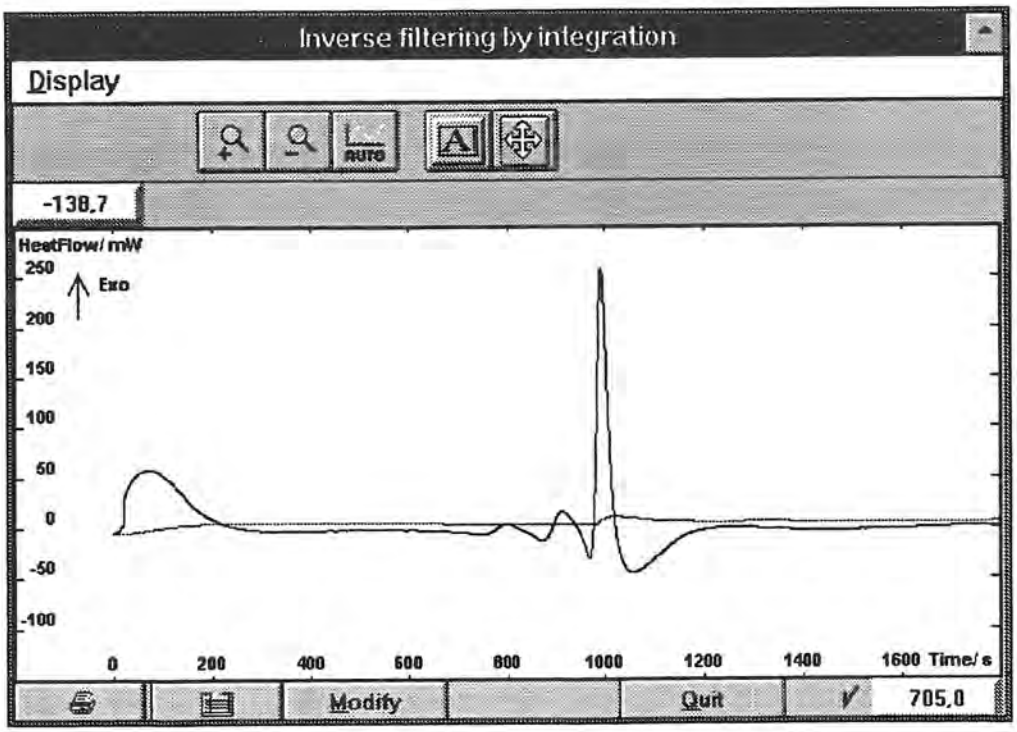

Figure 9: Inverse filtering screen

- This screen displays the different functions offered in the base software: ***Zoom, Write a label, Print, Go to the Clip board***, ...(refer to the ***Setsoft*** booklet). The initial signal(s) and the resulting signal are displayed.

Note The colour of the different curves can be changed: double click on the window background (as for changing the colour of the window background).

Click on ***Modify*** to change the calculation parameters.

Click on ***Quit***, and the window for saving a new curve appears (refer to *Saving a new signal (or resulting signal)*).

CHAPTER 7 - INTERPOLATION

1. Principle

This option provides for carrying out an interpolation on a part of the curve (e.g. to remove an erroneous point or to improve a part of the noisy curve).

Result : this option replaces the part of the selected curve by the segment of a straight line.

2. Utilisation

After selecting a curve in the palette (refer to *Chapter 3*), choose : ***Processing / Interpolation***. A window appears:

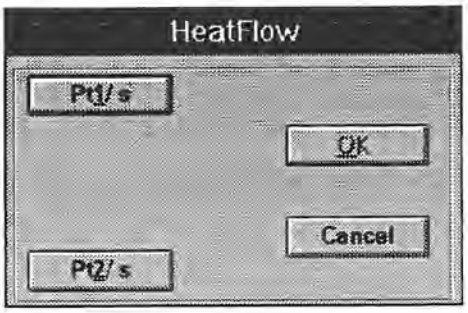

Figure 10

- Select the two points designating the interpolation.

Click on ***OK***. A window appears:

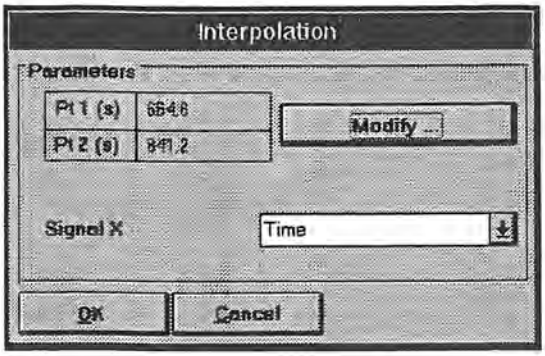

Figure 11: Interpolation

This screen displayed the selected points. Select the X axis to add the new signal on the graph.

Click on ***OK*** to start the calculation.

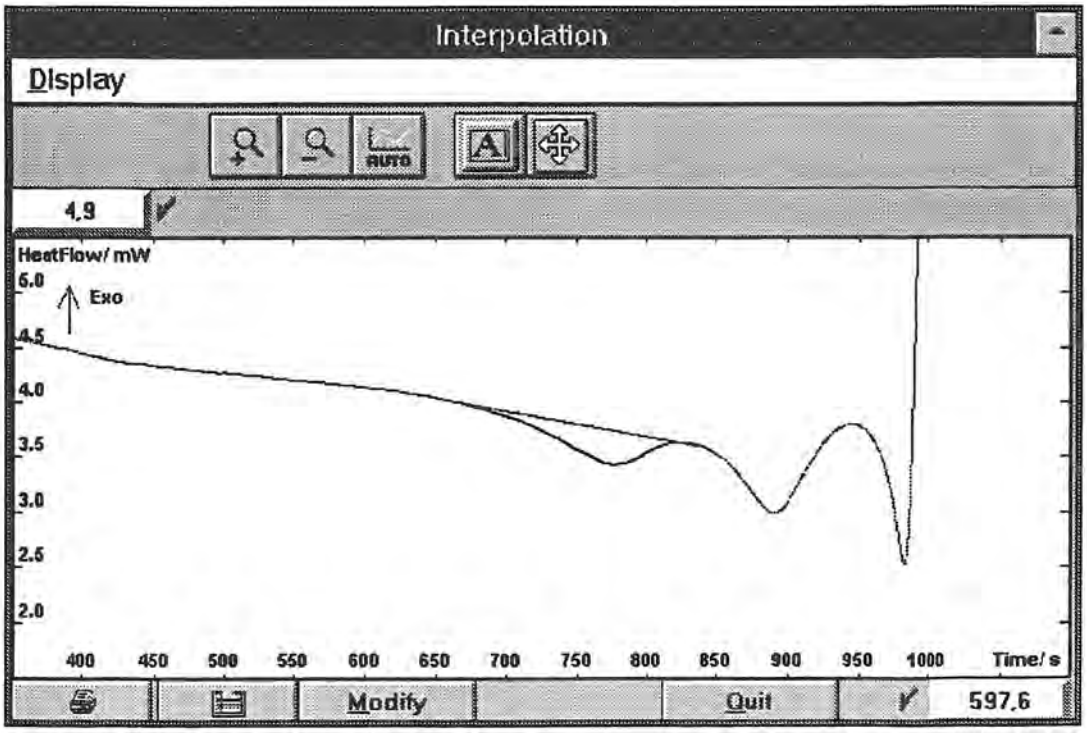

Figure 12: Interpolation

- This screen displays the different functions offered in the base software: ***Zoom, Write a label, Print, Go to the Clip board***, ...(refer to the ***Setsoft*** booklet). The initial signal(s) and the resulting signal are displayed.

Note The colour of the different curves can be changed: double click on the window background (as for changing the colour of the window background).

Click on ***Modify*** to change the calculation parameters.

Click on ***Quit***, and the window for saving the new signal appears. This window saves curve appears (refer to *Saving a new signal (or resulting signal)*).

CHAPTER 8 - SLOPE CORRECTION

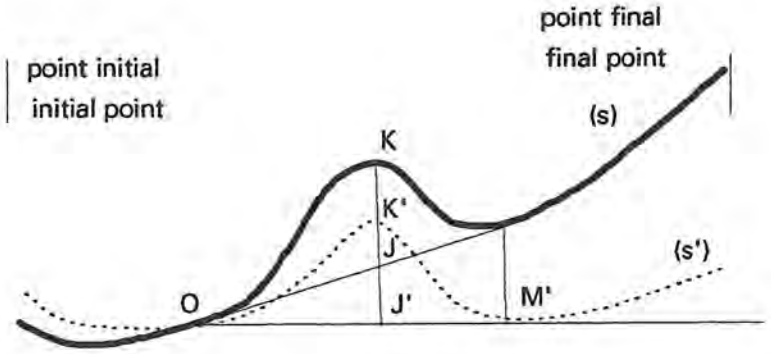

Figure 13

Let (S) be a curve which needs to be corrected to (S').

The two points O and M are selected and the curve (S) is made to flatten on to the horizontal plotted by O.

Thus the lineal point K will be moved to K' so that KK' = JJ'.

Let also be JK = J'K'

therefore JJ' = MM' x OJ'/OM'

This provides for easy calculation of all the curve S'.

This correction is applied **over the entire curve**.

This is to show that temperatures and surface areas have been conserved.

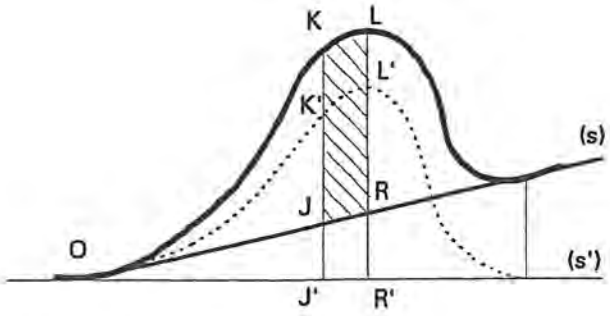

Figure 14

S (KJRL) = (JK +RL) x J'R'/2

S(K'J'R'L') = (J'K' + R'L') x J'R'/2

Now it has been shown that JK= J'K' so the outcome is clearly thus S(KJRL) = S(K'J'R'L').

After selecting the curve in the palette (see *Chapter 3*), choose: ***Processing / Slope correction***. A window appears :

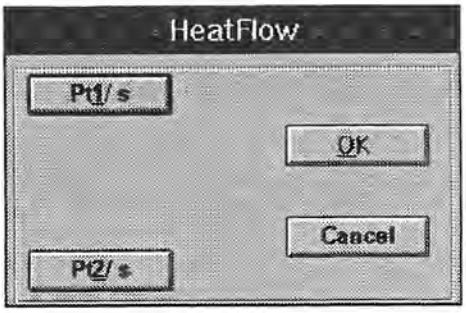

Figure 15

- Select the two points designating the slope correction.

Click on ***OK***. A window appears:

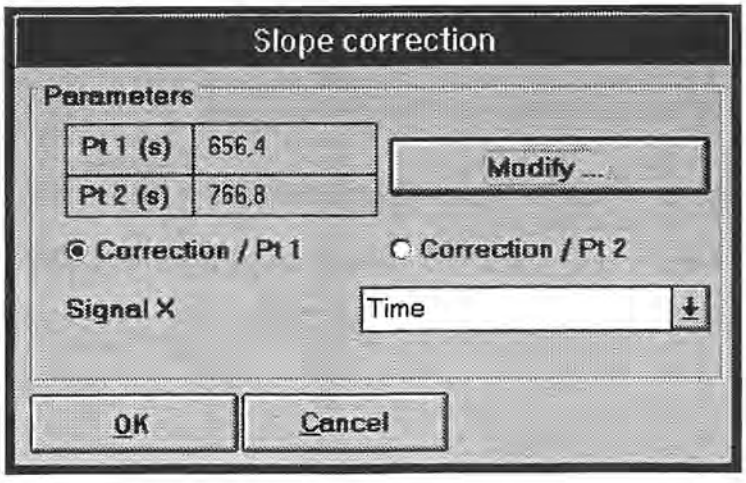

Figure 16: Slope correction

This screen displays the selected points. Select if the correction is on P1 or P2, that is to say is signal (P2) = signal (P1), choose ***Correction/Pt1***

Select the X axis to add the new signal on the graph.

Click on ***OK*** to start the calculation.

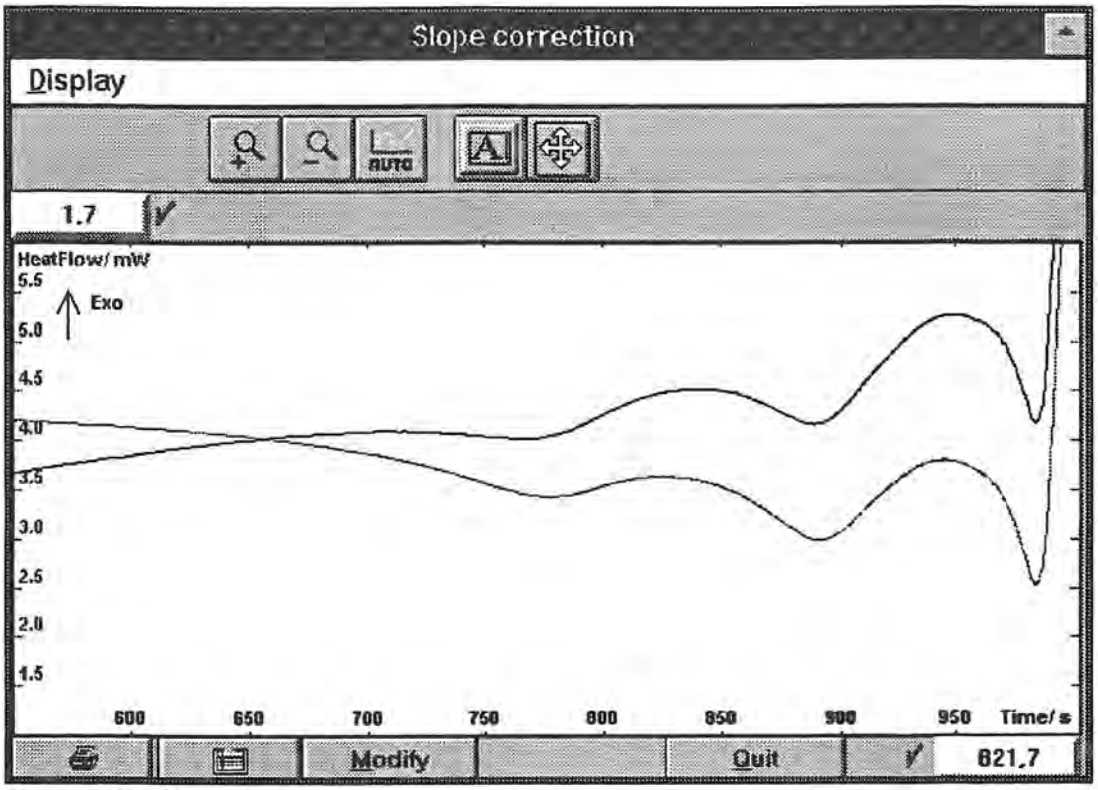

Figure 17: Slope correction

- This screen displays the different functions offered in the base software: ***Zoom, Write a label, Print, Go to the Clip board***, ...(refer to the ***Setsoft*** booklet). The initial signal(s) and the resulting signal are displayed.

Note The colour of the different curves can be changed: double click on the window background (as for changing the colour of the window background).

Click on ***Modify*** to change the calculation parameters.

Click on ***Quit***, and the window for saving a new curve appears (refer to *Saving a new signal (or resulting signal)*).

CHAPTER 9 - NAPERIANT LOGARITHM

1. Principle

This option enables a new curve to be produced:

S C(t) = log (ABS (SA (t)))

with S C(t) : value of the resulting curve at point t

log : naperian logarithm

ABS : absolute value

SA (t) : signal from the initial curve at point t

2. Utilisation

After selecting a curve in the palette (refer to *Chapter 3*), choose ***Processing / Naperian Logarithm***. A window appears:

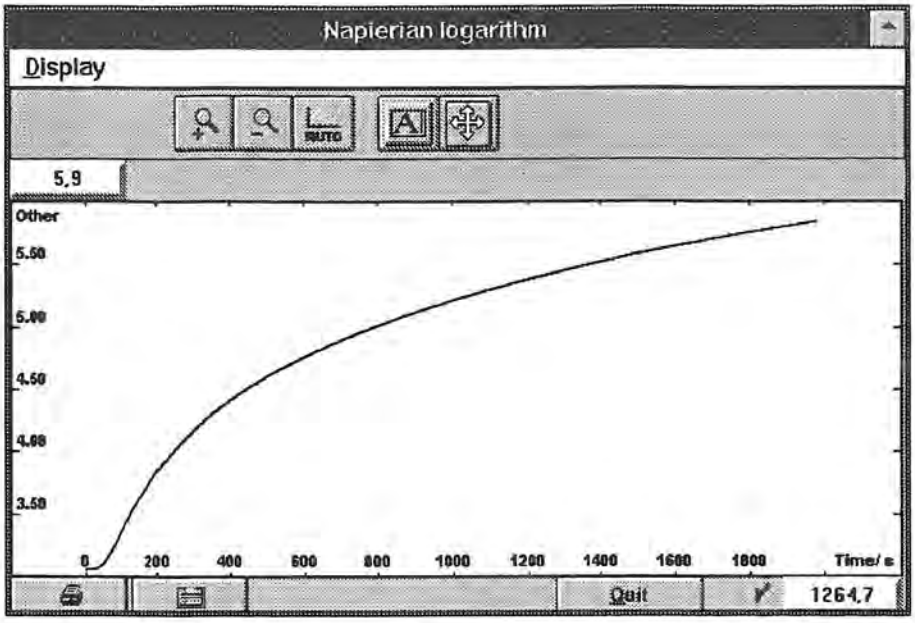

Figure 18: Naperian logarithm

Click on ***OK*** to start the calculation.

- This screen displays the different functions offered in the base software: ***Zoom, Write a label, Print, Go to the Clip board***, ...(refer to the ***Setsoft*** booklet). The initial signal(s) and the resulting signal are displayed.

Note The colour of the different curves can be changed: double click on the window background (as for changing the colour of the window background).

Click on ***Modify*** to change the calculation parameters.

Click on ***Quit***, and the window for saving the new signal appears. This window saves curve appears (refer to *Saving a new signal (or resulting signal)*).

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- micro DSCIII : -20 to 120°C ("batch and flow")
- micro DSCVII : -45 to 120°C ("batch")

CALVET PRINCIPLE DSC

- DSC 121 : -120 to 830°C
- DSC Robotic Sytem : -120 to 830°C

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- MS 80 : standard calorimeter from ambient to 200°C
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- C 80 : mixing and reaction calorimeter from ambient to 300°C
- Titrys : titration calorimeter from ambient to 75°C
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- DHT 96 : dilatometry
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Cp DETERMINATION

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CONTENTS

CHAPTER 1 - INSTALLATION

1. Foreword

This booklet is designed for people who are already familiar with the base version of SETARAM's thermal analysis software, ***Setsoft***. Indeed, most notions that are referred to in this booklet are detailed in the base software booklet.

2. Installing the Cp determination software package

2.1. Preparation

2.1.1. Verification of the hardware and software mapping

Remark Installing the ***Cp Determination*** software package first of all requires installing the base software on the hard disk. Refer to the base version booklet for the installation procedure (see *Chapter 1 - Installation*).

2.1.2. Back up copies of distribution disks

Before running the installation programme, back up copies of the SETARAM software package must be made with one of the following commands :

- ***Disk / Copy Disk*** in the Microsoft Windows™ manager file.
- The MS-DOS™ ***Diskcopy***

2.2. Installing the software package

Refer to the base version of the Setsoft booklet (see *Chapter 4 - Data Management / Installing New Software Collection*) for the installation procedure.

3. Starting the Cp Determination

To start the ***Cp Determination*** software, double click on the ***Cp*** icon (***SETSOFT*** group) from the program manager (see Figure 1).

Figure 1 : Determination of Cp icon

The main window must appear (see Figure 2).

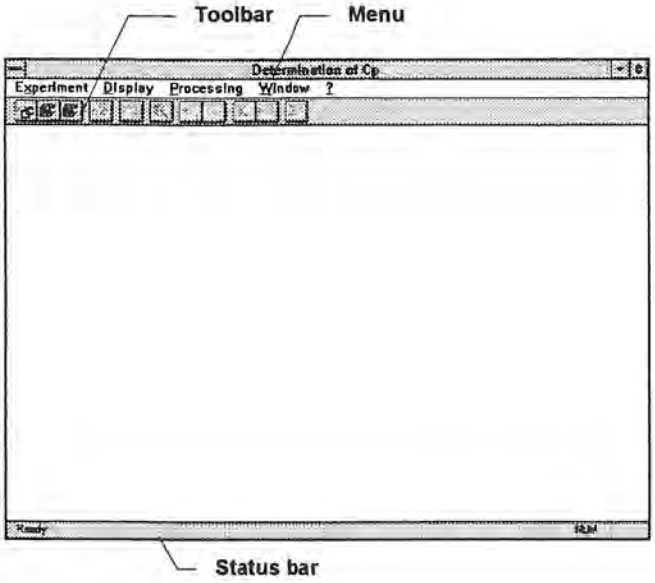

Figure 2 : Main Window

4. Menus and toolbar

4.1. Experiment menu

The ***Experiment*** menu made of the following sub-menus:

- ***Data Collection*** : to define a new experiment. .
- ***Processing / Continuous*** : to process an experiment done with the Cp continuous method.
- ***Processing / Cp Continuous with reference*** : to process an experiment allowing -according to the type of the instrument- to determine:
  - either a ***Specific heat capacity by reference***,

- ♦ or a ***Volumic heat capacity by reference***, depending on the continuous Cp method.

- ***Processing / Cp by step*** : to process an experiment done with the Cp by step method.
- ***Processing / Cp by step with reference*** : to process an experiment allowing -according to the type of the instrument- to determine:
  - ♦ either a ***Specific heat capacity by reference***,
  - ♦ or a ***Volumic heat capacity by reference***, depending on the Cp by step method.
- ***Print*** : to print the displayed curves.
- ***Print Setup...*** : to change the print parameters (orientation, printer, print quality, etc...).
- ***Page Setup...*** : to change the print margins.
- ***Quit*** : to quit the software.

4.2. Display menu

The ***Display*** menu is made of the following sub-menus:

- ***Real time drawing*** : to display the real time drawing when an experiment is currently running.
- ***Direct programming*** : to display the direct programming screen when an Experiment is currently running.
- ***Copy*** : to copy the displayed curves into the clipboard. The curves can be paste into many Windows software (Winword™ for example).
- ***Automatic scales*** : to display curves with an appropriate scale.
- ***Comments*** : to allow the move mode. During the move mode, the comments could be moved onto the curves.
- ***Icon Bar*** : to show or hide the toolbar.
- ***Status Bar*** : to show or hide the status bar.

4.3. Processing menu

The ***Processing*** menu is made of the following sub-menus:

- ***Smoothing*** : to smooth the ***Blank - Sample -Reference*** curves.
- ***Equation of Cp*** : to change the degree of the Cp equation.
- ***Filter*** : it is possible to :
  - ♦ change the filter used for computing the temperature derivative,
  - ♦ smooth the Heat Flow signal used for computing the continuous Cp (but the displayed signal is not smoothed).

- ***Temperature in K*** : to toggle temperature unit between °C an Kelvin.
- ***Cp in J/mol*** : to toggle Cp unit between J/mol and J/g.
- ***Add Cp coefficient on curves*** : to add the coefficients of the Cp equation on the curves.
- ***Add sensitivity coefficients on curves*** : to add the coefficients of the sensitivity equation on the curves. This option is available only when processing a Cp with reference.
- ***Export*** : to export signals under ASCII format in a file ou in the clipboard or to print digital values on the printer.

4.4. Toolbar

The toolbar (see Figure 3) provides for going directly to the most common menus described above.

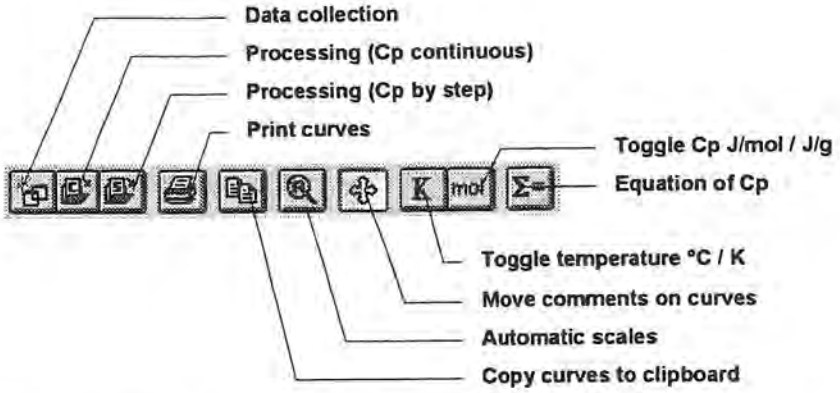

Figure 3 : Toolbar

CHAPTER 2 - DATA COLLECTION

1. Device, option and collection type selection

Before defining an experiment, the user has to select the apparatus, the option (if the apparatus has any) and the collection type (see Figure 4).

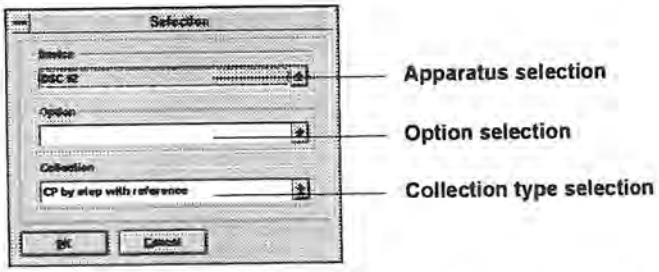

Figure 4 : Device, option and collection type selection

The options are listed in accordance with the selected apparatus. The collection types are listed in accordance with the apparatus and the option selected.

2. Experiment definition

2.1. Continuous Cp method

The determination of specific heat with the continuous mode is easy and rapid. Most calorimeters and DSCs scanned in temperature are suitable for such a measurement.

Two possible methods are available for the continuous Cp method:

1. continuous Cp without reference
2. continuous Cp with reference

Remark The user cannot choose the method, which depends on the type of apparatus.

2.1.1. Continuous Cp without reference

The precise determination of Cp requires two tests with identical experimental conditions :

- The first test is carried out with two empty cells without sample.
- The second test is carried out with the cells and the sample.

The difference between the two signals is proportional to the heat capacity of the sample. This amplitude is directly converted into heat power using the calibration curve of the DSC.

This method is a direct determination for any temperature and it does not need any standard sample (such as sapphire).

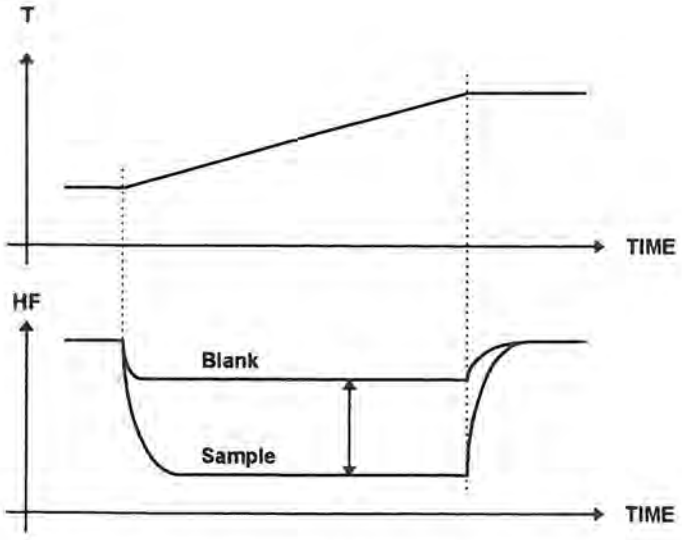

Figure 5 : Cp continuous without reference

The formula is given below:

$$Cp(T) = \frac{HF_{sample} - HF_{blank}}{Sensivity(T) \cdot Mass_{sample} \cdot \frac{dT}{dt}}$$

2.1.2. Continuous Cp with reference

2.1.2.1. Cp (specific) with reference

The precise determination of Cp requires three tests with identical experimental conditions :

- The first test with two empty cells without sample.
- The second test with the cells and the reference sample.
- The third test with the cells and the sample.

The reference sample is a material whose Cp equation is known.

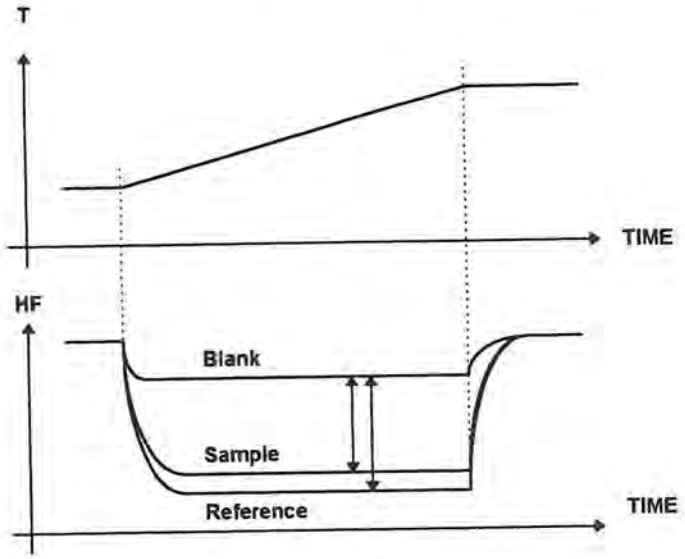

Figure 6 : Cp continuous with reference

The formula is given below:

$$Cp(T) = \frac{HF_{sample} - HF_{blank}}{HF_{ref} - HF_{blank}} \cdot \frac{Mass_{ref}}{Mass_{sample}} \cdot Cp_{ref}(T)$$

2.1.2.2. Cpv (volumic) with reference

The precise determination of Cp requires three tests with identical experimental conditions :

- The first test with two empty cells without sample.
- The second test with the cells and the reference sample.
- The third test with the cells and the sample.

The reference sample is a material whose Cpv equation is known.

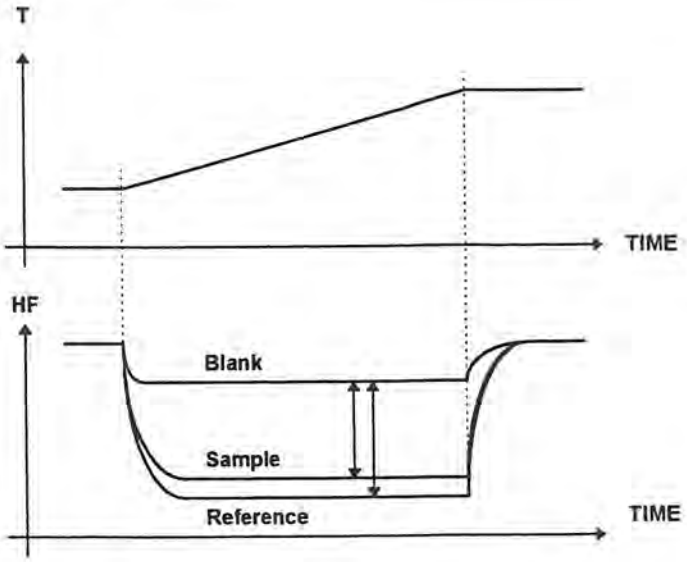

Figure 7 : Cp continuous with reference

The formula is given below:

$$Cpv(T) = \frac{HF_{sample} - HF_{blank}}{HF_{ref} - HF_{blank}} \cdot Cp_{ref}(T)$$

2.1.3. Defining the experiment

The user has to define the temperature, the delay and the rate for each sequence of the experiment.

- Case of the Cp (specific):

The mass is used in Cp calculation. Therefore, it must be defined. The molar mass field is optional, but it is necessary for obtaining the Cp unit in J/mol at the processing time.

Warning For the blank experiment, enter zero in the mass field.

- Case of the Cpv (volumic):

Select whether it is a blank, a sample or a reference.

It is possible to start from a stored procedure or from a previous experiment (click on the ***Catalog*** button). Obviously, it is possible to save the current procedure (see ***Saving the Experiment definition as procedure***).

To define collection parameters (such as PIDs, stop mode, etc...), refer to ***Defining the collection parameters***.

To start the experiment, click on the ***To Experiment*** button (see ***Starting the Experiment***).

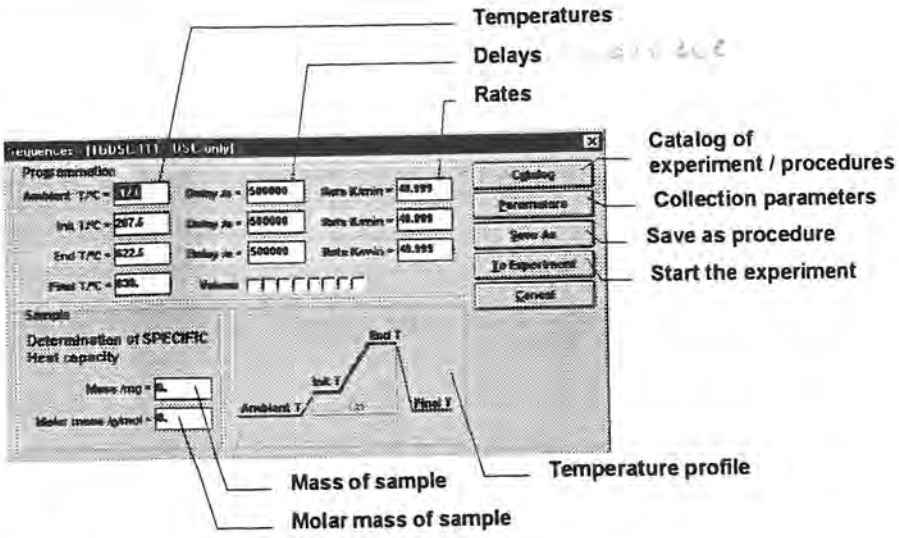

Figure 8 : Continuous (specific) Cp collection

In the case of Cpv (volumic) the window is as follows:

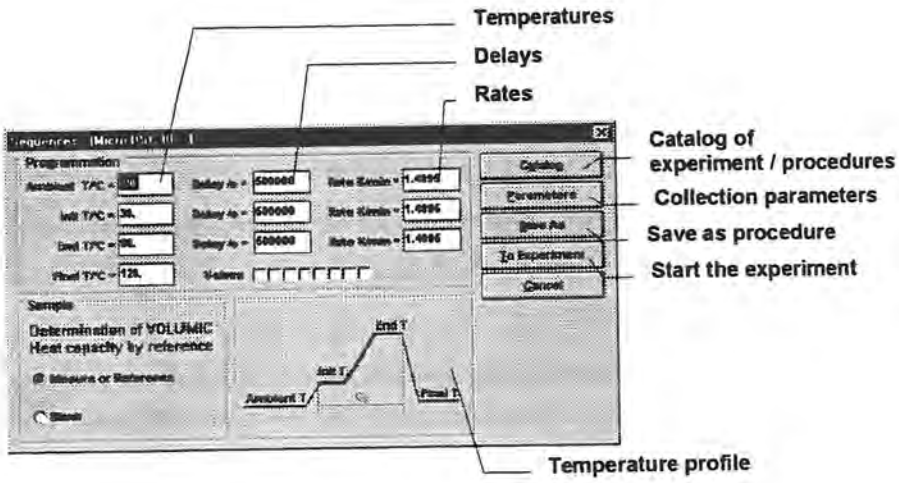

Figure 9 : Continuous (volumic) Cpv collection

2.2. Cp by step method

The common method for obtaining specific heat determination by DSC is the continuous heating mode. The difference in calorimetric signal between two successive tests with and without sample is evaluated.

Another method of specific heat determination, based on a step heating mode, is available. For a defined step of temperature, the thermal effect corresponding to the sample heating is integrated. With such a method, it is possible to reach the

thermal equilibrium of the sample after step of temperature. It gives the method a much better accuracy.

Two possible methods are available for the Cp by step method:

1. Cp by step without reference.
2. Cp by step with reference.

Remark The user cannot choose the method , which depends on the type of apparatus.

2.2.1. Cp by step without reference

The precise determination of Cp requires two tests with identical experimental conditions :

- The first test with two empty cells without sample.
- The second test with the cells and the sample.

The difference between the two signals is proportional to the heat capacity of the sample. This amplitude is directly converted into heat power using the calibration curve of the DSC.

This method is a direct determination for any temperature and it does not need any standard sample (such as sapphire).

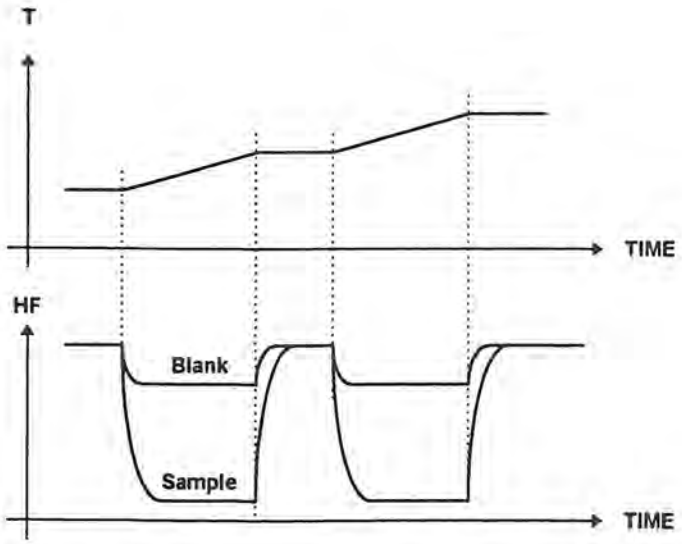

Figure 10 : Cp by step without reference

The formula is given below:

$$Cp_{moy}(T_i \to T_{i+1}) = \frac{\int_{T_i}^{T_{i+1}} HF_{sample} \cdot dT - \int_{T_i}^{T_{i+1}} HF_{blank} \cdot dT}{Sensitivity(\frac{T_i + T_{i+1}}{2}) \cdot Mass_{sample} \cdot (T_{i+1} - T_i)}$$

2.2.2. Cp by step with reference

2.2.2.1. Cp (specific) with reference

The precise determination of Cp requires three tests with identical experimental conditions :

- The first test with two empty cells without sample.
- The second test with the cells and the reference sample.
- The third test with the cells and the sample.

The reference sample is a material whose Cp equation is known.

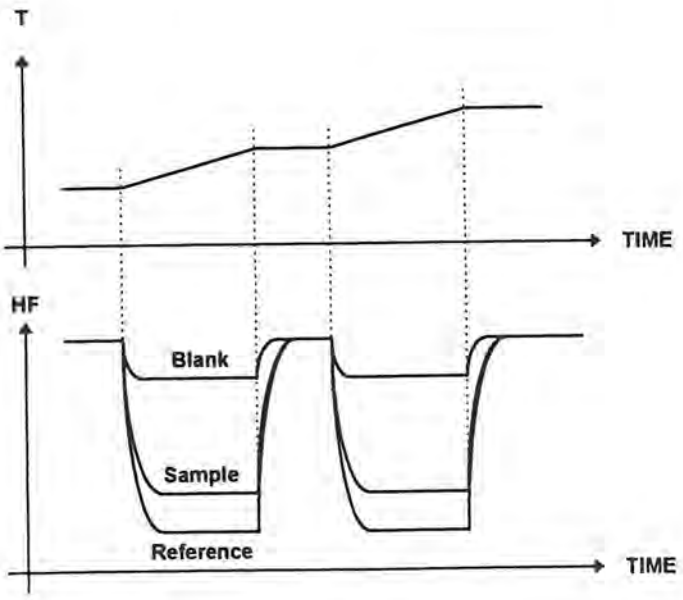

Figure 11 : Cp by step with reference

The formula is given below:

$$Cp_{moy}(T_i \to T_{i+1}) = \frac{\int_{T_i}^{T_{i+1}} HF_{sample} \cdot dT - \int_{T_i}^{T_{i+1}} HF_{blank} \cdot dT}{\int_{T_i}^{T_{i+1}} HF_{ref} \cdot dT - \int_{T_i}^{T_{i+1}} HF_{blank} \cdot dT} \cdot \frac{Mass_{ref}}{Mass_{sample}} \cdot Cp_{ref}(\frac{T_i + T_{i+1}}{2})$$

2.2.2.2. Cp (volumic) with reference

The precise determination of Cpv requires three tests with identical experimental conditions :

- The first test with two empty cells without sample.
- The second test with the cells and the reference sample.
- The third test with the cells and the sample.

The reference sample is a material whose Cpv equation is known.

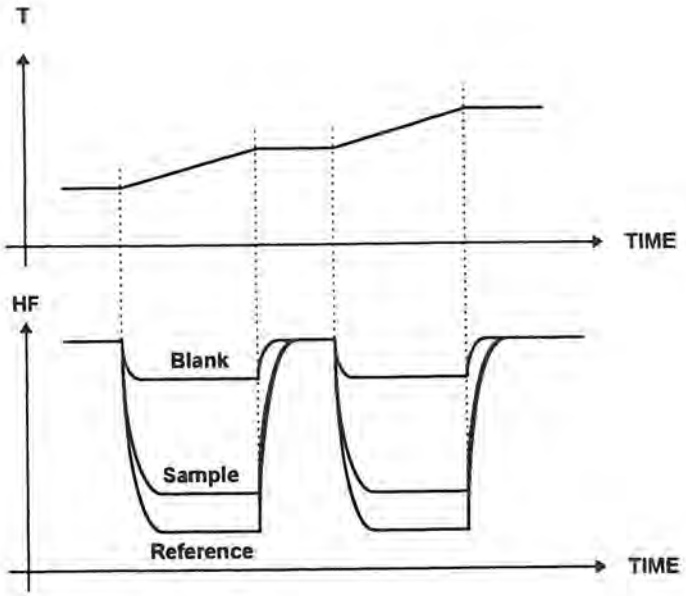

Figure 12 : Cpv by step with reference

The formula is given below:

$$Cp_{moy}(T_i \rightarrow T_{i+1}) = \frac{\int_{T_i}^{T_{i+1}} HF_{sample} \cdot dT - \int_{T_i}^{T_{i+1}} HF_{blank} \cdot dT}{\int_{T_i}^{T_{i+1}} HF_{ref} \cdot dT - \int_{T_i}^{T_{i+1}} HF_{blank} \cdot dT} \cdot Cp_{ref}\left(\frac{T_i + T_{i+1}}{2}\right)$$

2.2.3. Defining the experiment

The user has to define the temperature increment, the delay and the rate for the steps. The final temperature is given by the start temperature, the temperature increment and the number of steps.

- Case of the Cp (specific):

The mass is used in the Cp calculation. Therefore, it must be defined. The molar mass field is optional, but it is necessary to obtain the Cp unit in J/mol at the processing time.

Warning For blank experiment, enter zero in the mass field.

- Case of the Cpv (volumic)

Select whether it is a blank, a sample or a reference.

To perform a decreasing Cp by step enter a negative Delta T.

It is possible to start from a stored procedure or from a previous experiment (click on the ***Catalog*** button). Obviously, it is possible to save the current procedure (refer to ***Saving the Experiment definition as procedure***).

To define collection parameters (such as PIDs, stop mode, etc...), refer to ***Defining the collection parameters***.

To start the experiment, click on the ***To Experiment*** button (refer to ***Starting the Experiment***).

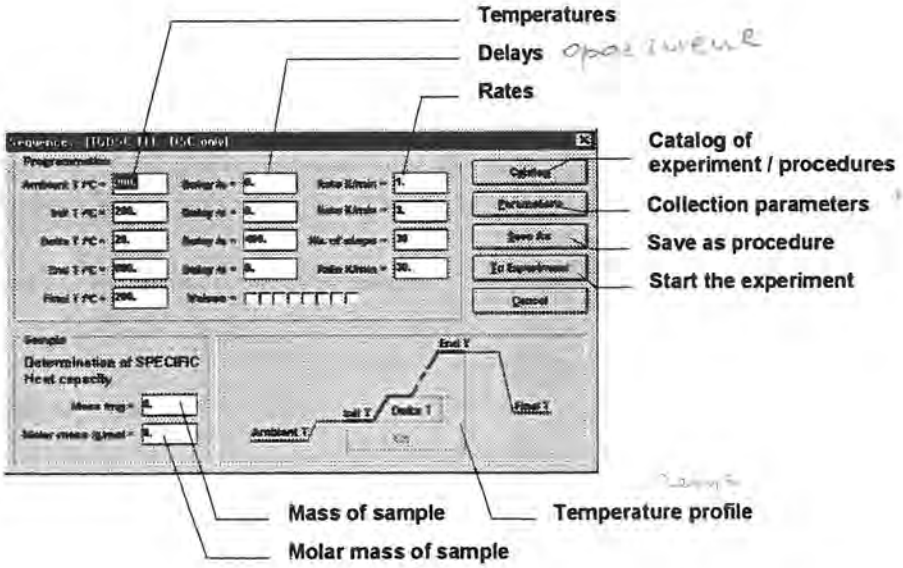

Figure 13 : Cp (specific) by step collection

In the case of Cpv (volumic) the window is as follows:

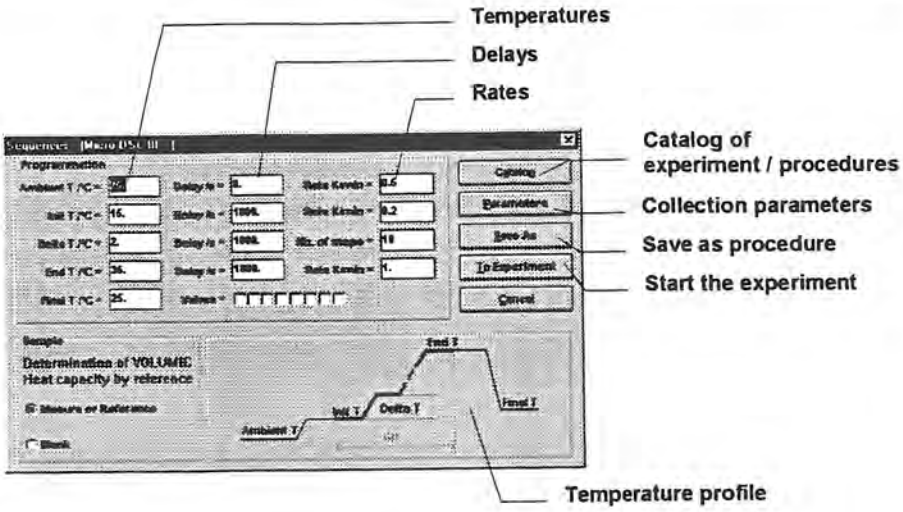

Figure 14 : Cpv (volumic) by step collection

3. Defining the collection parameters

The user can define the PIDs coefficients, the security temperature, the temperature correction coefficients, the heat flow attenuation and the stop mode.

For the Cp without reference (by step or continuous) method, the user must define the heat flow sensitivity coefficients.

Refer to the ***Setsoft*** booklet to have additional information about this window.

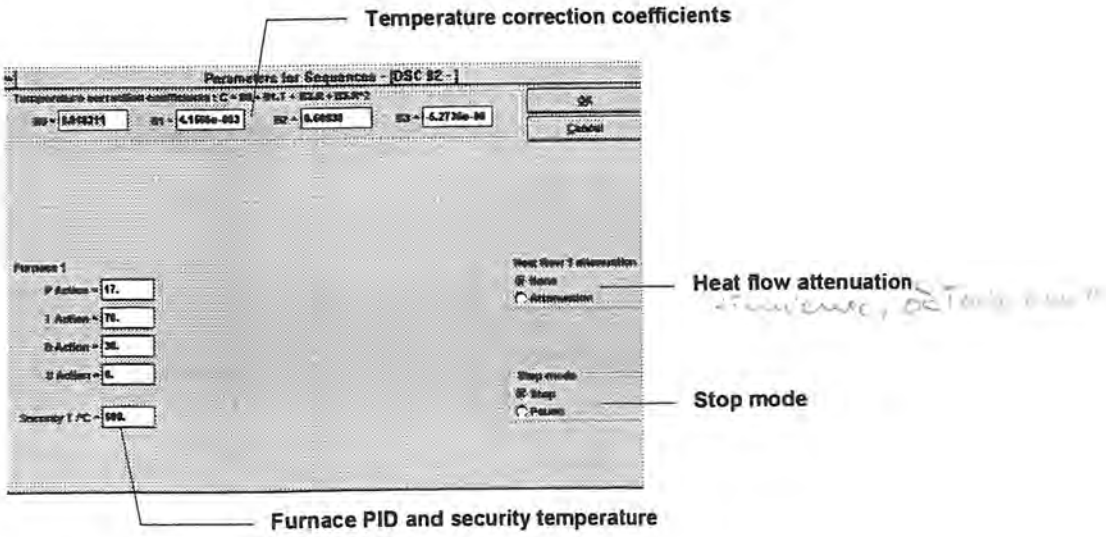

Figure 15 : Collection parameters

4. Saving the Experiment definition as procedure

The user can save the experiment definition as a procedure (like a template).

Refer to the ***Setsoft*** booklet to have additional information about this window.

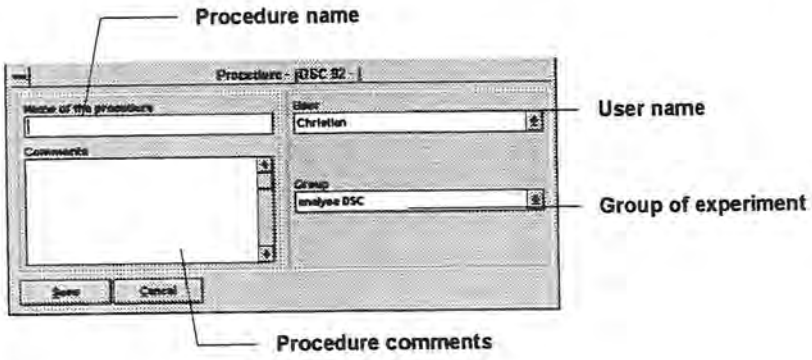

Figure 16 : Saving the procedure

5. Starting the Experiment

Refer to the ***Setsoft*** booklet to have additional information about this window.

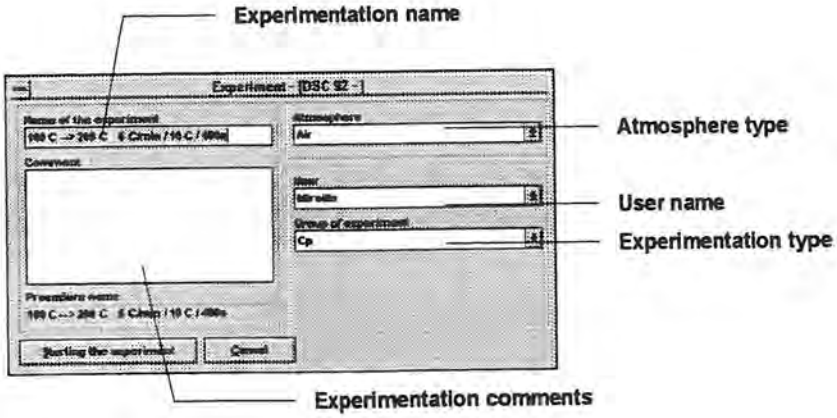

Figure 17 : Starting the experiment

CHAPTER 3 - DATA PROCESSING

1. Selecting the experiment

1.1. Catalogue of experiment

To have access to the catalogue of experiments, choose ***Processing*** from the experiment menu (or from the toolbar).

The user has to select two (without reference) or three (with reference) experiments from the catalogue.

To select the blank experiment, click on the ***Blank*** radio button and select the experiment. To select the sample experiment, click on the ***Sample*** radio button and select the sample experiment. To select the reference experiment, click on the ***Ref*** radio button and select the reference Experiment.

Remark When choosing the blank experiment, the experiments with a mass sample equal to zero only are listed. Otherwise, the experiments with a mass sample different from zero only are listed.

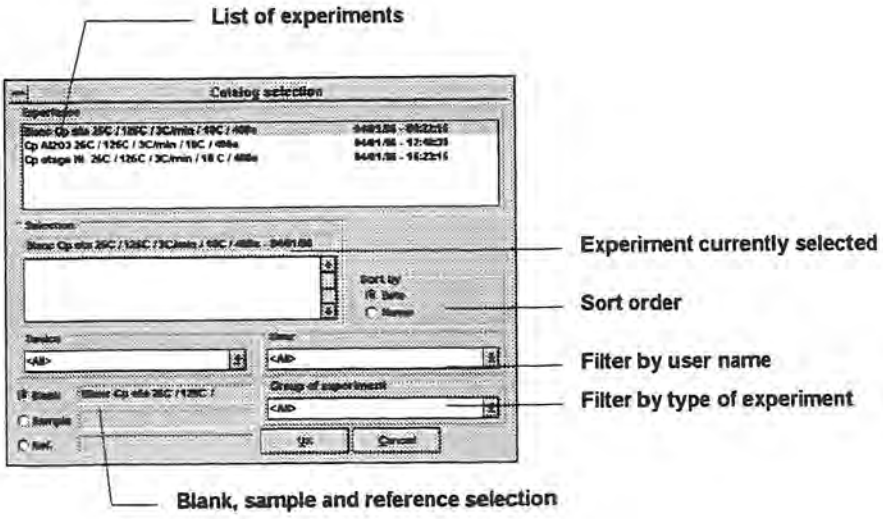

Figure 18 : Catalogue of experiment

1.2. Equation of Cp reference

1.2.1. Equation of Cp (specific) reference

In case of Cp with reference (continuous or by step), the user has to give the Cp reference coefficients before calculation. The last coefficients entered are automatically given when opening the window.

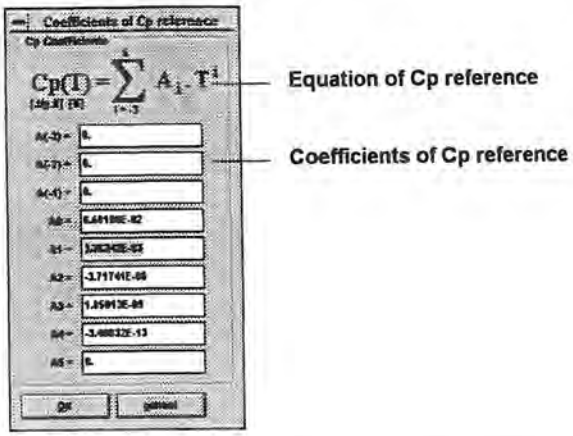

Figure 19 : Coefficient of Cp reference

The Cp reference equation is given below:

$$Cp_{ref}(T) = \sum_{i=-3}^{5} A_i \cdot T^i$$

1.2.2. Equation of Cpv (volumic) reference

In case of Cpv with reference (continuous or by step), the user has to give the Cpv reference coefficients before calculation. The last coefficients entered are automatically given when opening the window.

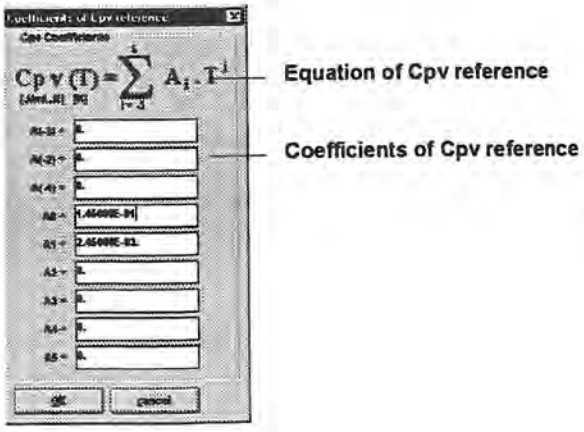

Figure 20 : Coefficient of Cpv (volumic) reference

The Cpv reference equation is given below:

$$Cpv_{ref}(T) = \sum_{i=-3}^{5} A_i \cdot T^i$$

2. Processing

2.1. Display overview

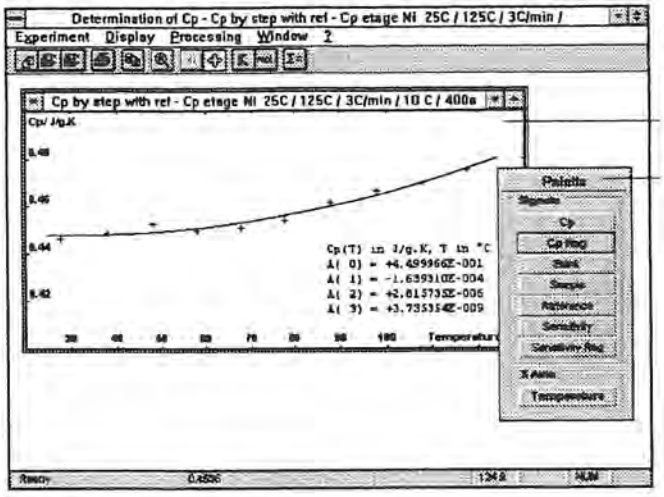

Figure 21 : Viewing experiment results

2.1.1. Palette

The palette (see Figure 22) allows the operator to have access to the signals properties (see Figure 23).

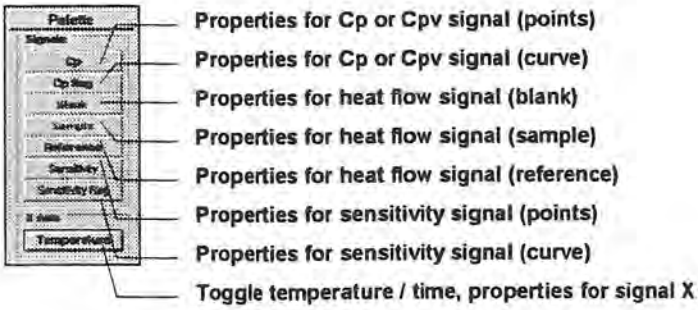

Figure 22 : Palette

2.1.2. Signal properties

The user can either hide or display the signal, and change the colour (see Figure 25) and the scale range.

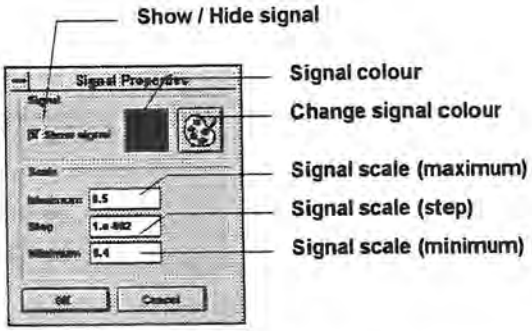

Figure 23 : Signal properties

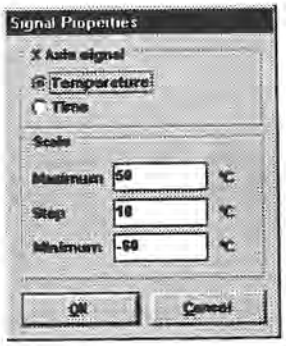

Figure 24 : Properties for signal X

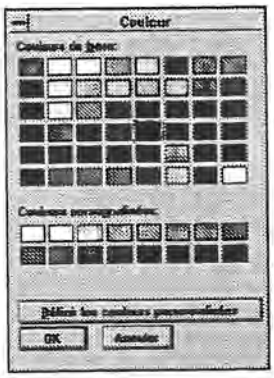

Figure 25 : Signal colour selection

2.2. Processing parameters

2.2.1. Smoothing

The blank, sample and reference curves can be smoothed (in the case of continuous Cp or Cpv).

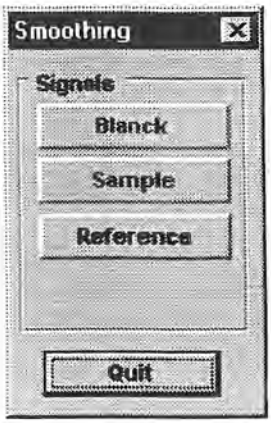

Figure 26: Choosing the signal to be smoothed

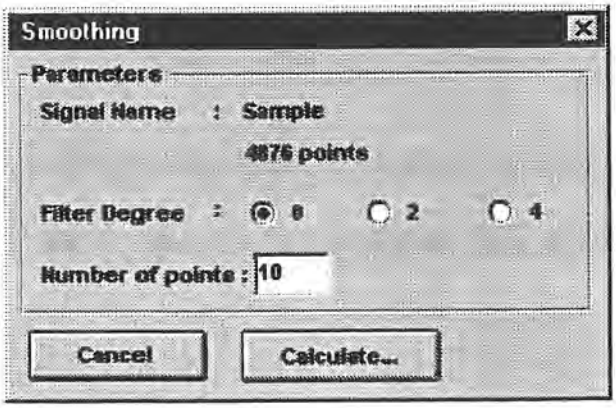

Figure 27: Smoothing according to the Savisky and Golay method

- Enter the filter degree and the number of points on which the filter will be applied.
- Press the ***Calculate*** button to perform the calculation.
- Press the ***Cancel*** button to cancel the smoothing.

Then, the result of the filtering appears in the following window :

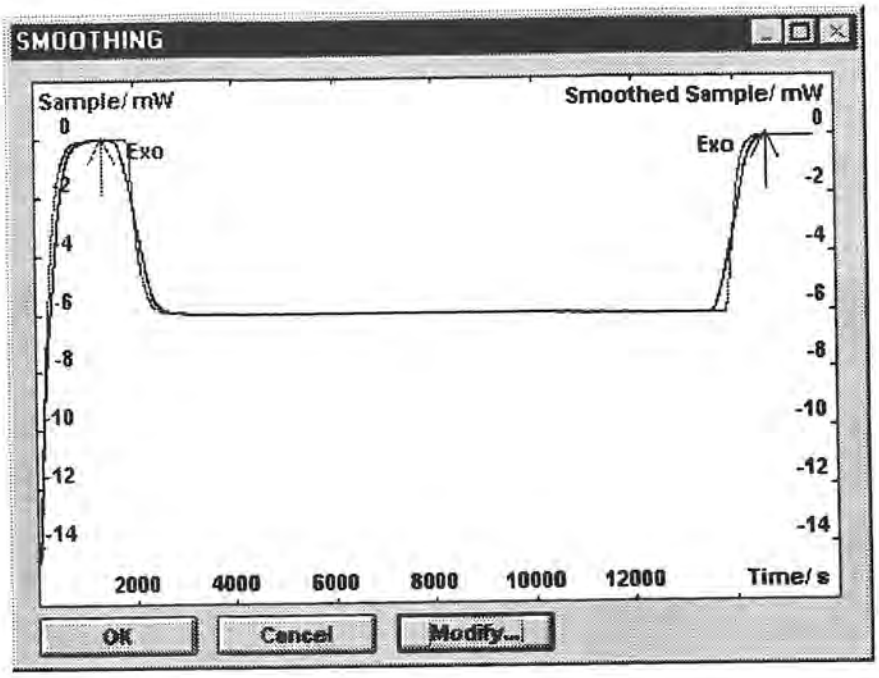

Figure 28 : Result of the filtering

It is therefore possible to:

- modify the smoothing parameters by pressing the ***Modify*** button,
- cancel the smoothing calculation by pressing the ***Cancel*** button,
- validate the smoothing by pressing the ***Ok*** button. In that case, confirm the validation by pressing the ***Ok*** button in the following window :

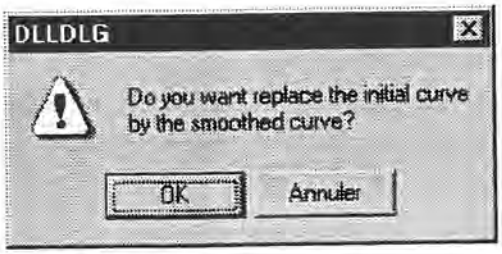

Figure 29 : Confirming the smoothing operation

- smooth a new curve if wanted.

2.2.2. Cp (specific) equation

The user can change the parameters of the Cp equation by changing the lower coefficient and / or changing the higher coefficient (see Figure 30).

It is possible to select an initial time and a final time for regression.

To have access to the Cp equation, choose ***Equation of Cp*** from the ***Processing*** menu or from the toolbar.

The Cp equation is given below:

$$Cp(T) = \sum_{i=l}^{h} A_i \cdot T^i \qquad l,h \in [-3;5]$$

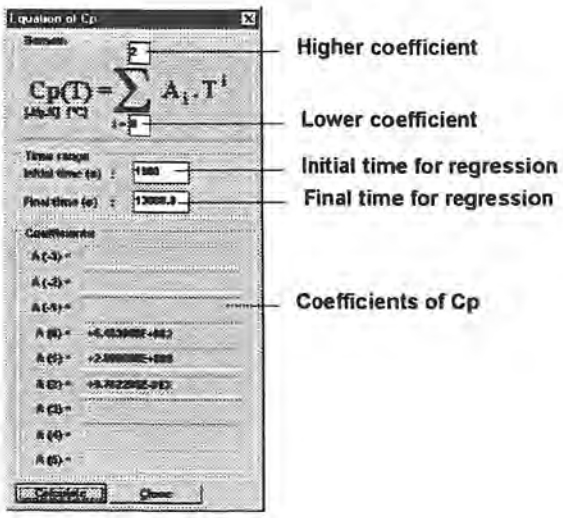

Figure 30 : Equation of Cp (specific)

2.2.3. Cpv (volumic) equation

The user can change the parameters of the Cpv equation by changing the lower coefficient and / or changing the higher coefficient (see Figure 30).

It is possible to select an initial time and a final time for regression.

To have access to the Cpv equation, choose ***Equation of Cpv*** from the ***Processing*** menu or from the toolbar.

The Cpv equation is given below:

$$Cpv(T) = \sum_{i=l}^{h} A_i \cdot T^i \qquad l,h \in [-3;5]$$

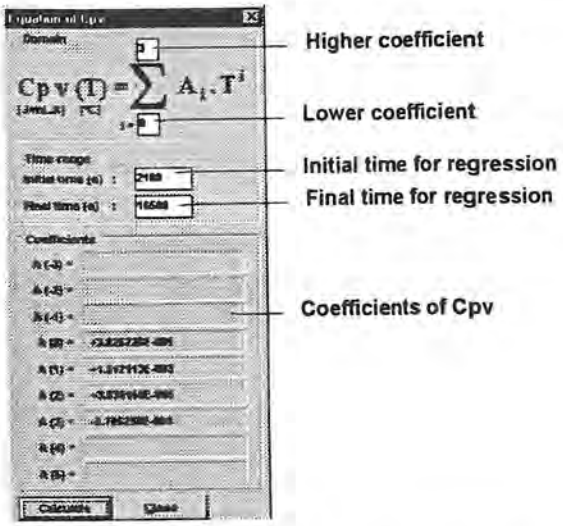

Figure 31: Equation of Cpv (volumic)

2.2.4. Units

Temperature signal : can be displayed in °C or in Kelvin. To change the temperature unit, click on the ***Temperature in K*** from the ***Processing*** menu or from the toolbar.

Cp signal :

- In case of Cp (specific) it can be displayed in J/g.K or in J/mol.K. To change the Cp unit, click on the ***Cp in J/mol*** from the ***Processing*** menu or from the toolbar.
- In case of Cpv (volumic) it is only displayed in J/mL.K

Remark The Cp coefficients (refer to sections 2.2.2 *and 2.2.3*) are computed with the units previously selected.

2.3. Adding results on curves

2.3.1. Cp equation

To add the Cp or Cpv coefficients on the curves, click on ***Add Cp coefficient on curves*** from the ***Processing*** menu.

Remark The text position may be adjusted. Click on ***Comments*** from the ***Display*** menu or from the toolbar and drag the text on the curves.

2.3.2. Sensitivity equation

To add the sensitivity coefficients on the curves, click on ***Add sensitivity coefficients on curves*** from the ***Processing*** menu.

Remark The text position may be adjusted. Click on ***Comments*** from the ***Display*** menu or from the toolbar and drag the text on the curves.

2.4. Exporting signals

The exporting under ASCII form of all the signals toward the clipboard, a file or the printer is possible. Click on ***Export...*** from the ***Processing*** menu.

Refer to the ***Setsoft*** booklet to have additional information about this window.

2.5. Printing curves

It is possible to print the curves displayed. Click on ***Print*** from the ***Experiment*** menu or from the toolbar.

2.5.1. Defining print margins

To change the margins, click on ***Page setup*** from the ***Experiment*** menu. The margins are defined in per cent of the paper size.

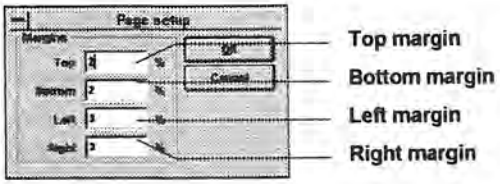

Figure 32 : Print margins

2.5.2. More printing options...

To change the printer, the orientation, the quality, printer specific options and more, click on ***Print setup*** from the ***Experiment*** menu.

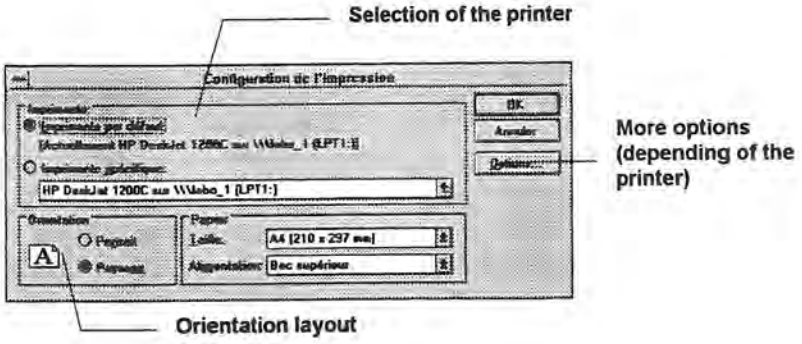

Figure 33 : Print options

SETARAM : excellence in thermal analysis

LABSYS™ : low cost series of multi-module thermal analyzers

- DSC131 : -150 to 700°C (heat flux sensor)
- DTA, TG/DTA : ambient to 1600°C
- DSC, TG/DSC : ambient to 1600°C
- TMA : ambient to 1000°C

SETSYS : top of range in thermal analyzers

- DSC141 : -150 to 600°C (power compensation)
- DTA, TG/DTA : -150 to 2400°C
- DSC, TG/DSC : -150 to 1600°C
- TMA, DLTMA : -150 to 2400°C

micro DSC : high sensitivity DSC and calorimetry

- micro DSCIII : -20 to 120°C ("batch and flow")
- micro DSCVII : -45 to 120°C ("batch")

CALVET PRINCIPLE DSC

- DSC 121 : -120 to 830°C
- DSC Robotic Sytem : -120 to 830°C

CALVET CALORIMETERS

- BT 2.15 : low temperature calorimeter from -196 to 200°C
- MS 80 : standard calorimeter from ambient to 200°C
- HT 1000 : high temperature calorimeter from ambient to 1000°C
- C 80 : mixing and reaction calorimeter from ambient to 300°C
- Tytris : titration calorimeter from ambient to 75°C
- calorimeters based on your analysis needs

96 LINE : high temperature and large volume thermal analyzers

- MULTI-HTC 96 : DSC and calorimetry
  calorimetric detectors up to 1500°C
  DSC detectors up to 1600°C
- TG 96 : thermogravimetry
  ambient to 1750°C
- DHT 96 : dilatometry
  1750°C and 2100°C versions

SYMMETRICAL THERMOGRAVIMETRY LINE

- TAG 24 : a line of symmetrical thermoanalyzers
  -150 to 2400°C
- TG-DSC 111 : the unique TG-DSC coupling
  -120 to 830°

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