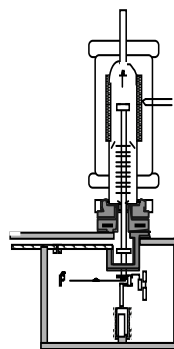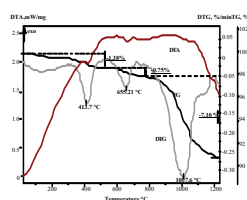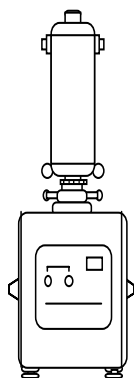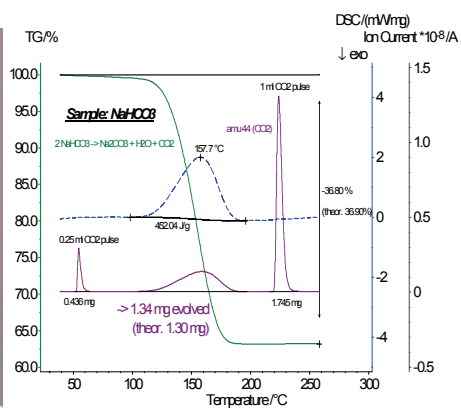# MìMeR

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CONTENTS

FIGURE CAPTIONS

THERMAL ANALYSIS

INTRODUCTION

Thermal analysis includes a group of methods by which the physical and chemical properties of a substance, a mixture and/or reaction mixtures are determined as a function of temperature or time, while the sample is subjected to a controlled temperature program. The program may involve heating or cooling (dynamic), or holding the temperature constant (isothermal), or any combination of these.

TGA stands for Thermo-Gravimetric Analysis. TGA can be used for the determination of decomposition weight loss, combustion analysis, temperature stability, and moisture content and reaction mechanism.

TGA monitors weight versus temperature. It can detect changes in weight of 1 ug. This is accomplished with an extremely sensitive balance hanging inside a furnace. A thermocouple mounted just a few millimeters from the sample pan ensures accurate temperature of the sample. There are several events that can be calculated for any run.

TA METHODS
Differential Thermal Analysis (DTA)
Differential Scanning Calorimetry (DSC)
Thermogravimetry (TG)
Simultaneous Thermal Analysis (STA)
Thermomechanical Analysis (TMA)
Dilatometry (DIL)
Dynamic Mechanical Analysis (DMA)
Combined (Hyphenated) Techniques (TA - MS, TA - FT-IR, PTA)
Thermal Conductivity Testing (TCT)
Thermal Diffusivity Measurement (LFA)
Refractories Testing (RUL, CIC, MOR)

THERMOGRAVIMETRY (TG)

This is a technique by which the mass of the sample is monitored as a function of temperature or time, while the sample is subjected to a controlled temperature program.

Dm = mass change

dm/dt	=	rate of mass change/decomposition
DTG	=	derivative thermogravimetry
DTG Peak	=	characteristic decomposition temperatures ® identification
Tonset	=	thermal stability
Composition	=	moisture content, solvent content, additives, polymer content, filler content , dehydration , decarboxylation, oxidation, decomposition.

The curve of thermogravimetry analysis is build around a furnace where the sample is mechanically connected to an analytical balance. The first thermobalance was developed by K. Honda in 1915. I t be came widespread from 1950s when the derivated thermogravimetric (DTG) was solved.

Balance, furnace and control/data handling system are the three essential parts of a modern TG instrument. There is three main possibilities to place the sample relative to the balance:

a- Suspended, b- horizontal, c- top-loading see figure 2.
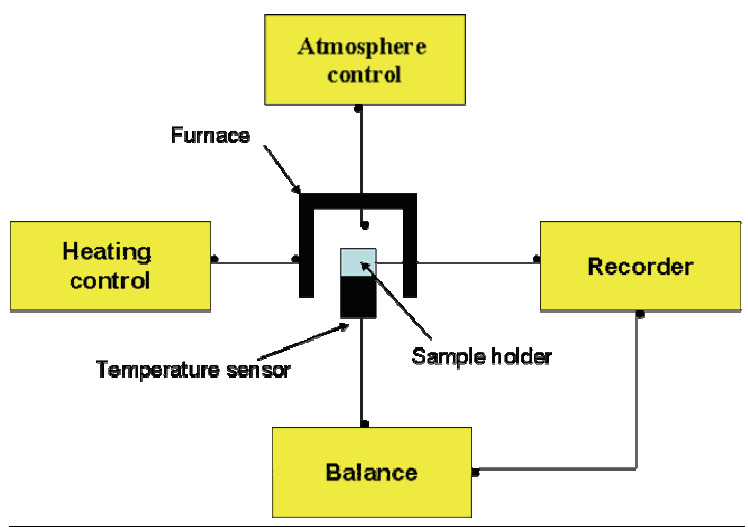
Figure1 – Schematic of Thermogravimetry system
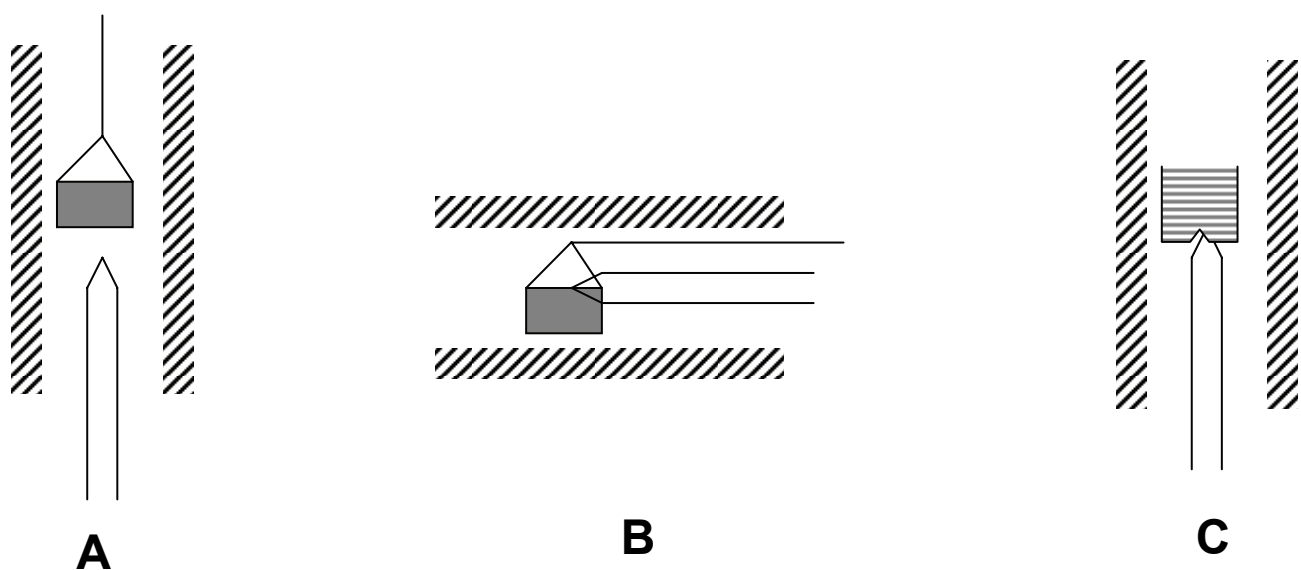
Figure 2 – Position of the sample in thermobalance

Differential Thermal Analysis (DTA)

DTA is a technique measuring the difference in temperature between a sample and a reference (a thermally inert material) as a function of time or the temperature, when they undergo a temperature scanning in a controlled atmosphere. The DTA method enables any transformation to be detected for all the categories of materials.

Applications: Melting and crystallisation behavior, Heat of melting and crystallisation, Heat of reaction, Reaction kinetics, Glass transitions, Oxidative stability, Thermal stability.

Differential Thermal Calorimetry (DSC)

DSC is a technique determining the variation in the heat flow given out or taken in by a sample when it undergoes temperature scanning in a controlled atmosphere. When heating or cooling, any transformation taking place in a material is accompanied by an exchange of heat; DSC enables the temperature of this transformation to be determined and the heat from it to be quantified. Calibration necessary.

1. Power compensated DSC
2. Heat flux DSC
3. Applications, see DTA

SIMULTANEOUS THERMAL ANALYSIS (STA)

This technique combines thermogravimetry with differential thermal analysis or differential scanning calorimetry in one run.

- Possible to consider the real sample mass at a given temperature in Cp determination.

- No temperature differences between signals of TG and DTA/DSC measurement.

Peak, Step, Onset, Delta Y, and First Derivative.
Runs can be measured in (Temp or Time) vs. (Wt% or mg)

DSC stands for Differential Scanning Calorimetry. DSC is used for the determination of endothermic or exothermic reactions or phase changes of a sample. Several characteristics can be determined such as: melting point, curing temperature, reaction kinetics, freezing point, glass transition, physical transitions, heat capacity, reaction mechanism, kinetics, purity, product identification.

DSC monitors heat change versus temperature input. It can detect changes in heat as low as 1 microwatt. This is accomplished with an extremely sensitive sensor array inside the heater cup. The heater cups have a weight less than 1 gm. This gives them a low thermal mass with extremely quick temperature response and extremely sensitive and accurate heat changes. (For a more complete description of operation SEE Advanced Guide to Microanalysis.)

MAIN THERMOANALYTICAL TECHNIQUES

Measured property	Technique	Accepted acronym
Mass (change)	Thermogravimetry or Thermogravimetric analysis	TG TGA
Temperature difference	Differential thermal analysis	DTA
Heat flux	Differential scanning calorimetry	DSC
Volatiles	Evolved gas analysis	EGA
Diffraction angle & intensity	High temperature X-ray diffraction	HTXRD
Mechanical properties	Thermomechanical analysis	TMA
Dimensional change	Thermodilatometry	TG
Radioactive decay	Emantionthermal analysis	ETA
Acoustic properties	Thermoacoustimetry	
Magnetic properties	Thermomagnetometry	
Optical propoerties	Thermooptometry	

STA APPLICATIONS

Simultaneous Thermal Analysis (STA) is used for the following applications:

Characteristic temperatures	Polymorphism
Identification	Solid-liquid ratio
Glass transitions	Specific heat capacity
Melting and crystallization behavior	Reaction behavior
Heat of melting and crystallization	Heat of reaction
	Reaction kinetics
	Oxidative stability

THERMOMECHANICAL ANALYSIS (TMA)
DILATOMETRY (DIL)

This is a technique by which the dimensional changes of the sample are monitored as a function of temperature or time, while the sample may be subjected to an additional mechanical load.

- negligible mechanical load ® dilatometry

- constant load ® (static) thermomechanical analysis

- oscillating force ® dynamic mechanical analysis

DL = length change , DL / L0 = relative length change, a = coefficient of linear thermal expansion, Tg = glass transition temperature, expansion / shrinkage / penetration behavior, dimensional stability ® design purposes softening / curing behavior, volumetric expansion (_ bulk density)

DYNAMIC MECHANICAL ANALYSIS (DMA)

This is a thermoanalytical method by which the mechanical behavior of a sample subjected to a specific temperature program is investigated under the effect of a load which changes with time. Determination of the storage and loss moduli and the damping factor of a sample as a function of temperature, time and frequency of an applied oscillating load.

COMBINED (HYPHENATED) TECHNIQUES

With these thermoanalytical methods, the gases evolved from the sample during a thermal analysis experiment are detected/analyzed.

THERMAL CONDUCTIVITY TESTING

This thermoanalytical method allows the measurement of the thermal conductivity of a sample (solid or powder) as a function of temperature.

THERMAL DIFFUSIVITY MEASUREMENT
(Laser Flash Method)

This is a thermoanalytical method which measures the thermal diffusivity of the sample (solid, liquid or powder) at constant temperatures while monitoring the temperature increase of the sample caused by the absorbed energy of a laser flash.

REFRACTORIES TESTING (RUL, CIC, MOR)
Refractoriness Under Load (RUL):
Creep In Compression (CIC)
Hot Modulus of Rupture (HMOR)

This thermoanalytical test method is used for the determination of refractoriness under load (RUL), creep in compression (CIC) and modulus of rupture (MOR) of solid samples.

APPARATUS (STA 409C)

Simultaneous Thermal Analysis: TG/DTA or TG/DSC

The STA 409C instrument consists of the following main parts (see figure 3):

1. Registration control cabinet, 2. Measuring part, 3. Computer system with printer, 4. Thermostat,
   5. Evacuating system (vacuum pump)
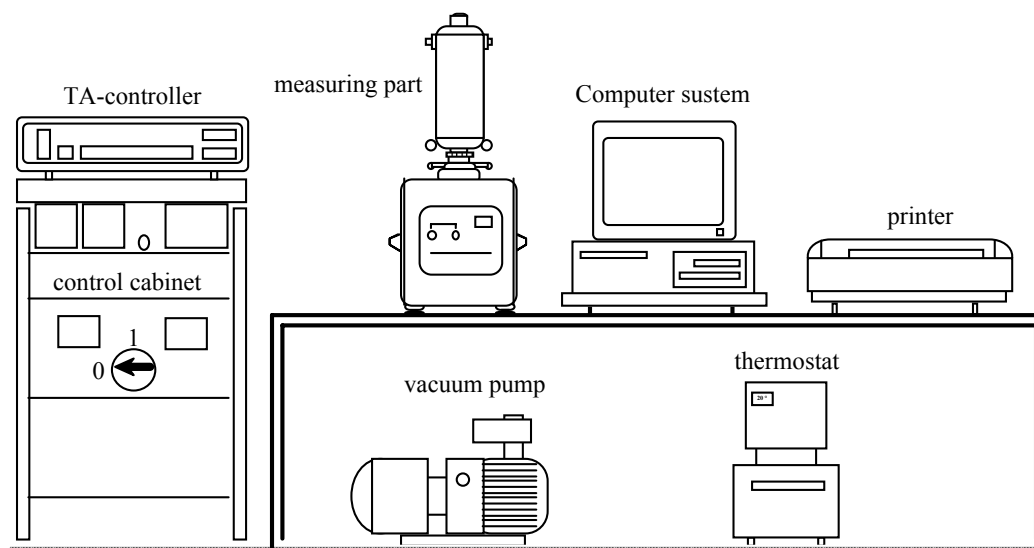
Figure 3 – Assembly diagram of STA 409 C/7/E measuring equipment

Figure 4 shows the measuring part, which is, consists on the balance (bottom) and furnace Top). The high temperature furnace is heated by graphite heating elements, which are protected by injection of inert gas. The furnace can be cooled down to room temperature very fast by water-cooling. The temperature of furnace is controlled by a W3% Re-W35% thermocouple. Sample and furnace chamber are separated by a gastight protective tube.

The schematics of STA 409C and STA with QMS are shown in figures 5 and 6 respectively. The balance and furnace was sequentially evacuated and purged with pure argon. Two programs were performed in this instrument. One for setting operating conditions, running the STA and data acquisition, another for evaluating the data obtained. In order to avoid buoyancy effect correction, TG/DTA must be run with empty crucibles and the data obtained by this way will be used as reference when running.

For all experiments of TG/DTA with the investigated samples, TG/DTA sample holder with different types of crucibles can be used, which are put on radiation shield in order to protect the balance. The sample carrier system is shown in annex. By using the correction data, the investigated samples can be tested in the mode TG/DTA sample + correction. The operating instrument is given in the next paragraph.

Figure 4 - Scheme of STA-409 C (A).
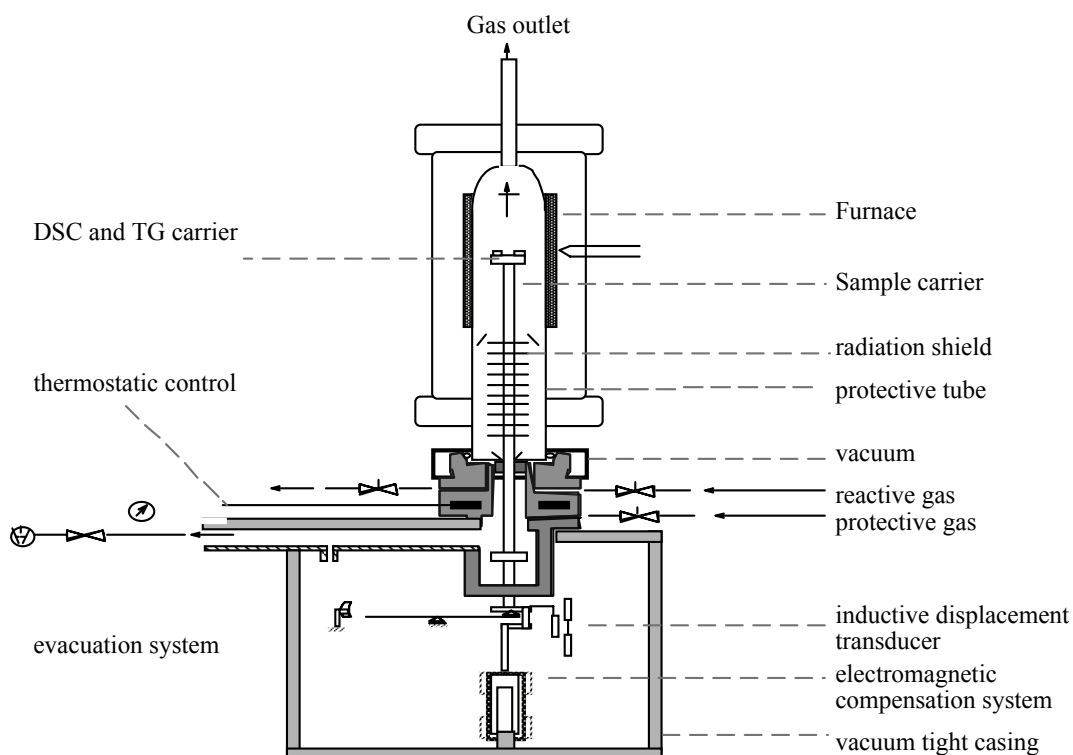
Figure 5 - Scheme of STA-409 C (B).
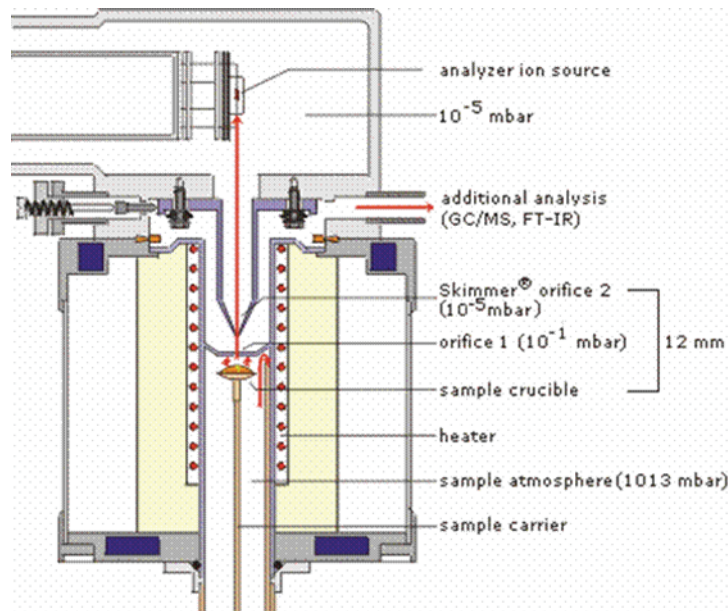
Figure 6 – Schematic of Skimmer

The quadrupole mass spectrometer

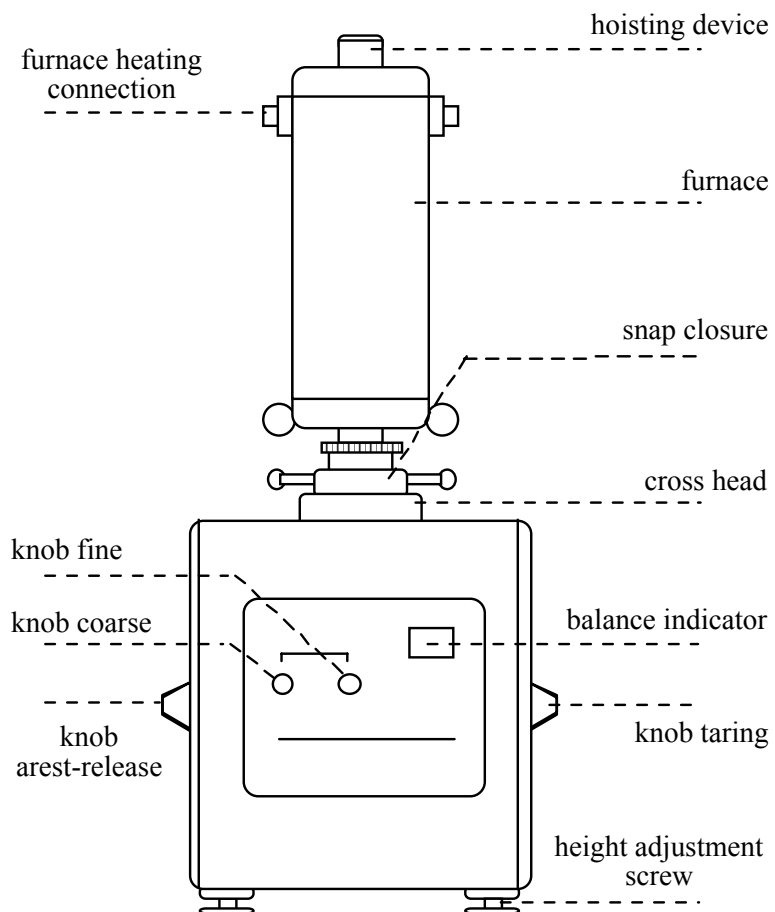The quadrapole mass filter was originally proposed by W. Paul Its basic design is illustrated in figure 7. In a high-frequency, quadrupole electric field, which in the ideal case is generated by four hyperbolic rod electrodes a distance of 2ro apart at the tips, it is possible to separate ions according to their mass/charge ratio (m/e). The hyperbolic surfaces are approximated with sufficient accuracy by cylindrical rods of circular cross-section. The voltage between these electrodes is composed of high-frequency alternating component V$\cos\omega t$ and a superposed direct voltage U.

If ions in the direction of the axis of the axis of the field, perpendicular to the plane of the picture, are injected into the separating system, the influence of the high-frequency electric field causes them to oscillate at right-angles to the axis of the field.

The equations of motion of these ions are called Mathieu differential equations, the solutions of which are known and classifiable in two groups. In the first class, the amplitudes of the oscillations remain limited for any length of the time. These solutions are referred to as stable. The others – unstable solutions are characterized by a continuous increase in the amplitude.

Physically this means that some ions would pass through the mass analyser, while others would strike the rods, be neutralized and pumped away as gas. Here the term "mass filter" is often applied to quadrupoles.
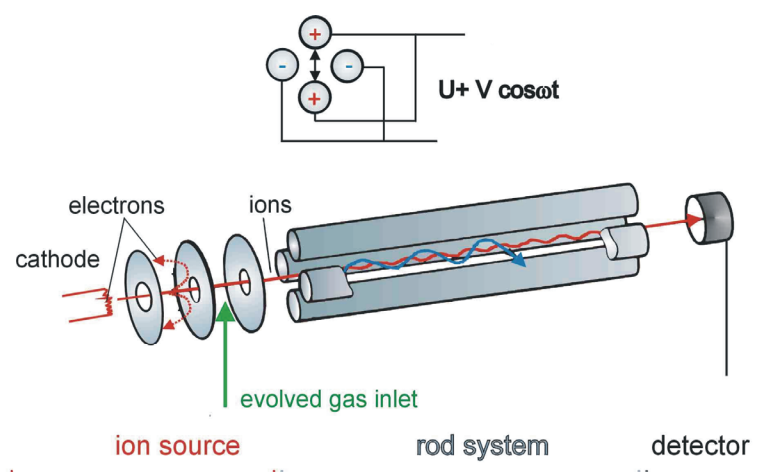
Figure 7 – Structure of quadrapole analyser

OPERATING THE INSTRUMENT
TG/TDA
BALANCE STA 409 C

Protection gas for balance

1.   Close gas inlet valve 11 and exit valve 8 and vacuum valve 2,

2.   Start vacuum pump on panel,

3.   Open vacuum valve (big red), carefully at the beginning,

4.   Close vacuum valve (big red) after 3 minutes (-1 on scale),

5.   Open gas inlet to fill Ar,

6.   Go to 1,

**Balance and sample. 3 times for glass-carbon furnace tube.
2 times for Alumina furnace tube**

7.   When over pressure has been build up (0.1 bar) open red exit
      valve 8. Adjust flow to approx. 100 ml/min on the flow meter.

Protection gas for furnace

1.   Close gas inlet valve 4 and vacuum valve 5,

2.   Switch to "Vacuum" on the panel,

3.   Open vacuum valve 5 (Big black) carefully,

4.   Close vacuum valve 5 after 3 minutes (-1 on scale),

5.   Switch to "Fill" on the panel,

6.   Open inlet valve 4 carefully to 0.05 bar over pressure,

7.   Go to 1,

8.   Last time open inlet valve 4 carefully to 0.05 bar over pressure. Open valve fully,

9.   Switch to "Dynamic" on the panel,

10.   Adjust gas flow to 4-5 units on the panel.

Protection gas for furnace. Always evacuate and fill 3 times.

Classification of TG curve

Figure 8 shows different types of TG curves can be obtained from TA 409C equipment. Their classification is as following:

Type A. It shows no mass change over temperature range selected. DSC can be used to investigate if non - mass changing processes have occurred.

Type B. Large initial mass loss followed by mass plateau evaporation of volatile compounds during polymerization drying and deposition give rise to such a curve.

Type C. Single stage decomposition.

Type D. Multi-stage decomposition, where the reaction steps are easily resolved.

Type E. The individual reaction steps are not well resolved, DTG curve is preferred to characterize this type of curve.

Type F. Presence of an interacting atmosphere, a mass increase is observed, surface oxidation reactions.

Type G. Mass increase followed by decomposition, such as surface oxidation followed by decomposition of the reaction products.
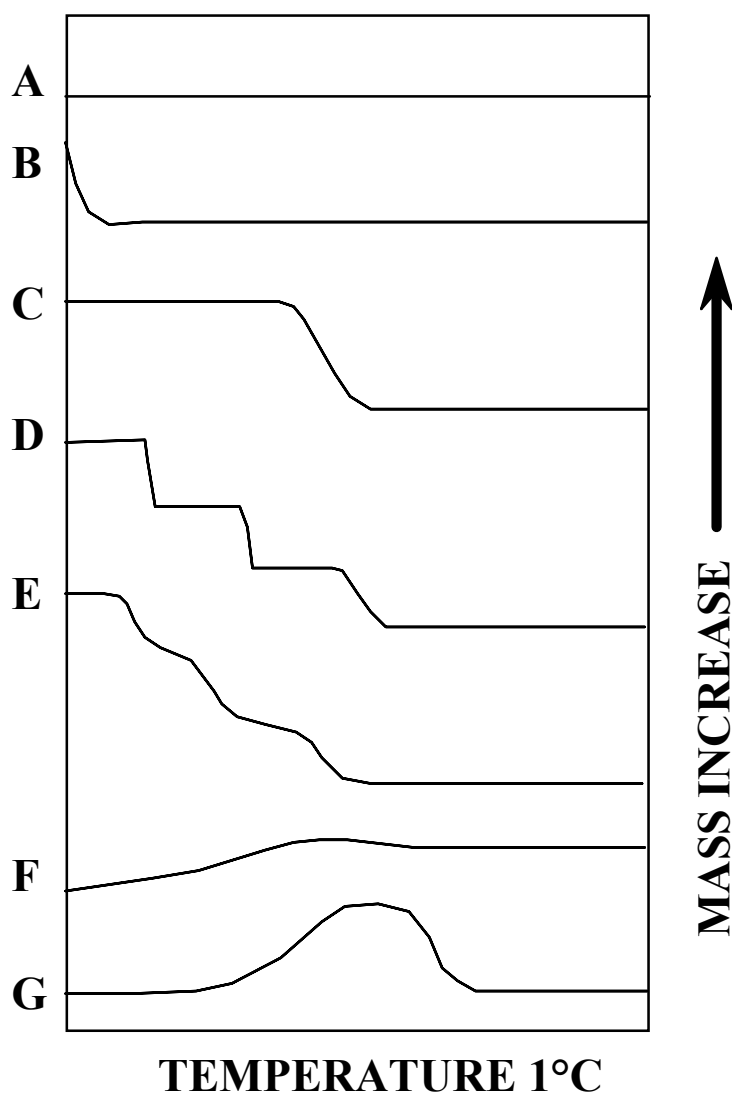

Figure 8 – Behavior of different TG curves.
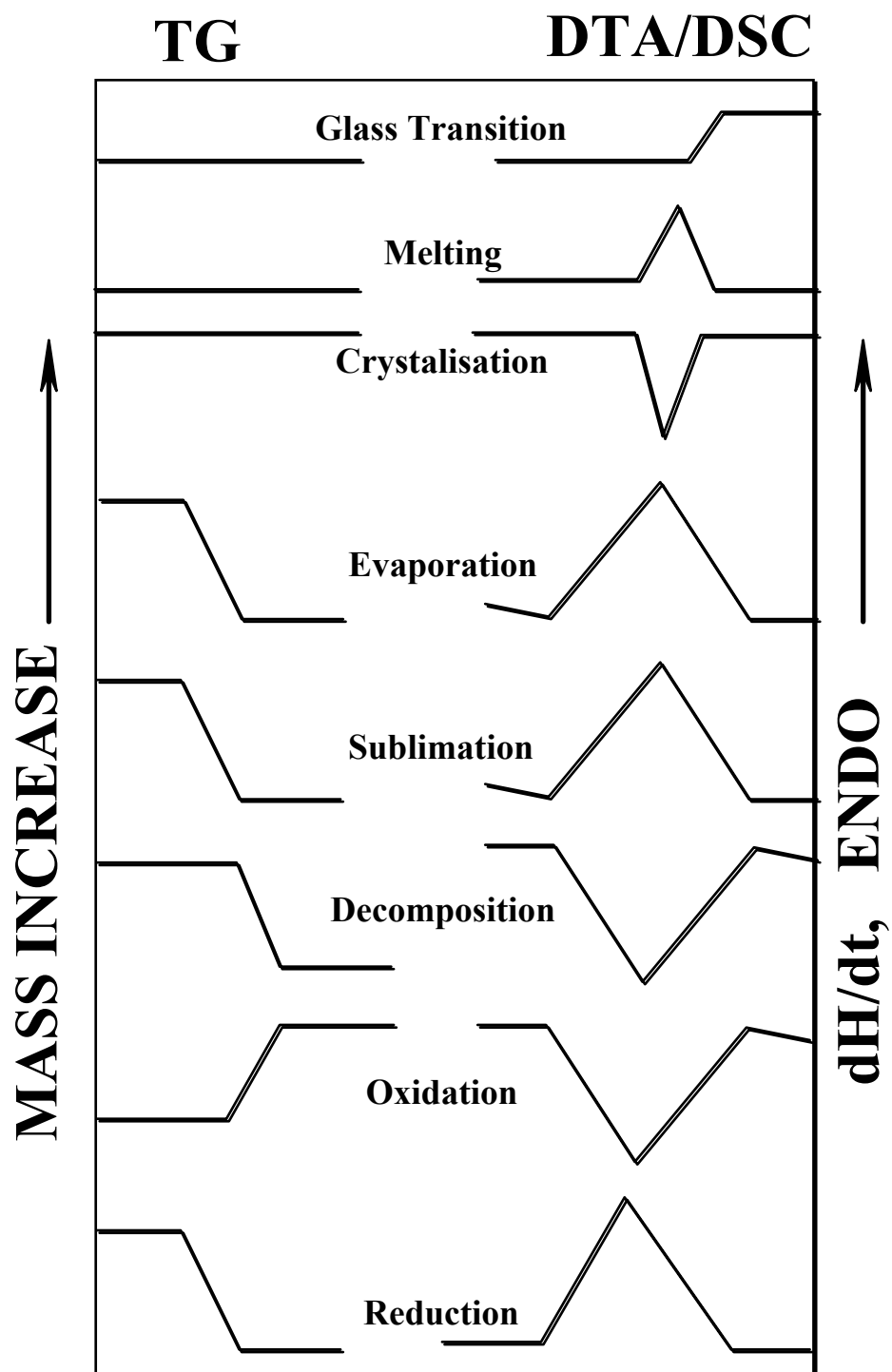
Behavior of TG/DTA curves

Figure 9 – Comparison of TG and DTA curves

Introduction to Thermogravimetry (TG)

In this technique (TG or TGA), changes in the mass of a sample are studied while the sample is subjected to a controlled temperature program. The temperature program is most often a linear increase in temperature, but isothermal studies can also be carried out, when the changes in sample mass with time are followed. (There is also a family of newer control techniques - i.e. Controlled Rate methods, and Hi-Res™ TG, described elsewhere.)

The main processes amenable to study are listed below

Process	Weight gain	Weight loss
Ad- or absorption		
Desorption		
Dehydration/desolvation		
Sublimation		
Vaporization		
Decomposition		
Solid-solid reactions		
Solid-gas reactions		

TG is inherently quantitative, and therefore an extremely powerful thermal technique, but gives no direct chemical information. The ability to analyse the volatile products during a weight loss is of great value.

Factors affecting the TG curve

Many factors influence the form of the TG curve, both sample- and instrument-related, some of which are interactive. The primary factors are heating rate and sample size, an increase in either of which tends to increase the temperature at which sample decomposition occurs, and to decrease the resolution between successive mass losses. The particle size of the sample material, the way in which it is packed, the crucible shape, and the gas flow rate can also affect the progress of the reaction. Careful attention to consistency in experimental details normally results in good repeatability. On the other hand, studying the effect of deliberate alterations in such factors as the heating rate can give valuable insights into the nature of the observed reactions

TG has been applied extensively to studying analytical precipitates for gravimetric analysis. One example is that of calcium oxalate monohydrate, as shown below see figure 10. This material has become popular for demonstrating thermobalance performance, as it gives three distinct weight losses over a wide temperature range.
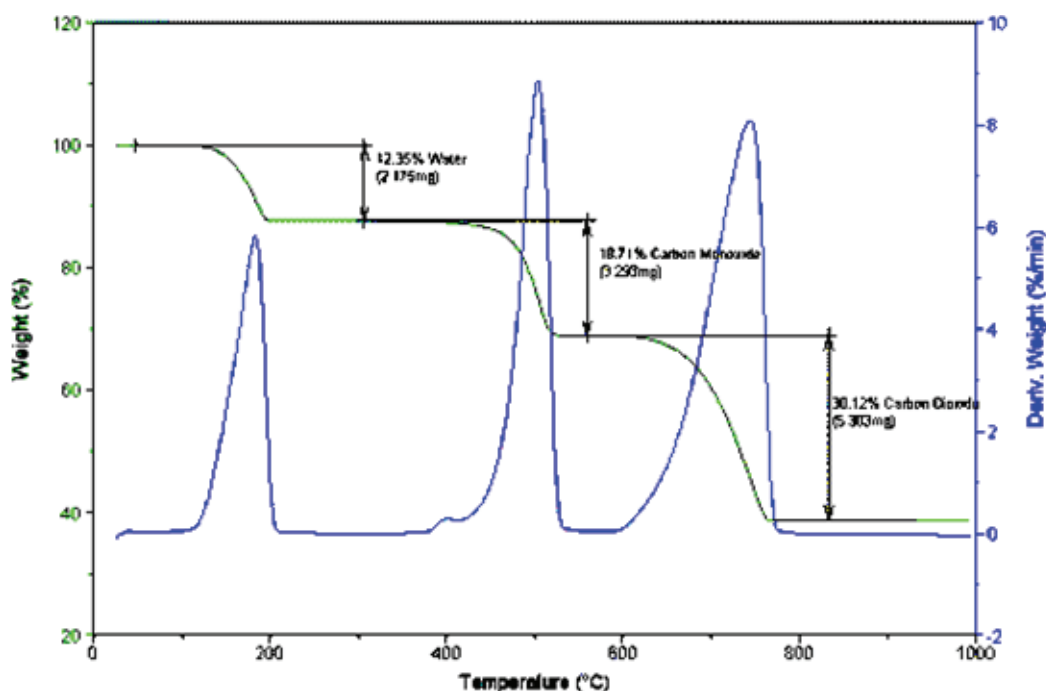
Figure 10 – decomposition of calcium oxalate

The plot also shows the derivative of the TG curve, or the DTG curve, which is often useful in revealing extra detail, such as the small event around 400°C, which would not have been seen on the TG curve itself. The DTG curve is sometimes used to determine inflection points on the TG curve, to provide reference points for weight change measurements in systems where the weight losses are not completely resolved.

The measured losses above agree well with the theoretical losses, according to the usual scheme

$$CaC_2O_4.H_2O \rightarrow CaC_2O_4 \rightarrow CaCO_3$$

apart from that due to decomposition of the anhydrous oxalate to calcium carbonate around 500°C. The curve gives a value of 18.7% lost, as compared to the theoretical value of 19.2%. This is due to the disproportionation of carbon monoxide into carbon dioxide and carbon. CO_2 has been seen to evolve in parallel with CO by evolved gas analysis. The residual calcium oxide from an experiment such as that above is pale grey, due to the carbon deposited. Changing the atmosphere in the thermobalance to air after the decomposition of the carbonate around 700°C would initiate a weight loss due to the oxidation of this carbon. The extent to which the disproportionation reaction occurs is influenced by several factors including the nature and cleanliness of the material from which the sample container is made, and it is difficult to obtain reproducible results for this reaction step. It is therefore unwise to use this material as a weight change standard, as has been sometimes suggested, when operating in inert atmosphere. Even in an oxidizing atmosphere, difficulties may arise in obtaining a reproducible result. In this case, the CO produced on decomposition is oxidized quantitatively to CO_2, in a strongly exothermic process. The heat generated raises the sample

temperature, and accelerates the reaction, resulting in a sharper DTG peak. The sharpness of the peak however depends on the catalytic activity of the sample holder material. Careful cleaning is needed to restore the activity of a new platinum holder, which is the most commonly used pan material.

The absence of a grey residue after running calcium oxalate in an inert atmosphere would probably be due to traces of air in the system. A good test of the inert atmosphere quality in a thermo balance is to hold a sample of carbon black at 1000°C, and measure the rate of weight loss. A well-made instrument, after thorough initial purging with inert gas, should be able to give a result of below 1μ g/min. For the best results with highly sensitive materials (e.g. finely-powdered metals) it may well be necessary to deliver the inert gas via metal pipes, and to use an oxygen scrubber

Introduction to DTA and DSC

Both Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) are concerned with the measurement of energy changes in materials. They are thus the most generally applicable of all thermal analysis methods, since every physical or chemical change involves a change in energy

DTA
DTA is the older technique. The principle of the "classical" arrangement is readily explained with reference to the following figures
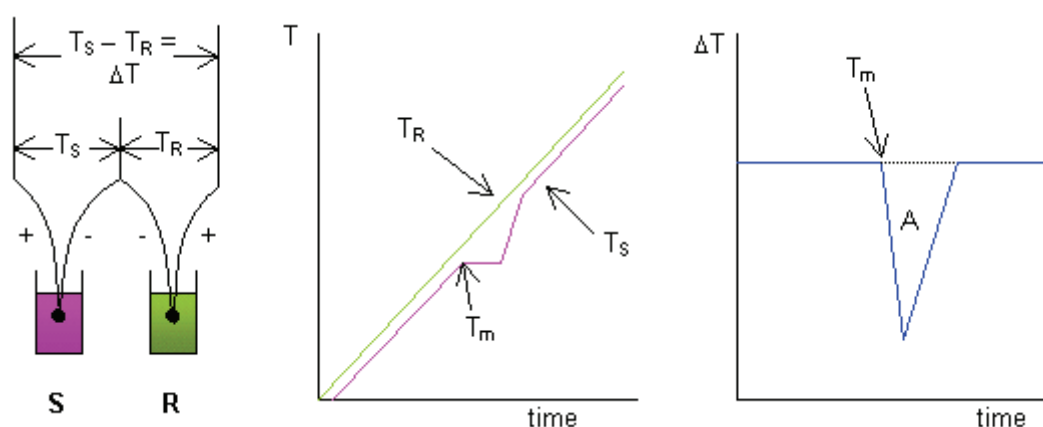
Figure 11 – principle of DTA

S and **R** are containers holding the Sample and an inert Reference material. In these are thermocouples measuring their respective temperatures. By connecting the thermocouples in opposition, the difference in temperature (DeltaT) is also measured. If **S** and **R** are heated at the same rate, by placing them in the same furnace, their temperatures will rise as in the middle figure. T_R rises steadily, as the reference material is chosen to have no physical or chemical transitions. T_S also rises steadily in the absence of any transitions, but if for instance the sample melts, its temperature

will lag behind T_R as it absorbs the heat energy necessary for melting. When melting is complete, steady heating is resumed. The right-hand figure shows the DTA curve - a plot of DeltaT against time, or more usually, sample temperature. The curve shows an endothermic (heat-absorbing) peak. If an exothermic (heat-producing) event had occurred, the curve would show a peak in the opposite direction. The area **A** on the curve is proportional to the heat of the reaction:

$$\Delta H \ KA = \int \Delta T . dt$$

The constant **K** comprises many factors, including the thermal properties of the sample, and varies with temperature. The generation of quantitative data using the "classical" arrangement above is laborious

Nowadays the thermocouples are rarely, if ever in the sample itself, but are placed below the container, which has the effect of reducing the influence of sample properties on the area of the DTA peak. With such designs, it is easier to determine the variation in **K** with temperature, and quantitative data are more readily obtained. This approach led to the development of heat-flux DSC.

DTA instruments are still valuable, particularly at higher temperatures (>1000°C), or in aggressive environments, where true heat-flux DSC instruments may not be able to operate.

DSC

Most DSC instruments are of the heat-flux design, a schematic of which is shown in figure 12. There is another type of instrument, "power-compensated DSC", which is discussed in standard texts, and for most practical purposes gives equivalent results to good heat-flux designs. The figure most closely resembles the TA Instruments design of cell, but the features are common to most. Small, flat samples are contained in shallow pans, with the aim of making a good thermal contact between sample, pan and heat flux plate. Symmetrical heating of the cell, and therefore **S** and **R**, is achieved by constructing the furnace from a metal of high thermal conductivity - silver in the case of the TA Instruments design. Note the provision for establishing a gas flow through the cell, to sweep away volatiles, provide the required atmosphere, and to assist in heat transfer
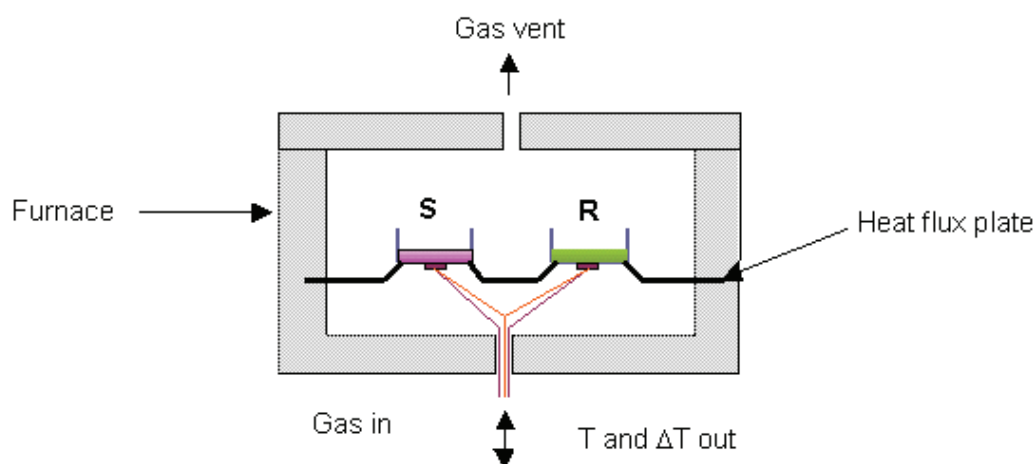
Figure 12 – Principle of DSC

The control of the furnace, signal acquisition, and data storage and analysis are of course handled by a computer. The primary signals from the cell are of the order of mV for the temperature, and µV for DeltaT. Low noise high gain amplifiers are necessary to boost these signals before data logging. Reproducible construction results on a known variation in sensitivity to heat flow with temperature, and software correction results in an effectively constant sensitivity over the working range, which is typically up to 700°C, and down to ca. -140°C with a liquid nitrogen cooling system

Temperature calibration is carried out by running standard materials, usually very pure metals with accurately known melting points. Energy calibration may be carried out by using either known heats of fusion for metals, commonly indium, or known heat capacities. Synthetic sapphire (corundum, or aluminium oxide) is readily available as a heat capacity standard, and the values for this have been accurately determined over a wide temperature range. The absolute accuracy for measurements of heat capacity and transformation enthalpies are more often limited by the lack of appropriate standards, and difficulties in assigning a baseline construction, than by limitations of the instrument itself

A variety of sample pans can be used for different purposes. The best quantitative results for polymers are obtained from thin samples crimped flat between the pan and a lid. Hermetically-sealed pans capable of holding a few atmospheres pressure are used for liquids, or when it is necessary to retain volatiles. Very high-pressure seals can be achieved using O-ring or screw-threaded seals. For materials that react with aluminium, or for higher temperatures, pans may be made from stainless steel, inconel, gold, alumina, graphite, silica or platinum

Typical purge gases are air and nitrogen, though helium is useful for efficient heat transfer and removal of volatiles. Argon is preferred as an inert purge when examining samples that can react with nitrogen. The experiment can also be carried out under vacuum or under high pressure using instruments of the appropriate design.

EXAMPLES

1. Characterisation of metallurgical By-products

TG/DTG/DT ANALYSES

Figure 13 shows the TG/DTA/DTG diagrams of the dust generated from metallurgical process treated in argon. It can be seen that the first transition takes place at about 100 - 450°C with a mass loss of 1.38% with an endothermic peak on the DTA curve. This transition is probably attributed to the volatilisation of chemically bounded water. The second transition occurs at 500 – 800°C with a mass loss of 0.75% with an endothermic peak. The third transition takes place at 800 - 1200°C with a mass loss of 7.1 %, with an endothermic peak. The total weight loss of the dust treated in argon is about 9% at 1200°C. DTG curve shows different temperature effects on the sample in the temperature range between 200 and 1200 °C. These effects are: 413.7°C, 655.21 °C and 1007.6 °C.
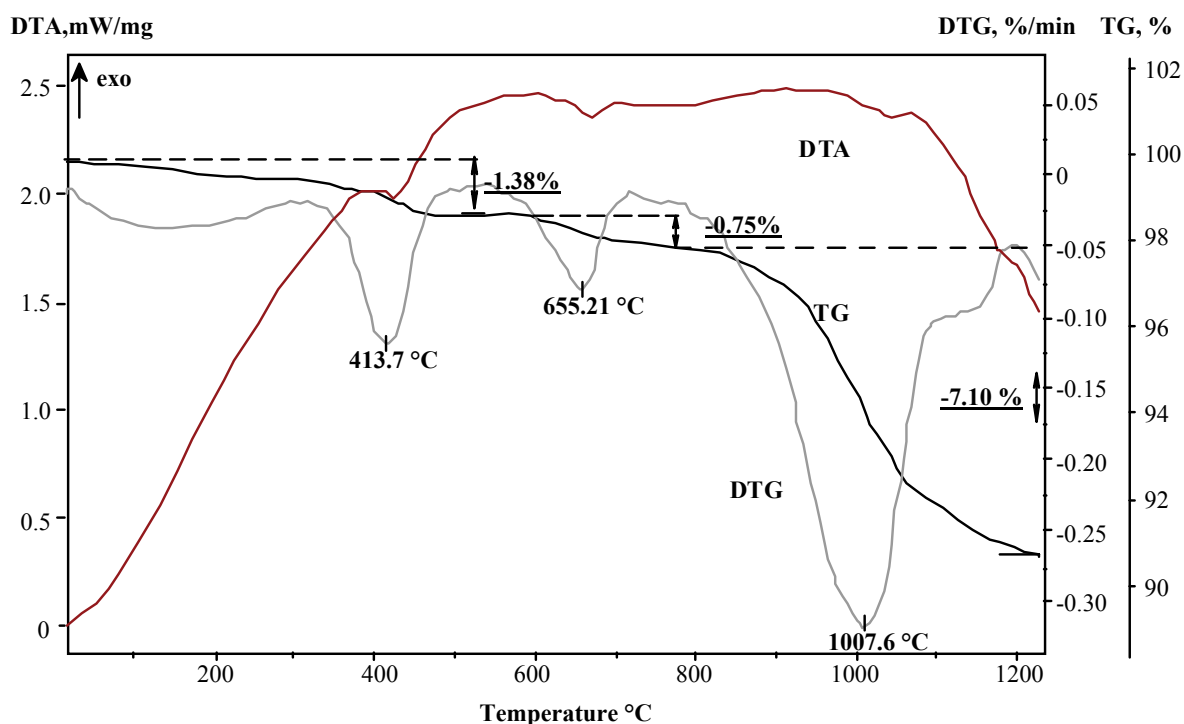

Figure 13 - TG/DTG/DTA diagram of dust generated from metallurgical processes, in argon.

2. Characterisation of Plastics

Figure 14 shows the thermal properties of PET plastic between 30 and 330 °C. It shows clearly the glass transition at 80 °C, the crystallization peak at about 158 °C and melting peak at approximately 258 °C. The measurement was conducted in He atmosphere with a heating rate of 10 k/min. It can be seen that the weight of PET sample is stable in the temperature range of 30 °C to 330 °C.
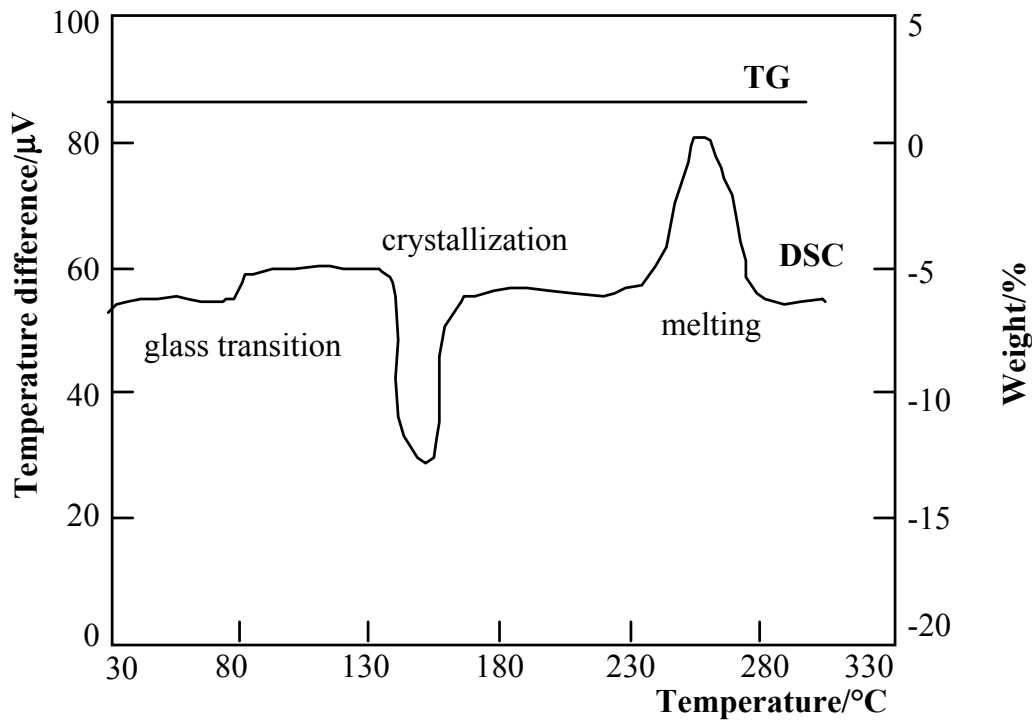
Figure 14 – STA measurement of PET plastic. (4).

3. Characterisation of Electric and Electronic scrap

Using TGA/DTA" NETZCH STA 409/QMS", the results of an electronic waste sample are shown in Figures 12 to 16. The evolution of the waste sample weight and differential analysis as function of temperature are given in Figure 15. It can be seen that the sample lose about 30% of its initial weight, this is due to degradation of plastics contained. At 500 °C the reaction is endothermic with enthalpy of 95 J/g. At high temperature of 800 °C, the reaction is exothermic with enthalpy of -127.6 j/g.

Figure 16 shows STA/QMS measurement of printed circuit boards. Figure 19 (a) gives TG curve with three fragments of epoxy resin. The mass numbers shown represent fragments of epoxy resin contained in printed circuit boards.

The fragments with higher mass numbers detected during the decomposition of this material are shown in Figure 19 (b). It can be noted that from, figures 19 (c and d), the mass number 79, 80 and 82 show two peak maxima between 250 and 550 °C, these fragments are [79]Br+, [81]Br and H[81]Br+, as well as aromatic fragments.
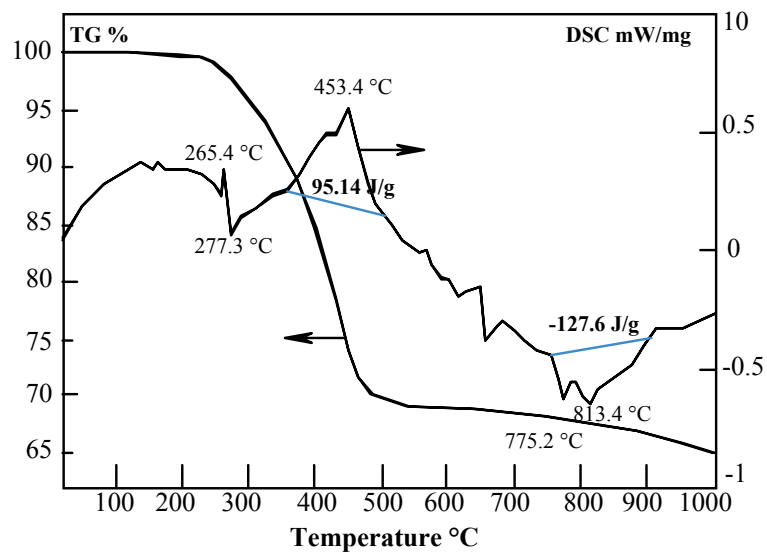
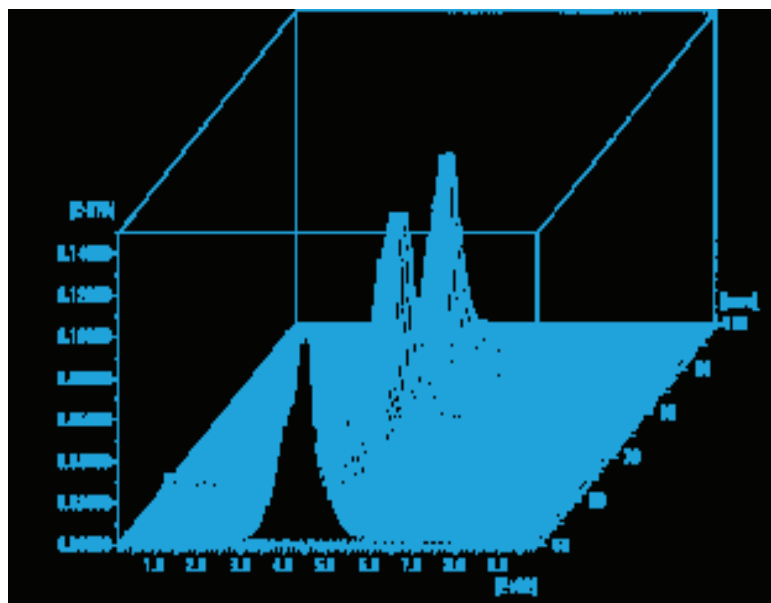**Figure 15** - TG/DTA of an electronic wastes.

Figure 16 - STA/QMS measurement of an electronic scrap material
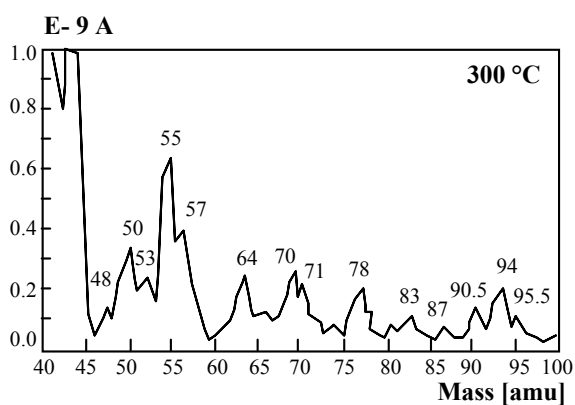in the temperature range of 25 to 1000 °C.

Figure 17 - STA/QMS measurement of PC
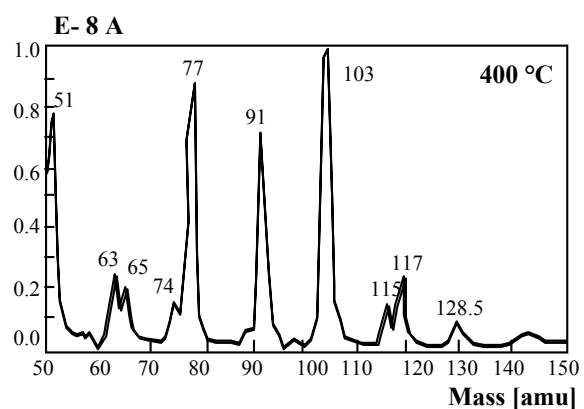scrap at 300 °C
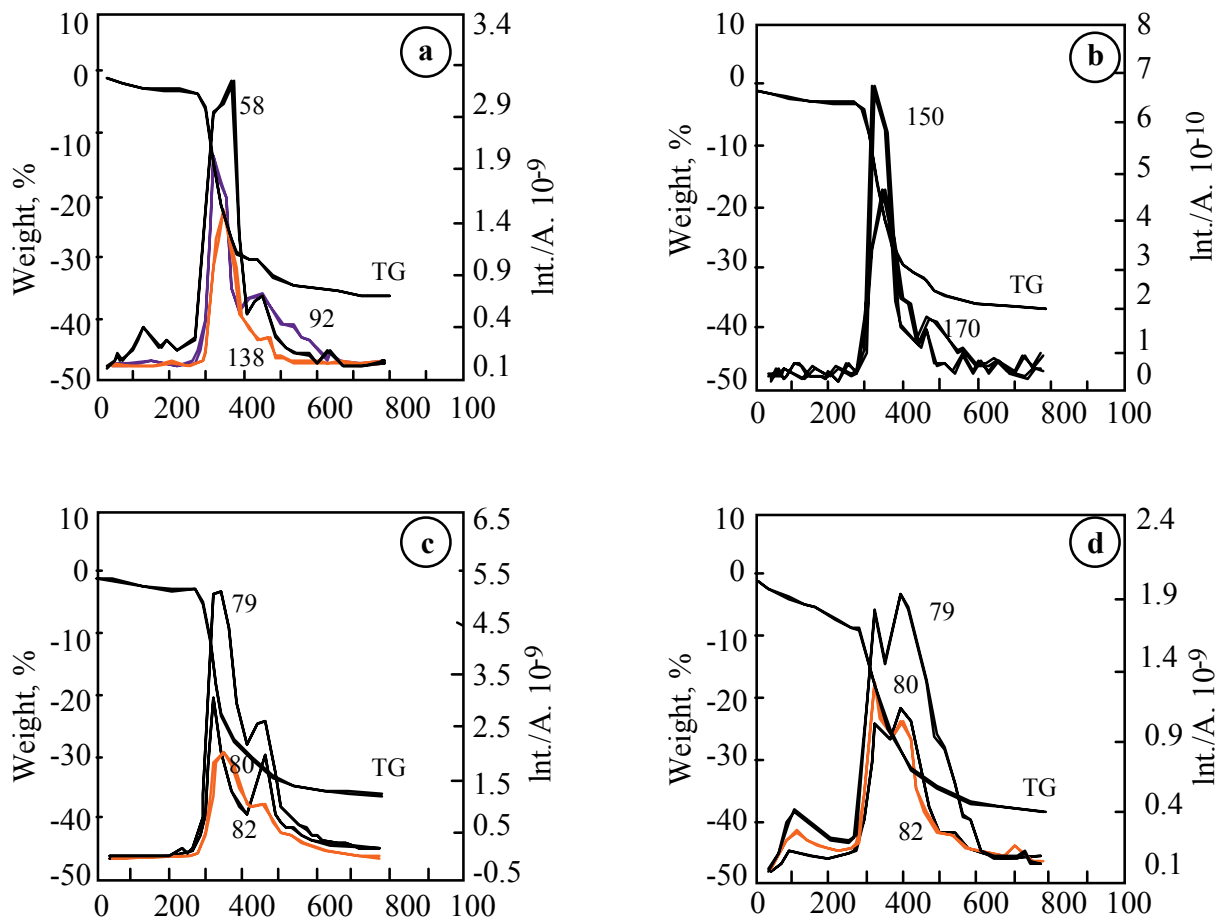

Figure 18 - STA/QMS measurement of PC
scrap at 400 °C

Figure 19 - STA/QMS measurement of Printed circuit boards
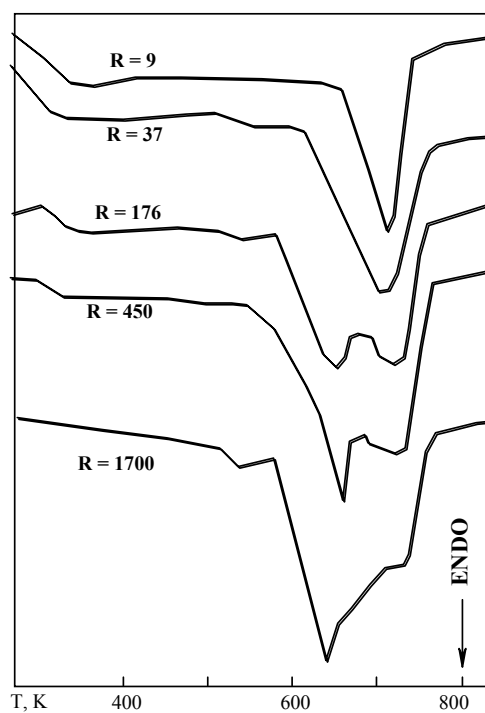
4. Characterisation of Zeolites

Figure 20 – DTA curves of different Zeolites.

The behavior of different Zeolites at temperatures lower than 800 K is given in figure 20. This figure shows the DTA measurement of some ZSM-5 samples, with different Si/Al rations (R). It can be seen different peaks of endothermic effects for different Zeolites.

*5. Decomposition of Calcium oxalate ($CaC_2O_4.H_2O$)

The behavior of calcium oxalate ($CaC_2O_4.H_2O$) in inert atmosphere is shown in figures 21 and 22. Figure 21 illustrates thermogram obtained from TG + QMS. It shows the evolution of weight in % and the composition of compounds in the gas mixture generated during heat treatment of $CaC_2O_4.H_2O$. It can be seen the following mass units: 18 (H_2O), 28 (CO), 44 (CO_2).
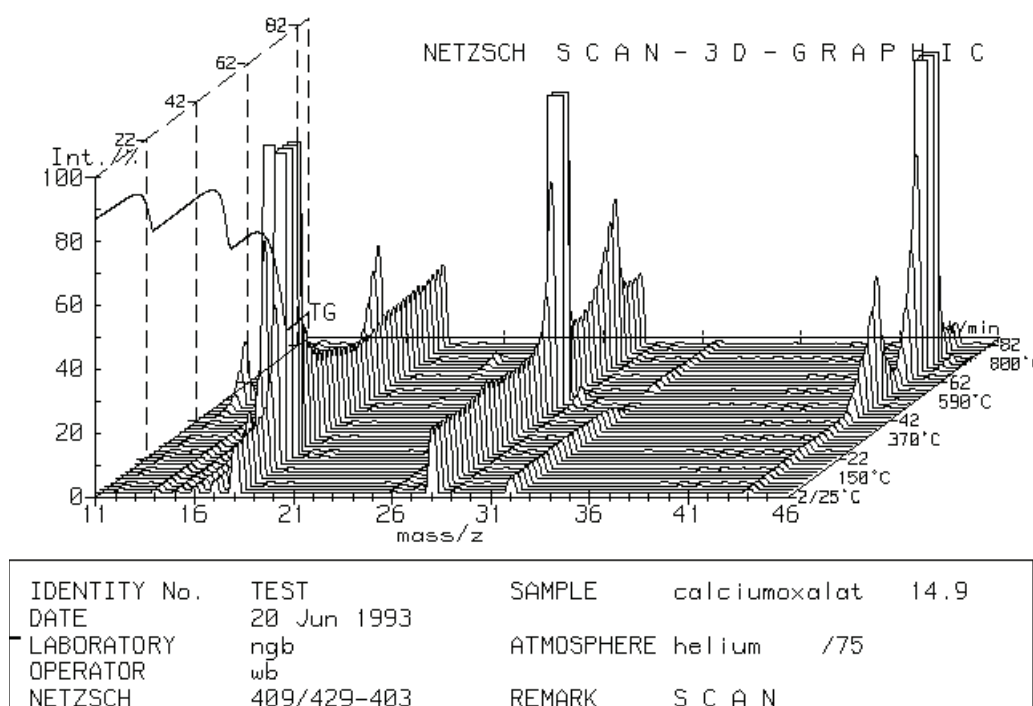

Figure 21 – TG+MS of the Calcium oxalate treated in helium atmosphere.

Figure 19 is a recorded thermogram obtained by increasing the temperature of pure calcium oxalate at a rate 5°C/min. The clearly defined horizontal regions correspond to temperature ranges in which the indicated calcium compounds are stable. The decomposition of calcium oxalate in inert atmosphere is as follow:

Temperature °C	Compounds	Residue	Volatiles
100 - 226	$CaC_2O_4.H_2O$	CaC_2O_4	H_2O
346 - 420	CaC_2O_4	$CaCO_3$	CO
660 - 840	$CaCO_3$	CaO	CO_2
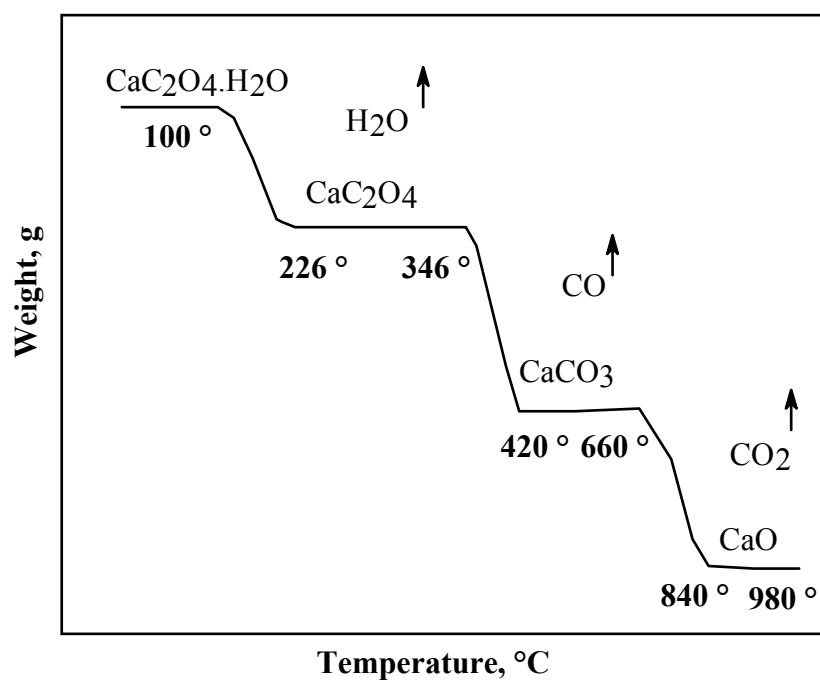
Figure 22 – Decomposition of $CaC_2O_4.H_2O$ in an inert atmosphere (4).

Figure 23 shows the derivative of the thermogram shown in figure 22. This derivative curve may reveal information that is not identified in ordinary thermogram. For example, the three peaks at 140 °C, 180 °C and 205 °C, related to three hydrates lose moisture at different temperatures. At 450 °C it appears the weight lost of carbon monoxide.

Figure 23 – DDTG of $CaC_2O_4.H_2O$ in an inert atmosphere (4).

Annexes

A1. Sample carrier systems

head

radiation shield

socket

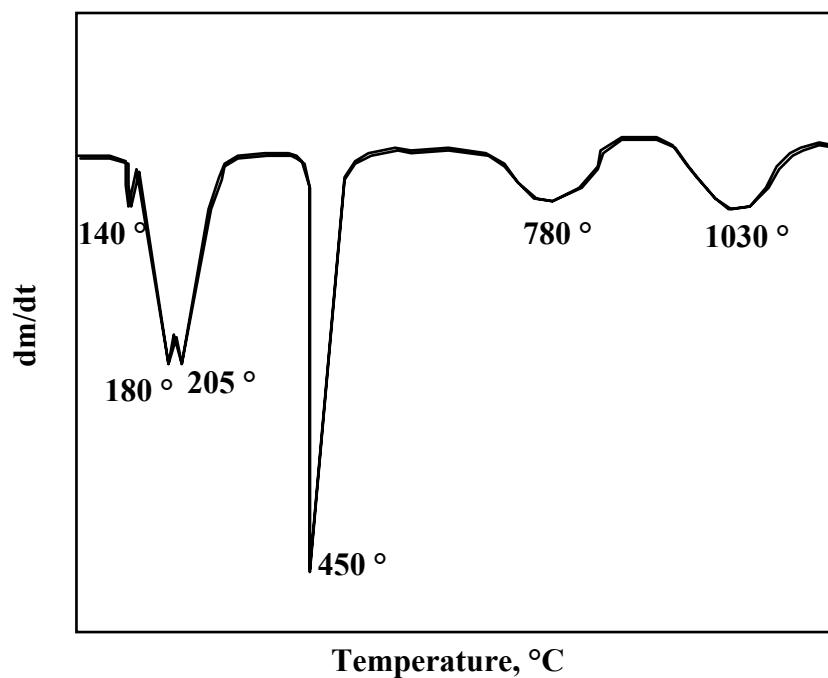plug

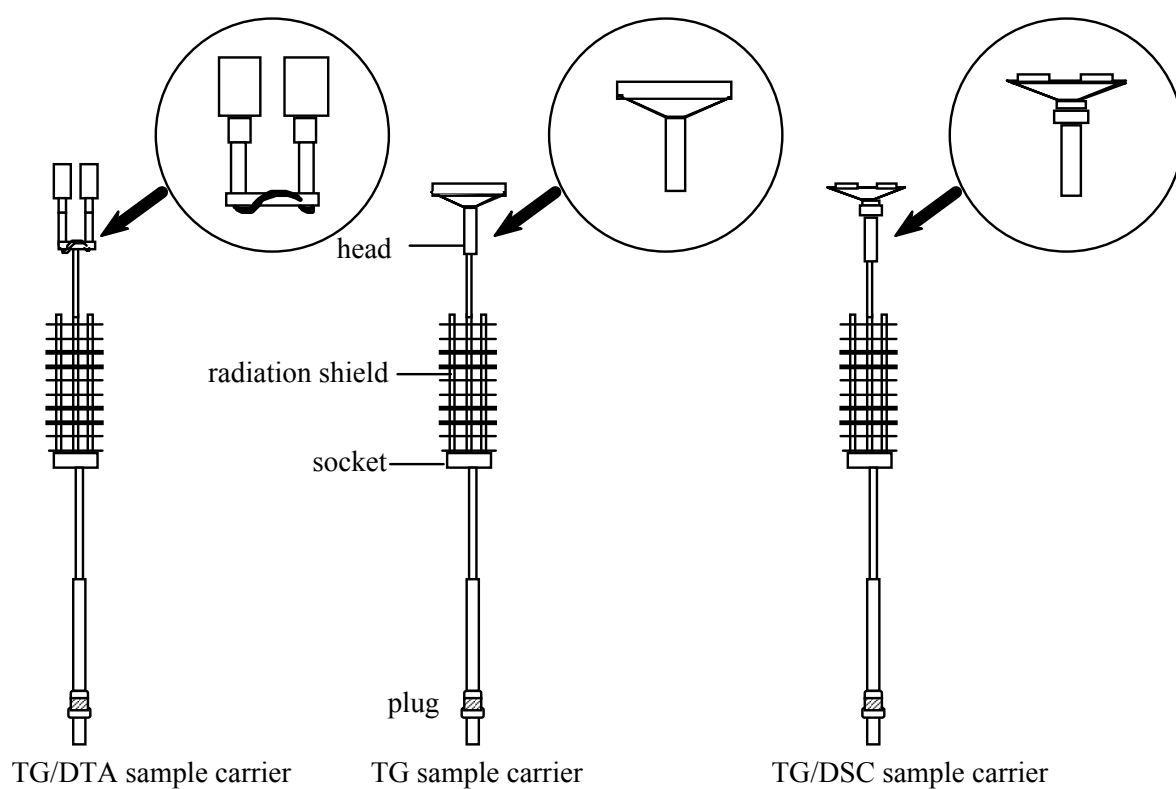TG/DTA sample carrier   TG sample carrier   TG/DSC sample carrier

Figure 24 – Sample holders

A2. The Buoyancy effect

It is generally recommended for all balance systems that buoyancy corrections be carried out for the evaluation of TG measurements, with the extortion of those made under a vacuum. What are buoyancy corrections anyway and why are they necessary?

Every substance found in a gas atmosphere is subjected to a buoyant force, this results in "apparent" mass changes. The degree of buoyancy, and thus the degree of mass change as well, are basically dependent on the volume of the substance and the density of the prevailing gas. However, for thermogravimetric investigations, it is not the absolute value of the buoyancy at a certain temperature that is decisive, but rather its change as a function of temperature. A typical buoyancy curve is shown in figure 25. It was recorded using a NETZSCH STA 409 with a DSC sample carrier in a static air atmosphere. A mass change of 0.85 mg is apparent at 500°C.

Due to the volume-dependence of the buoyancy, it is important to specify the sample carrier type in addition to the gas atmosphere, since different sample carrier/crucible combinations give rise to different "apparent" mass changes. For this reason, it is possible to predict a buoyancy effect of about half the size for a DSC sample carrier with DSC crucibles (volume in the "hot" range approx. 1 cm^3) as for a DTA sample carrier with corresponding crucibles (volume approx. 2 cm^3).

The gas atmosphere enters into the determination of dm ("apparent" increase in mass) with the density in our example from Figure 26, there is a change in the density of air of about 0.8 mg/cm^3 over the temperature range of 0°C to 500°C (derived from tabulated values for an open system). Inclusion of the total volume given above of 1cm^3 for DSC sample carrier and DSC crucible in the following equation yields a theoretical mass increase of 0.8 mg.

$$Dm = V \, d \, Rho$$

Where:

d Rho = density change
V   = volume

This agrees quite well with the experimental data although the total volume of the sample carrier/crucible combination was estimated and the STA 409 is not a completely "open" system (sample chamber ends with the narrowing of the protective tube), additionally, the same temperature does not prevail over the entire sample carrier. Because of differing initial densities and density changes displayed by different gases over the selected temperature range, different buoyancy curves will appear when the gas atmosphere is changed even when the same sample carrier and crucible type are used.

Therefore, it is advisable to run a blank test with either empty crucibles or crucibles filled with inert material to determine the buoyancy, and then subtract that from an applicable sample measurement. The question remains of why the buoyancy curve initially shows such a drastic rise.

At low temperatures, heat transfer from the furnace to the sample thermocouple is exclusively through convection. Since a certain amount of time is required before the crucible material is evenly heated and the warm air preferably flows along the inside of the protective tube, and thus does not reach the crucible immediately, the actual temperature of the gas atmosphere is far higher, particularly at the beginning of a measurement, than the temperature sensor indicates.

This means, that if one were to plot dm against the true temperature of the gas atmosphere rather than the sample temperature, the buoyancy curve and the curve of the gas density change would be exactly mirror inverted (Figure 26). The time required for uniform heating of the sample chamber is dependent on the heating rate the time constant of the sample carrier system and the thermal conductivity of the gas atmosphere.
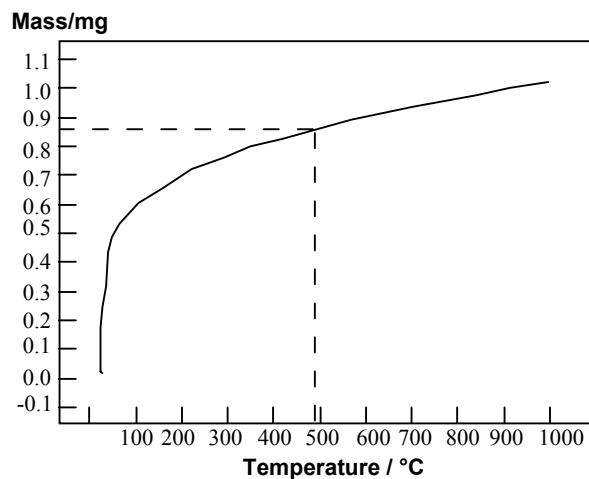

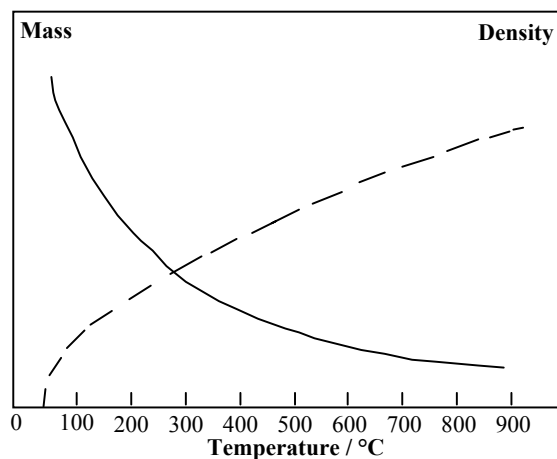**Figure 25 -** Typical buoyancy curve measured with STA 409 C.

Figure 26 – Schematic comparison of the density change of a gas
and the change in the buoyancy.

A3. Exothermicity and Endothermicity

Exothermic

With this command you can set the direction for display of exothermic and endothermic reactions. The direction of display is indicated in the graphic by an arrow on the y-axis. In ASCII format, -1 stands for exotherm down.

NOTE

The direction of display of exothermic (endothermic) reactions must be set before loading the measurement curves. Accordance with DIN 51007, an ordinate direction with negative sign (exo down) must be selected for an exothermic process. ASTM E 472-86 specifies a representation in the positive ordinate direction (exo up) for exothermic reactions.

Exo up or exo down - two thermodynamic observation modes

If, during thermal treatment, heat is released from the sample, this is an indication of an exothermal process. If such a process is studied using dynamic differential calorimetry (DSC), two forms of presentation are possible. In some countries, e.g. Germany, Switzerland, Austria, an exothermal signal is generally marked with a negative sign, i.e. exothermal down. In other countries, e.g. USA, GB, France the presentation exothermal up is preferred. The type of presentation is strictly defined in relevant standards (e.g. in Germany). Because there have been repeated questions on this in the past, the purpose here is to show the respective method of thermodynamic observation. To begin with, we agree that for the X (temperature or time) and Y (DSC signal) axes the values increase from left to right or from bottom to top, respectively.

Exotherm up

The observer is outside the sample. With the start of the exothermal reaction, he receives energy from the sample; therefore, the presentation of the DSC signal is positive.

Observer   **heat flux**   **sample**
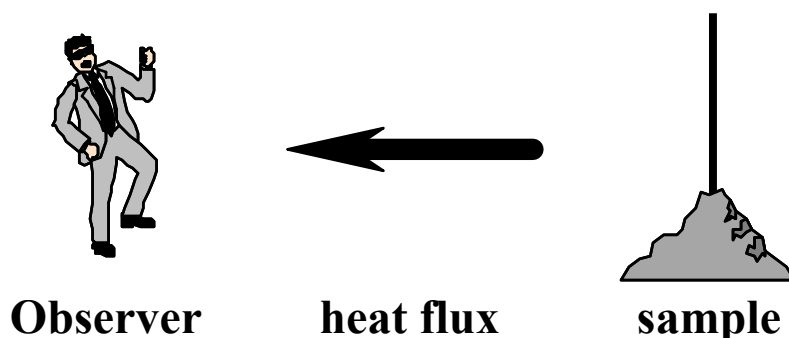
Exotherm down

The observer is on the sample. With the start of the exothermal reaction energy is lost; therefore the presentation of the DSC signal is negative.

Observer

environment   **heat flux**   **sample**
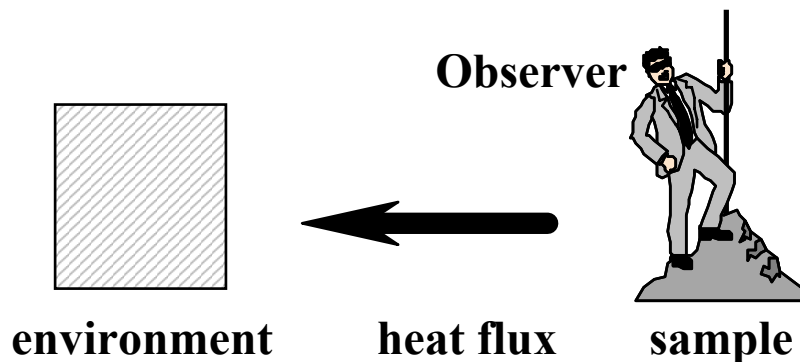
Peak Area

The peak area is calculated over time according to formula (1) as an integral of the difference between the DSC signal and the baseline, even if temperature scaling was selected for the X axis. The integration is always carried out from the lesser time t1 to the greater time t2, because heat is determined over a running process. Therefore the integral is always positive, if the difference DSC(t) - baseline(t), is positive for the integration range and negative, if DSC(t) - baseline(t) is negative over the integration range. To change the direction for display of exothermic (endothermic) reactions:

- Select the command Exo... from the Extras Menu.

- The Exo Window appears.

- Click the button Up or Down to establish the presetting for the display direction.

- Confirm with OK.

- Open your measurement curve(s).

NOTE

The setting of the DSC analysis values are automatically accepted into the DSC data acquisition graphic.

References

1. Menad N. and Bo, Björkman, "Characteristics of Electronic Wastes", EPD congress, USA, March, 2000.

2. Menad N. and Bo. Björkman, "Combustion of Plastic contained in Electric and Electronic scrap", Report N°2, Luleå University, (Sweden), 59 pp. October 1996.

3. Menad N. and Qixing Yang, "Charaterisation of EAF dusts", Luleå University of Technology, (Sweden), 20 pp. Sept, 1999.

4. Skkoo.Holler.Nieman," Instrumental analysis", 5th edition, Chapter 31.