

# Principles and Practice of Analytical Chemistry

Fifth Edition

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Blackwell  
Science

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## Thermal Techniques

Thermal methods of analysis may be broadly defined as methods of analysis in which the effect of heat on a sample is studied to provide qualitative or quantitative analytical information. Such studies have a long history, but it is only in the last thirty years that instrumental improvements have led to methods which are both simple and reliable to operate. This has been accompanied by a steadily widening applicability. Such techniques are now applied across a wide range of areas in which analytical chemistry is used. Thermal analysis may be defined as a group of techniques in which a property of the sample is monitored against time, or temperature while the temperature of the sample, in a specified atmosphere, is programmed. There are a substantial number of sample properties on which the effect of heat has been studied, which has led to the development of a number of recognized techniques for which the appropriate instrumentation is commercially available. The most important of these are summarized in Table 11.1. In this text, only *thermogravimetry* (TG), *differential thermal analysis* (DTA) *differential scanning calorimetry* (DSC), *pyrolysis – gas chroma-*

**Table 11.1** The main thermal analysis technique (from *Introduction to Thermal Analysis*, M. E. Brown, Chapman & Hall)

Property	Technique	Abbreviation
mass	thermogravimetry	TG, TGA
	derivative thermogravimetry	DTG
temperature	differential thermal analysis	DTA
enthalpy	differential scanning calorimetry	DSC
dimensions	thermodilatometry	
mechanical properties	thermomechanical analysis (thermomechanometry)	TMA
	dynamic mechanical analysis	DMA
optical properties	thermoptometry or thermomicroscopy	
magnetic properties	thermomagnetometry	TM
electrical properties	thermoelectrometry	
acoustic properties	thermosonimetry and thermoacoustimetry	TS
evolution of radioactive gas	emanation thermal analysis	ETA
evolution of particles	thermoparticulate analysis	TPA

*tography* (pyrolysis-GC) and *thermomechanical analysis* (TMA) will be discussed in any detail.

*Thermal events* are usually studied by recording the change in thermal property as the temperature is varied to give a *thermal analysis curve* or *thermogram*. The main thermal events are summarized in Table 11.2. Such curves are characteristic of a sample in both qualitative and quantitative senses. However, they can be complex, leading to difficulties in assigning the detail of the curve to particular thermal events. Nevertheless, complex curves can still be used as a 'fingerprint' for identification of the sample. Derivatives may often be of help in interpretation. The best results may be obtained by using a combination of thermal techniques, e.g. TG with DSC or DTA. It should be recognized that results in thermal analysis are very dependent upon the conditions and parameters surrounding their measurement. For example, the history of the sample and its mass, the nature of the sample holder, the rate of heating or cooling, the surrounding atmosphere and its flow rate, will all have an effect.

**Table 11.2** Thermal events. (From *Introduction to Thermal Analysis*, M. E. Brown, Chapman & Hall)

$A(s_1)$	$A(s_2)$	phase transition	
	$A(l)$	melting	
	$A(g)$	sublimation	
	$B(s) + \text{gases}$	decomposition	{ thermal radiolytic
	gases		
$A(\text{glass}) \rightarrow A(\text{rubber})$		glass transition	
$A(s) + B(g) \rightarrow C(s)$	{	oxidation	
		tarnishing	
$A(s) + B(g) \rightarrow \text{gases}$	{	combustion	
		volatilization	
$A(s) + (\text{gases})_1 \rightarrow A(s) + (\text{gases})_2$		heterogeneous catalysis	
$A(s) + B(s) \rightarrow AB(s)$		addition	
$AB(s) + CD(s) \rightarrow AD(s) + CB(s)$		double decomposition	

## 11.1— Thermogravimetry

### Summary

### Principles

Study of the change in mass of a sample as the temperature is varied.

### Instrumentation

Sensitive balance with the sample pan inside a furnace whose temperature can be accurately controlled and programmed for change. Facilities for

controlling the atmosphere of the sample. Electronic integration and derivative curve presentation.

### *Applications*

Qualitative and quantitative analysis for a wide range of sample types, especially for inorganic materials and polymers. Kinetic studies where weight changes can be clearly attributed to a particular reaction. Chemical reactions, volatilization, adsorption and desorption may be studied. Relative precision at best *ca.* 1% but very variable.

### *Disadvantages*

Limited to samples which undergo weight changes, thus melting, crystal phase changes etc. cannot be studied. Complex thermal traces are often difficult to interpret.

*Thermogravimetry* (TG), formerly known as *thermogravimetric analysis* (TGA), is based on the very simple principle of monitoring the change in weight of a sample as the temperature is varied. By controlling the atmosphere, e.g. with O<sub>2</sub> or N<sub>2</sub>, it may be possible to encourage or suppress oxidation reactions, thus controlling to some extent the nature of the thermal events occurring. When heated over the range of temperatures, ambient to approximately 1000°C, many materials undergo weight changes giving characteristic curves. Where the changes can be linked to a particular thermal event, such as oxidation, or loss of water of crystallization, the size of the step in the curve can be used for quantitative analysis. Where thermograms are complex, or where changes are subtle, derivative curves (DTG) can be valuable in interpretation. Figure 11.1 shows an example of a straightforward thermogram and Figure 11.2 a more complex one illustrating the value of DTG.

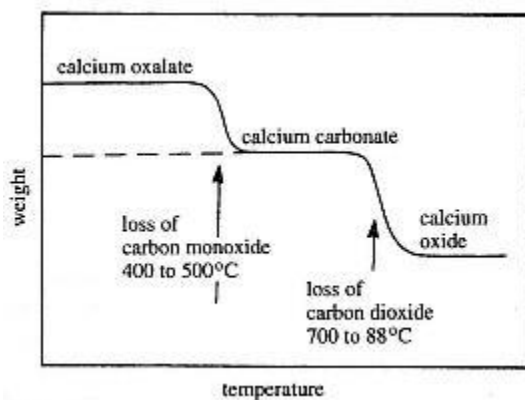


Figure 11.1  
TG curve for calcium oxalate.

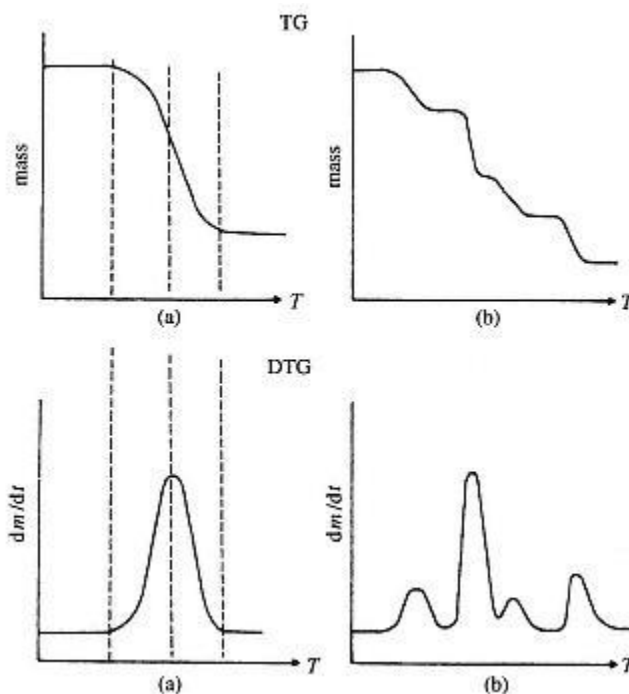


Figure 11.2  
Comparison of TG and DTG curves.

## Instrumentation

Early designs of thermobalances consisted of little more than a good quality chemical balance with one pan suspended in an electric furnace. Linked chart recorders provided a trace of temperature and mass changes. In some senses this experimental arrangement can still be seen in modern instruments.

However, the evolving requirements of greater sensitivity, both in terms of sample size and mass change, mean that current instruments are based on the use of electronic micro-balances. The schematic arrangement of such a thermobalance is shown in Figure 11.3. For use in TG, a null-point mechanism is to be preferred, as this ensures that the sample remains in the same part of the furnace, even when the mass changes. Thus any effects due to thermal gradients within the furnace tube remain constant.

The design and operation of the furnace are of critical importance in obtaining good quality, reproducible thermograms. Most instruments use electrical resistance heaters, although heating techniques using infrared, laser irradiation or microwave induction heating have been investigated. The latter has a particular attraction as it would enable uniform heating to be employed throughout the sample. The arrangement of the sample pan may be of horizontal, toploading, or suspended design. The effects of

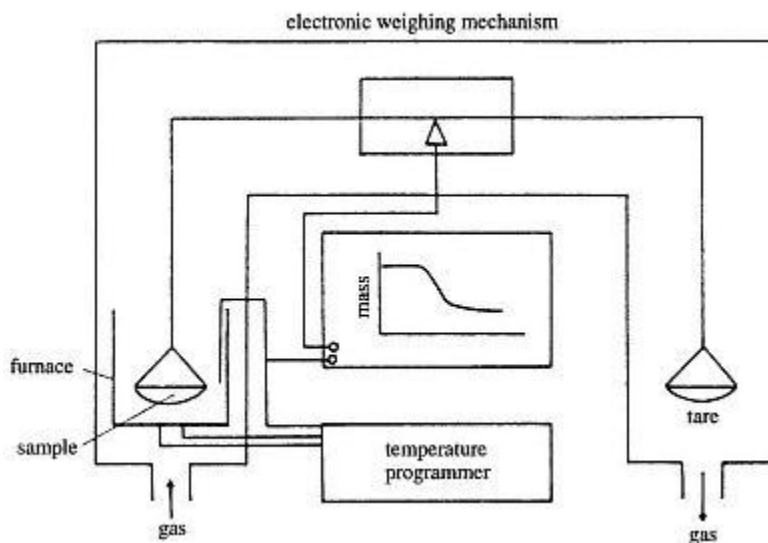


Figure 11.3  
A schematic thermobalance.

convection currents within the furnace tube, which can lead to uneven heating, can be minimized by a series of baffles. Even so, there will still be a thermal gradient within the furnace, and careful temperature calibration is needed. One method of calibration which has been used effectively is the *Curie-point* method. Ferromagnetic materials lose their magnetism on heating at exactly reproducible temperatures or Curie points. A range of metals or alloys with Curie points between 150 and 1000°C is available. If suitable ferromagnetic calibration standards are placed in the sample pan of the balance, and a large permanent magnet is placed below the pan, the sample will experience a downward attraction leading to an apparent increase in weight (Figure 11.4). At the Curie point the loss of the ferromagnetism will be reflected by an apparent loss of weight, enabling the temperature experienced by the balance pan to be accurately known. Using a range of standard materials, an accurate calibration curve of the furnace can be produced. However, this does not completely solve the problem of accurate assessment of the temperature actually experienced by the sample. With the exception of microwave induction heating, the heat is absorbed by the exterior of the sample and transferred to the interior by conduction. Thus a temperature gradient will exist within the sample. Many materials that are the subject of TG investigation, will have low thermal conductivities whence this effect will be pronounced. The only remedy is to reduce the sample size to the absolute minimum, e.g. 10 mg, and avoid rapid heating programmes.



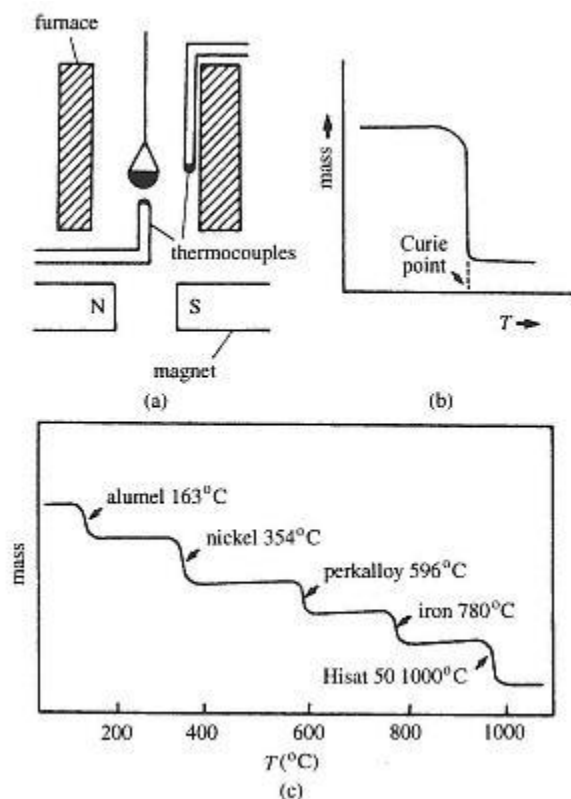


Figure 11.4  
Curie -point method of temperature calibration.

## Applications of TG

TG may be used to characterize and compare samples using the thermogram as a fingerprint. Where the thermal processes taking place are known or where a step in the thermogram of a mixture may be clearly related to one component, quantitative analysis may be possible. Weight changes in chemical reactions may be monitored in order to follow the kinetics of the reaction. The earlier developments of modern TG methods in the 1950s and 1960s were exploited largely in the field of inorganic chemistry and produced a revolution in inorganic gravimetric analysis. Some analyses have already been exemplified in Figures 11.1 and 11.2. Subsequently however the use of TG has spread into more diverse fields. Noteworthy are applications to polymers for thermal stability studies, as well as qualitative and quantitative analysis, whilst in pharmaceutical preparations both active ingredients and excipients can be analysed. Figures 11.5 and 11.6 show examples of these applications.

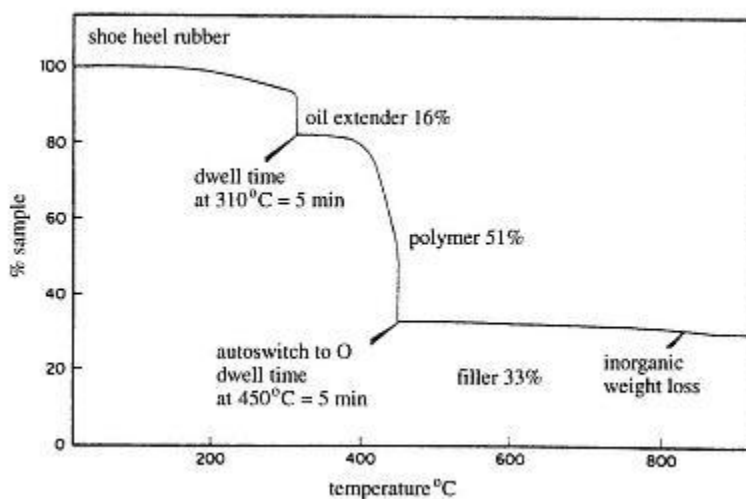


Figure 11.5  
Determination of extender, polymer and filler in an elastomer.

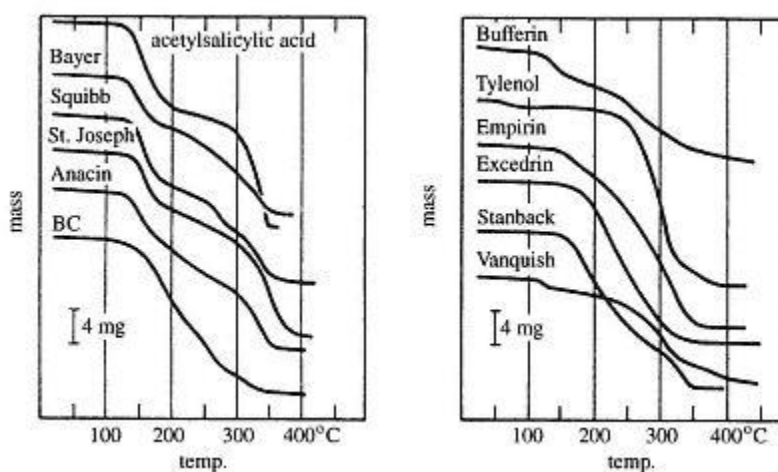


Figure 11.6  
TG curves of commercially available analgesics as determined by Wendlandt and Collins.

## 11.2— Differential Thermal Analysis (DTA)

### Summary

### Principles

Monitoring of the temperature difference between a sample and an inert reference as they are heated uniformly. Endothermic or exothermic changes in the sample lead to characteristic deviations in temperature, which can be used for qualitative and quantitative analyses.

### ***Instrumentation***

Programmed electric furnace containing sample and reference. Sensitive thermocouples and recorders to produce a  $\Delta T$  vs  $T$  plot. Facility to control atmosphere of sample.

### ***Applications***

Fingerprinting by the pattern of thermograms, qualitative and quantitative analyses by peak area or height for a wide range of materials.

Study of thermal characteristics, stability, degradation and reaction kinetics on small samples, over a temperature range of  $-175^{\circ}\text{C}$  to  $1000^{\circ}\text{C}$  and above. In some cases precision may be good (1%) but it is variable and may be much poorer.

### ***Disadvantages***

Small sample sizes are often required to minimize thermal conductivity problems. Less satisfactory than DSC with regard to resolution of thermal traces and quantitative data.

Differential thermal analysis (DTA) is based upon the measurement of the temperature difference ( $\Delta T$ ) between the sample and an inert reference such as glass or  $\text{Al}_2\text{O}_3$  as they are both subjected to the same heating programme. The temperature of the reference will thus rise at a steady rate determined by its specific heat, and the programmed rate of heating. Similarly with the sample, except that when an exothermic or endothermic process occurs a peak or trough will be observed. Typical behaviour is shown schematically in Figure 11.7.

In practice,  $\Delta T$  vs furnace temperature is plotted giving a thermogram of the type illustrated in Figure 11.8. Figure 11.9 shows a curve for the DTA

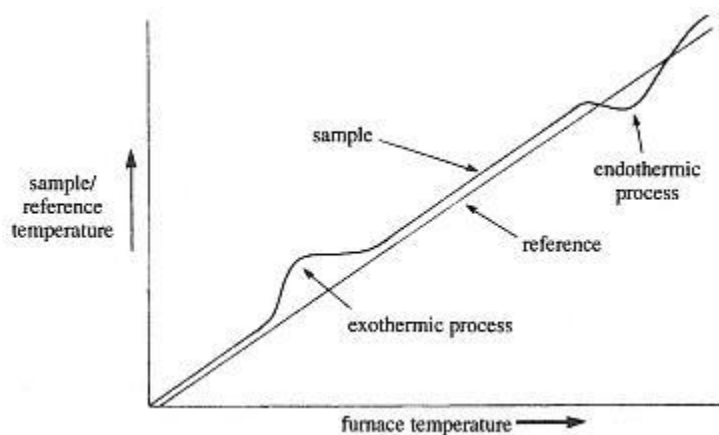


Figure 11.7  
Schematic representation of the variation of sample and reference temperature in DTA.

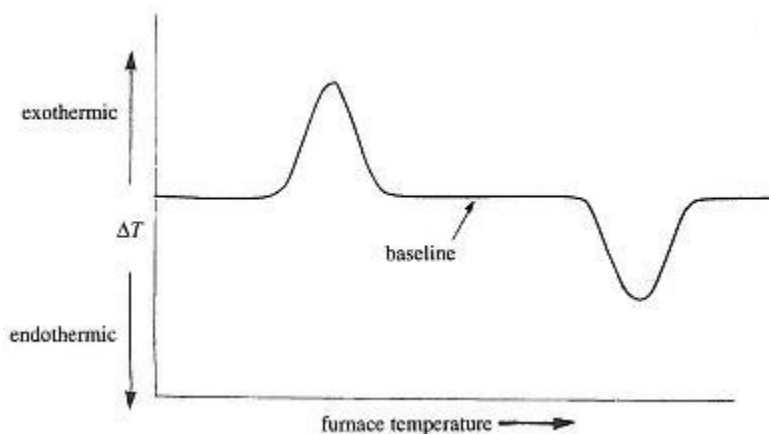


Figure 11.8  
 $\Delta T$  vs  $T$  plot to give a schematic DTA trace.

examination of calcium oxalate monohydrate exemplifying also the effect of changing the atmosphere from nitrogen to air.

Mostly, the convention with exothermic peaks (*exotherms*) shown as positive and endothermic peaks (*endotherms*) as negative is accepted. However, there are exceptions and care should always be exercised in the interpretation of recorded data.

### Instrumentation

The essential instrumentation for DTA involves a single furnace containing both the sample and reference, which are heated at the same rate. The temperatures of the sample and reference are measured separately by individual thermocouples. A thermogram is then plotted of the difference in temperature between sample and reference against overall furnace temperature. Two differing conformations for sample and reference heating may be found in use. In the first the sample and reference are heated in recesses in the same heating block (Figure 11.10(a)). This arrangement is known as a *classical* DTA instrument. In the second arrangement, the sample and reference pans are placed on separate heating blocks or heat sinks, with the temperature of the block being measured, rather than the sample itself (Figure 11.10(b)). Such an arrangement comprises a *calorimetric* or *Boersma* DTA instrument. The two variations provide essentially the same data, but the latter, whilst less dependent on the thermal properties of the sample, has a slower response to thermal changes. The temperature range of DTA instruments is obviously dependent upon the nature of the furnace and thermocouples and the limitations imposed by them. Typically instruments are designed to operate in the range from room temperature to *ca.* 1000°C. However, considerable extension to both higher and lower temperatures is possible with suitably modified equipment.

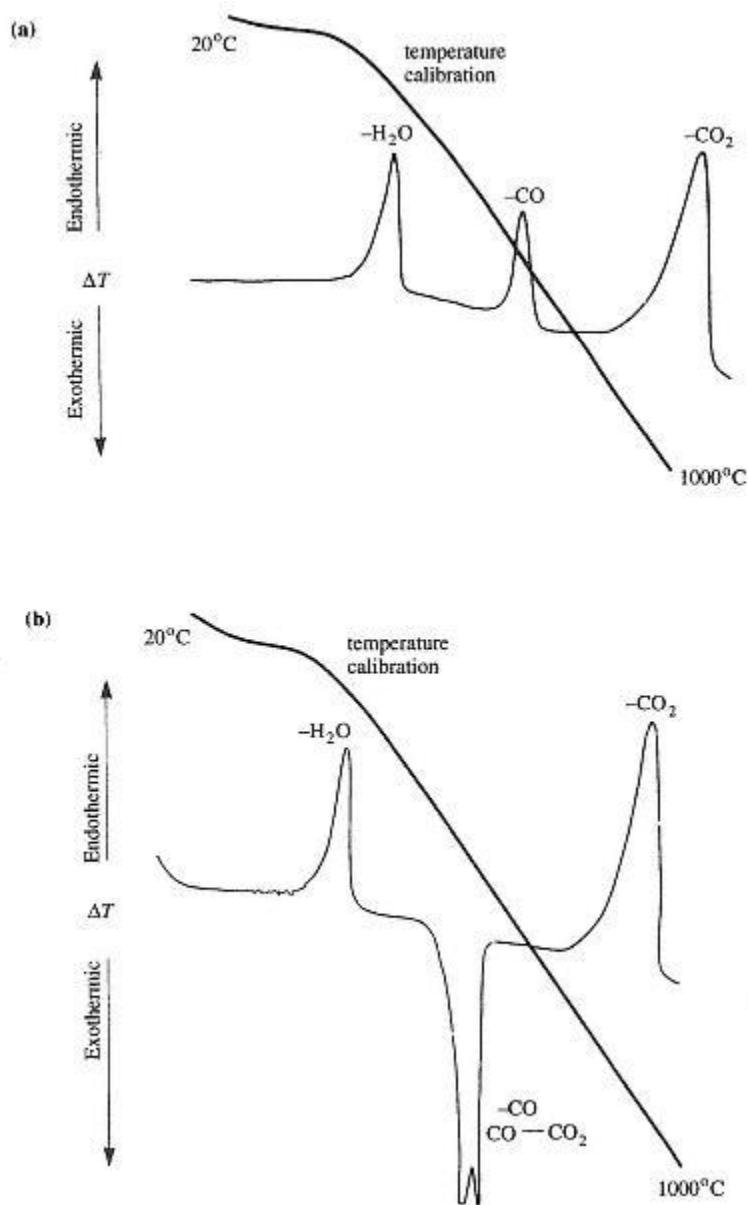


Figure 11.9

DTA study of calcium oxalate  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  showing the effect of changing the atmosphere from (a) nitrogen to (b) air.

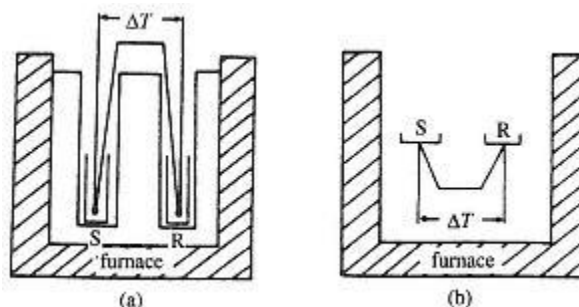


Figure 11.10  
Differential thermal analysis (DTA).  
(a) Classical apparatus (S = sample; R = reference).  
(b) Calorimetric.

Calibration is by heating known reference materials of accurately known external characteristics.

### Applications of DTA

Typical DTA curves have been illustrated in Figures 11.8 and 11.9. The combination of exotherms and endotherms will be unique to a particular sample composition. Thus the pattern of the thermogram can be used as a finger print for qualitative analysis, whilst the areas under the curve may be used for quantitative analysis. These principles can be widely applied to samples of very different types, e.g. minerals, inorganic compounds, pharmaceuticals, polymers, foodstuffs and biological specimens. Typical samples sizes are from 1 mg upwards allowing, where necessary, for measurements to be made on small samples. DTA may be used effectively in a simple characterization or a purity estimate by studying the melting characteristics of a specimen. On the other hand much more complex systems may be usefully studied. Figure 11.11 illustrates a complex behaviour pattern for an inorganic compound and Figure 11.12 the characterization of starch in foodstuffs. Reaction kinetics may be studied and measurements of enthalpy changes made.

Applications in polymer analysis are illustrated in Figures 11.13 and 11.14. The former shows schematically the typical thermal processes which can occur on heating a polymer, and the latter an analysis of a seven-component mixture based upon melting points.

Probably the main weakness of DTA as a method of analysis remains the difficulty of linking the thermal changes shown on the thermogram, with the actual thermal processes taking place. It should be noted that data obtained by DTA are often similar to those available for differential scanning calorimetry. Indeed the two techniques overlap extensively and may be seen as complementary. A comparison of the two techniques is made at the end of the next section.

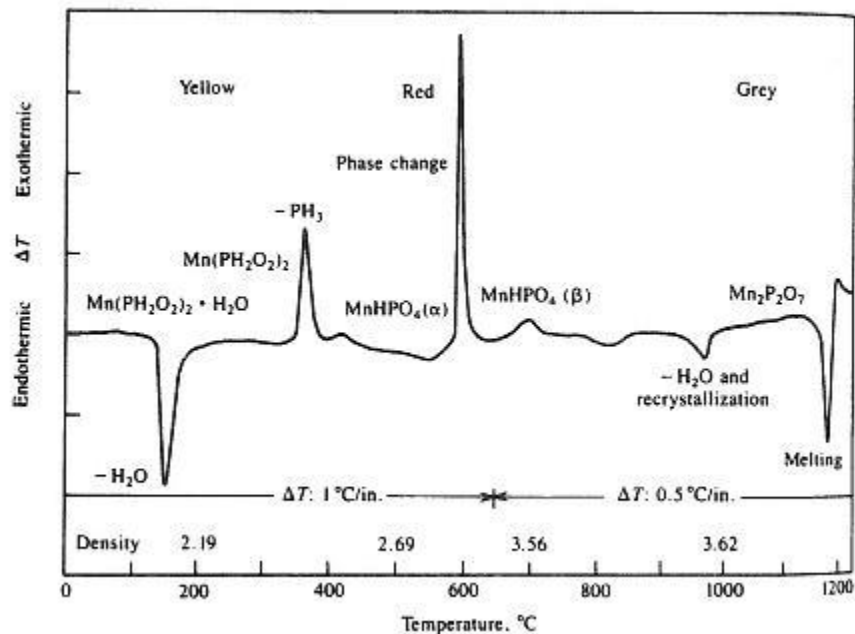


Figure 11.11  
DTA curve for  $\text{Mn}(\text{PH}_2\text{O}_2)\text{H}_2\text{O}$ .

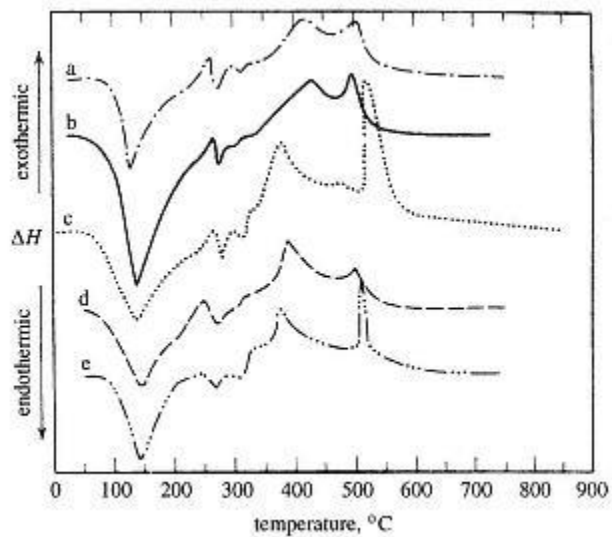


Figure 11.12  
DTA curves of potato and corn starch.  
(a) Potato starch;  
(b) potato starch, duplicate run;  
(c) corn starch;  
(d) methanol-extracted corn starch;  
(e) ammonia-pregelatinized corn starch.

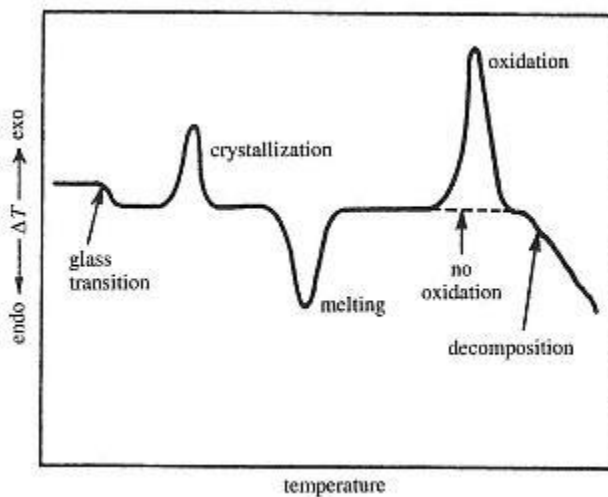


Figure 11.13  
Schematic DTA curve of a typical polymer. Note: glass transitions reflect a heat capacity change and thus they are seen as 'steps' on the baseline rather than peaks.

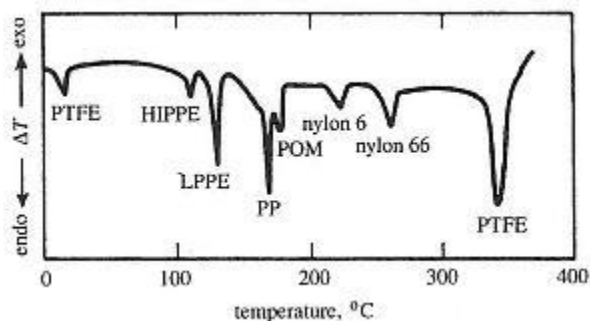


Figure 11.14  
DTA curve of a seven-component polymer mixture showing endothermic peaks associated with melting.

### 11.3— Differential Scanning Calorimetry (DSC)

#### Summary

#### Principles

Sample and an inert reference heated separately, with the power supply to the sample heater variable so that the temperature difference can be maintained at zero even when endothermic or exothermic changes occur. The difference in power supplied to the two heaters is monitored as the analytical signal ( $\Delta E$ ). Alternatively, the differential heat flow to sample and standard when they are heated from the same source is monitored.



### ***Instrumentation***

Sample and reference crucibles with separate heaters. Thermocouples with feedback to sample heater so that the power is varied to maintain  $\Delta T = 0$ . Data output equipment to provide  $\Delta E$  vs temperature curves, derivative curves and peak integration. Facility to vary atmosphere of sample.

### ***Applications***

Widespread study of thermal properties on an extensive range of sample types. Qualitative and quantitative analyses. Relative precision is very variable, at best *ca.* 1% but can be much poorer.

### ***Disadvantages***

Usually limited to small sample sizes. Thermograms are often complex and thus difficult to interpret fully.

*Differential scanning calorimetry* (DSC) is a technique which aims to study the same thermal phenomena as DTA, but does so on a rather different principle. Hence, although the data obtained are very similar, they may differ in detail. Typical DSC equipment will operate over the temperature range from ambient to *ca.* 700°C. However, as with DTA, specially modified equipment can extend this substantially in both directions.

In principle, like DTA, DSC involves the heating of the sample and an inert reference in parallel. However, for *power/compensated* DSC, the two are heated quite separately with separate electrical heaters. The heaters are programmed to ensure that the temperatures of both sample and reference advance at exactly the same rate. It follows that when endotherms or exotherms occur in the sample, the power to the heater will need to be varied in order to maintain  $\Delta T = 0$ , (Figure 11.15). Thus by monitoring the difference in power supplied to the heaters ( $\Delta E$ ) the thermal changes in the sample may be followed. Figure 11.16 illustrates a typical DSC thermogram schematically. It is worthy of note that the measurement of  $\Delta E$  is effectively a direct measurement of the energy change in the sample. This makes DSC particularly appropriate as a technique for the measurement of  $\Delta H$  values which can be derived from the areas of the peaks obtained. *Heat flux* DSC attains similar results by heating sample and reference from the same source. Thermocouples are used to sense the differential heat flow (supply) to the sample and standard.

A comparison of Figures 11.15 and 11.16 with 11.17 and 11.18 will show the peaks for endotherms and exotherms reversed in direction for DTA relative to DSC. This is a commonly met presentation but as there is no agreed convention, different authors may use different presentations. Confusion can arise unless care is exercised in the interpretation of the thermograms.

### ***Instrumentation***

The equipment for power-compensated DSC involves two parallel temperature measurement systems. Sample (*ca.* 50 mg) and reference in

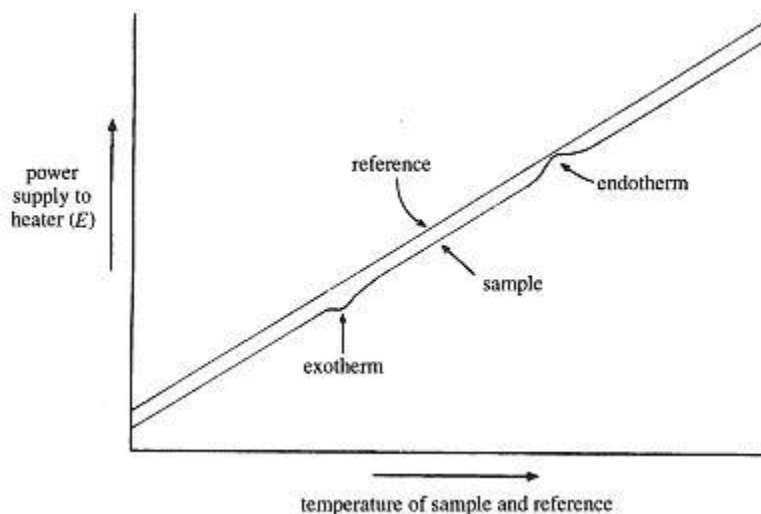


Figure 11.15  
Schematic representation of the variation of power supply to the sample and reference in DSC.

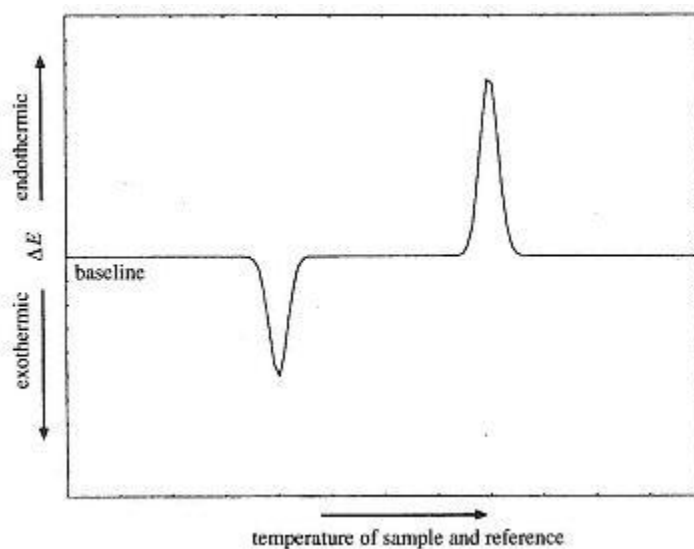


Figure 11.16  
Schematic DSC curve.

small pans are placed on the separate blocks (Figure 11.17). Each block is provided with a separate heater and thermocouple with feedback to the heaters so that the power supply can be varied as necessary to ensure that  $\Delta T = 0$  at all times as the temperature is raised overall. A thermogram is then generated by monitoring the difference in power supplied to

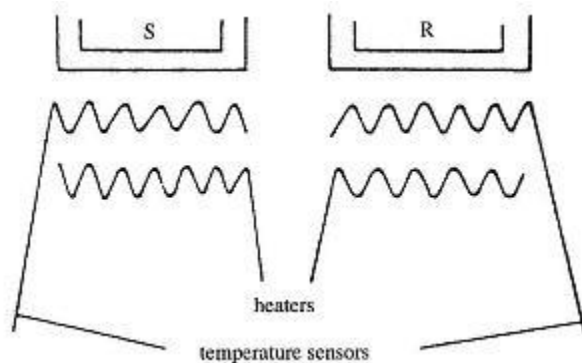


Figure 11.17  
Power-compensated differential scanning calorimetry  
(DSC) apparatus (S = sample; R = reference).

the two heaters ( $\Delta E$ ) and plotting this against the overall temperature (Figure 11.16). Data presentation at its simplest may be on a chart recorder, but increasingly microcomputers or microprocessors are used to give added flexibility to the presentation. Built into the system will be a facility to control the atmosphere of the sample. For heat flux DSC the sample and reference in separate containers are placed on separate platforms which sit on a heated metal (Cu/Ni alloy) disc. Thermocouples are placed to monitor the heat flow from the disc to the sample and standard. The differential heat flow will then reflect the different thermal behaviour of the sample and standard. A plot of this against overall temperature produces a graph analogous to those from power-compensated DSC. Calibration is by use of standards (e.g. indium) with accurately known thermal characterization.

### Applications of DSC

DSC essentially studies the same thermal phenomena as DTA, albeit using a different principle. Thus DTA and DSC provide very much the same information and their applications are similar. Reference back to the section on the applications of DTA will suffice to indicate the scope of DSC. Some differences in the quality of the information obtained sometimes exist however, leading to a preference for one technique over the other for particular purposes.

### DTA and DSC

The experimental set up for heat flux DSC is very similar to that for calorimetric or Boersma DTA. Thus heat flux DSC will have the same freedom from the thermal properties of the sample and slower response times associated with Boersma DTA. DSC will generally have better resolution, as illustrated in Figure 11.18. Finally, as has been discussed earlier, by measuring the power differential, DSC is making a direct

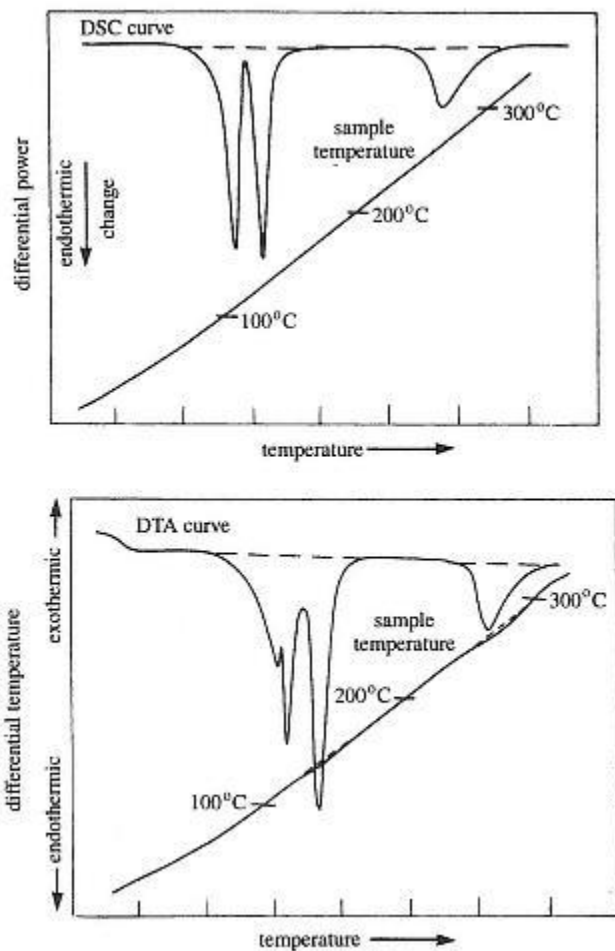


Figure 11.18

Comparison of DSC and DTA for  $\text{CuSO}_4 \cdot 4.5\text{H}_2\text{O}$ .

measurement of enthalpy changes and is thus the more satisfactory tool for thermodynamic measurements.

#### 11.4—

#### Thermo-mechanical Analysis (TMA) and Dynamic Mechanical Analysis (DMA)

##### Summary

##### Principles

Measurement of the effect of heat on the mechanical properties of a sample, e.g. expansion, compression, penetration, extension and resonant frequency of oscillation.

### ***Instrumentation***

Quartz probes fitted with thermocouples to measure the temperature, and follow the movement of the sample. Linked transducer, i.e. a linear variable density transformer to sense the probe movement and produce a related electrical signal. Sample furnace, programmers and various output devices.

### ***Applications***

Investigation of the mechanical properties of a range of materials, especially polymers, and their change with heating over the range – 100°C to 1000°C. Quality control of mechanical properties.

### ***Disadvantages***

Information is restricted largely to mechanical properties and cannot easily be related to the actual composition of a sample.

One of the more recently exploited forms of thermal analysis is the group of techniques known as *thermomechanical analysis* (TMA). These techniques are based on the measurement of mechanical properties such as expansion, contraction, extension or penetration of materials as a function of temperature. TMA curves obtained in this way are characteristic of the sample. The technique has obvious practical value in the study and assessment of the mechanical properties of materials. Measurements over the temperature range – 100°C to 1000°C may be made. Figure 11.19 shows a study of a polymeric material based upon linear expansion measurements.

### **Instrumentation**

A TMA analyser will need to measure accurately both the temperature of the sample, and very small movements of a probe in contact with the surface of the sample. A typical analyser, as illustrated in Figure 11.20(a) and (b), uses a quartz probe containing a thermocouple for temperature measurement, and is coupled to the core of a linear variable differential transformer (LVDT). Small movements at the sample surface are transmitted to the core of the LVDT and converted into an electrical signal. In this way samples ranging from a few microns to centimetre thicknesses may be studied with sensitivity to movements of a few microns. For studying different mechanical properties the detailed construction of the probe will vary as is illustrated in Figure 11.20(c).

### **Applications of TMA**

TMA has mainly been used in the study of polymers. The mechanical properties study may be used to characterize a polymer as well as to assess its mechanical utility. There is an obvious application to quality control. The ability to study small specimens gives the technique a distinct advantage over more traditional methods of mechanical testing if sample size is limited. A typical TMA study has already been exemplified in Figure 11.19.

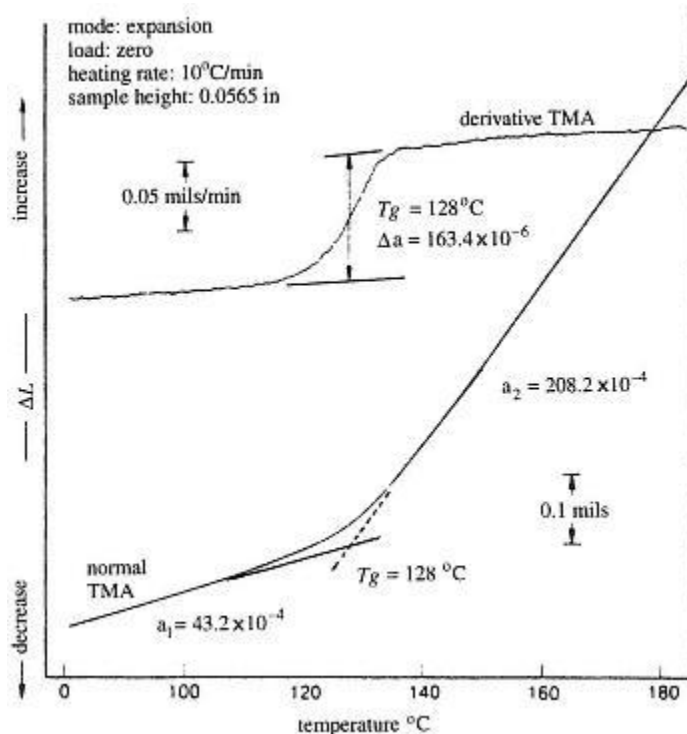


Figure 11.19  
TMA expansion study of an epoxy printed circuit board  
showing the determination of the glass point ( $T_g$ ).

## Dynamic Mechanical Analysis

An associated technique which links thermal properties with mechanical ones is dynamic mechanical analysis (DMA). In this, a bar of the sample is typically fixed into a frame by clamping at both ends. It is then oscillated by means of a ceramic shaft applied at the centre. The resonant frequency and the mechanical damping exhibited by the sample are sensitive measurements of the mechanical properties of a polymer which can be made over a wide range of temperatures. The effects of compositional changes and methods of preparation can be directly assessed. DMA is assuming a position of major importance in the study of the physico-chemical properties of polymers and composites.

## 11.5—

### Pyrolysis-gas Chromatography

#### Summary

#### Principles

Controlled pyrolysis of small samples followed by GC separation of the products. Identification by MS or FT-IR.

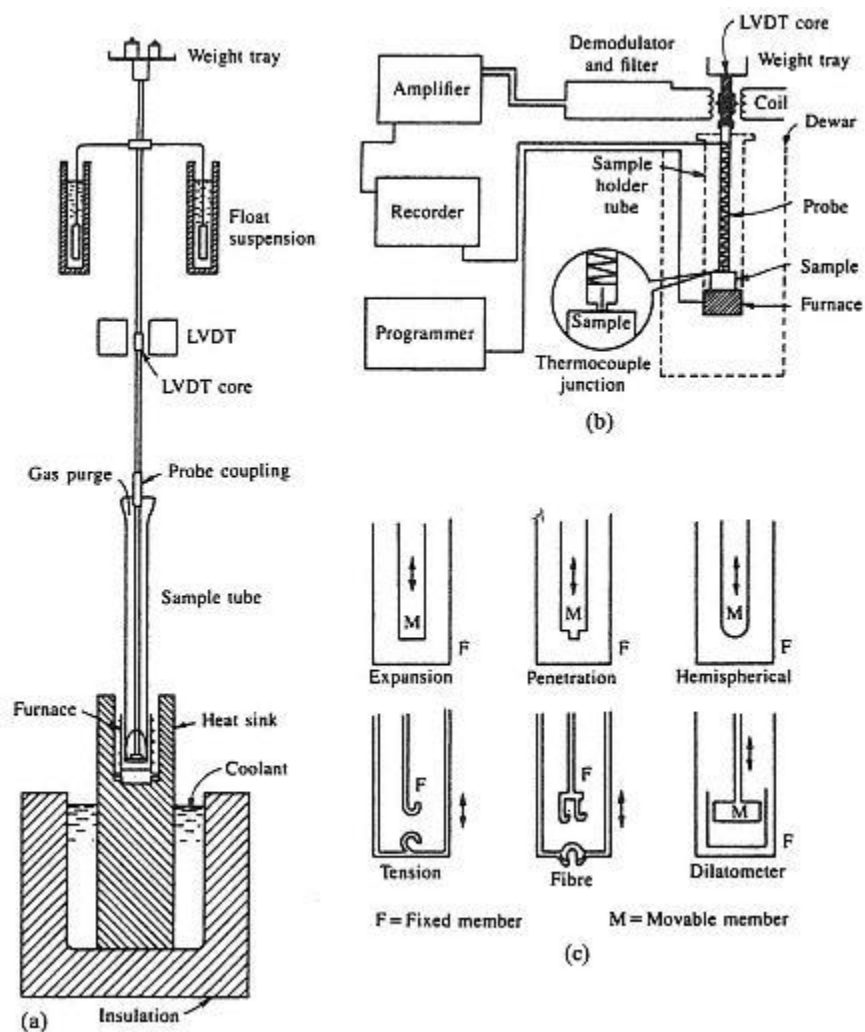


Figure 11.20  
Schematic representation of a thermomechanical analyser (a) and (b) with various probe configurations (c).

### ***Instrumentation***

Furnace, Curie-point or heated filament pyrolysers linked to packed column or capillary column gas chromatograph. GC-MS or GC-FT-IR interfaces.

### ***Applications***

Potentially applicable to a wide range of organic materials. Most use has been made in the analysis of polymers and oils. Essentially a qualitative technique with poor precision for quantitative measurements.

### Disadvantages

Relatively poor reproducibility because of the dependence on accurately reproduced heating profiles and the use of very small samples.

*Evolved gas analysis* (EGA) is based on the study of gases or volatile breakdown products emitted by a sample on heating. The identity and properties of the volatile materials emitted serve as a basis for the analysis of the sample. One particular technique of EGA which has attracted sub-

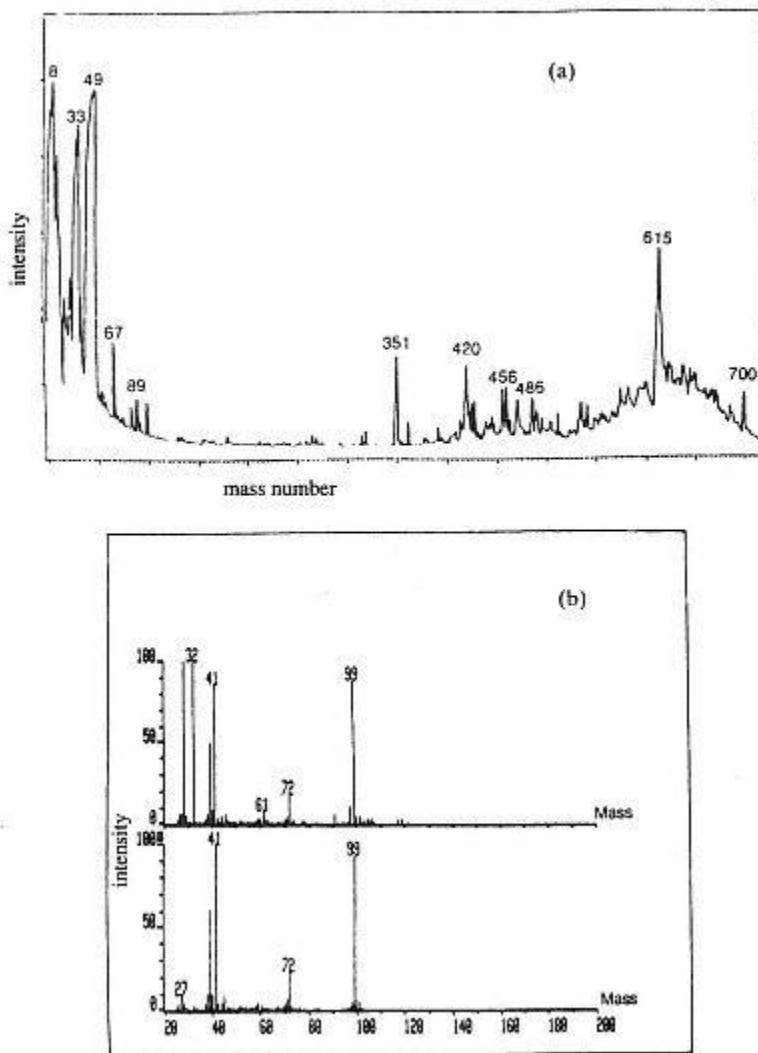


Figure 11.21

(a) Pyrogram of polystyrene cement.

(b) Mass spectrum of peak 36 from polystyrene cement and its first library fit: 3-isothiocyanatopropene.



stantial attention is *pyrolysis-gas chromatography* (Py-GC). As the name suggests this technique uses gas chromatography to separate the breakdown products of the sample which have been produced by carefully controlled pyrolysis. The pyrogram thus obtained will generally show a complex pattern of peaks which may be used for both qualitative and quantitative analyses in the ways discussed in section 4.3.1. Identification of the peaks present in the pyrogram has been carried out for some time by standard GS-MS procedures. However, more recently, with the development of FT-IR

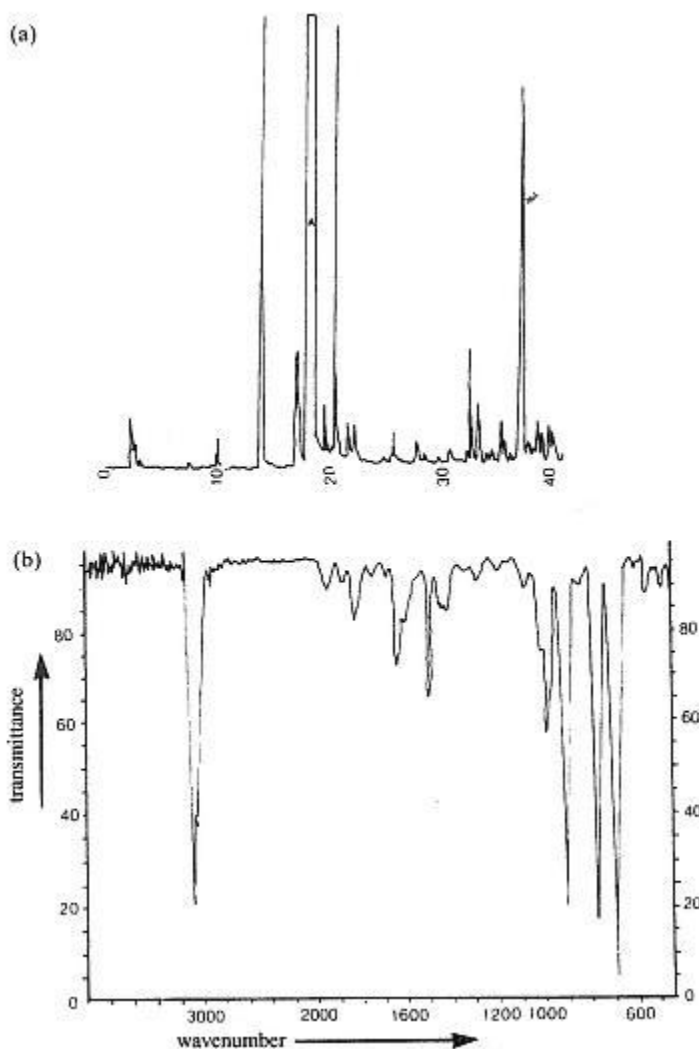


Figure 11.22

- (a) Py-GC trace for polystyrene.  
(b) FT-IR spectrum of 'peak A' identifying it as styrene.  
(Courtesy of P. J. Haines, Kingston University).

instruments, GC-FT-IR is also being exploited in this way. An example of Py-GC-MS analysis is given in Figure 11.21 and of Py-GC-FT-IR in Figure 11.22.

### Instrumentation

The essential instrumentation is divided into three parts: (a) the pyrolyser, (b) the gas chromatograph and (c) the MS or FT-IR instruments. In this chapter interest focuses on pyrolysers as the other instruments are discussed elsewhere.

It has been recognized that best results are obtained when the temperature of the sample is raised rapidly and reproducibly to the pyrolysis temperature and then held closely at that temperature for the desired pyrolysis time. One obvious way of achieving this aim is by the use of an electrically heated microfurnace. Considerable difficulties were encountered in the development of such furnaces with suitable characteristics, and although pyrolysers of this type are now readily available and in use, they still suffer from the relative disadvantage of rise times of several seconds. A design for a modern furnace is shown in Figure 11.23.

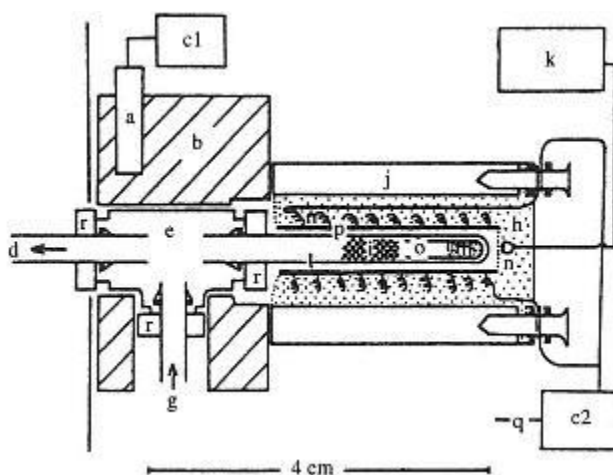


Figure 11.23

Controlled furnace -type pyrolyser: a, heater; b, Al block; c, variable transformer; d, gas outlet to column; e, Swagelok union; f, column oven; g, gas inlet; h, cement; i, glass wool plug; j, insulating block; k, pyrometer; l, stainless steel chamber; m, sample; n, heater thermocouple; o, pyrolysis tube; p, ceramic tube; q, line voltage.

(Reprinted from Irwin, *Analytical Pyrolysis*, Marcel Dekker Inc., NY, 1982).

An alternative approach has been to use *Curie-point pyrolysers*. The use of the Curie point in accurately reproducing a temperature has already been discussed for the calibration of TG furnaces (p. 481). In a slightly different way the Curie point can be used for accurately reproducing pyrolysis conditions with the added advantage that the rise time is only about 0.4 s. The

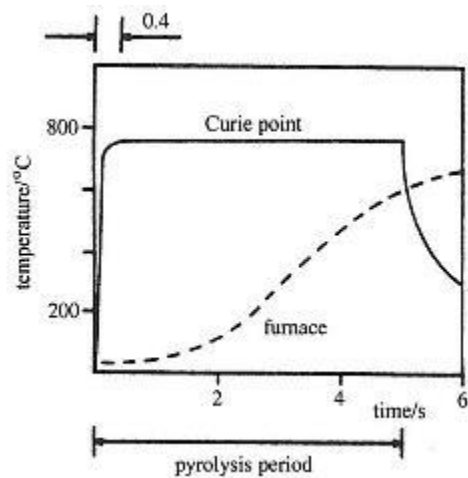


Figure 11.24  
Comparison of pyrolysis times for Curie-point  
pyrolysis and furnace pyrolysis.

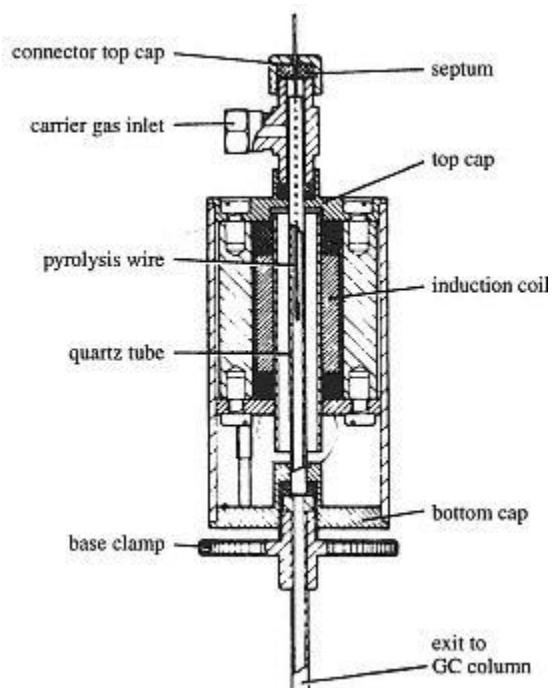


Figure 11.25  
A Curie -point pyrolyser.  
(Reprinted from Irwin, *Analytical Pyrolysis*, Marcel  
Dekker Inc., NY, 1982.)

sample, typically 50  $\mu\text{g}$ , is either placed on or encapsulated in the end of a pyrolysis wire composed of the appropriate ferromagnetic alloy. Induction heating can then be used to raise the temperature rapidly to the Curie point where it can be accurately maintained until the induction coil is switched off. The heating profile for a Curie-point pyrolyser is contrasted with that for a typical microfurnace in Figure 11.24 and the construction of a pyrolysis unit in Figure 11.25 with typical pyrolysis wires in Figure 11.26.

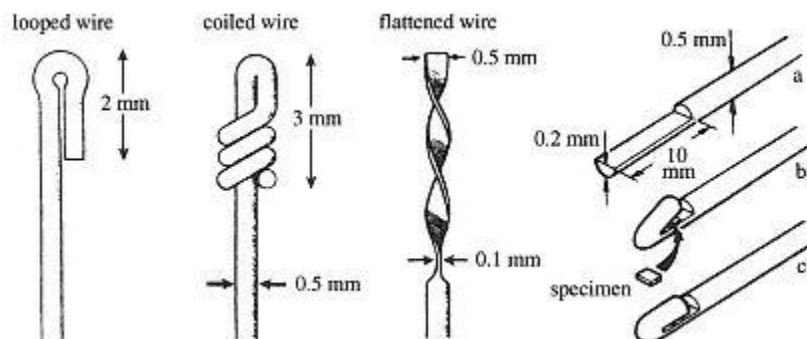
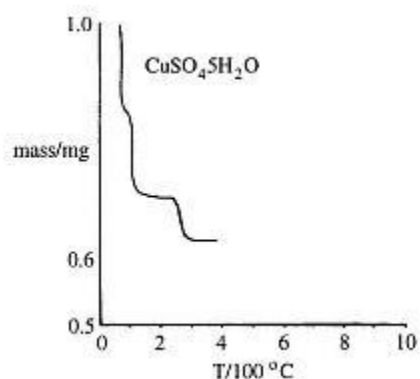


Figure 11.26  
Various pyrolysis wire configurations.  
(Reprinted from Irwin, *Analytical Pyrolysis*, Marcel Dekker Inc., NY, 1982.)

A third type of pyrolyser sometimes utilizes a filament heated by its own electrical resistance. The most effective pyrolysers of this type use an initial pulse of heating at a high voltage to produce a high current and rapid heating to the pyrolysis temperature, i.e. 700°C in 12 ms, followed by reduction to an accurately controlled maintenance voltage to maintain the pyrolysis temperature.

## Problems

(1) The decomposition of copper(II) sulphate pentahydrate follows the course shown below. Analyse the graph and calculate the most likely reactions.



(2) A sample of silica packing material with 5  $\mu\text{m}$  particles for use in liquid chromatography has been reacted with various silanizing reagents. A sample of 400 mg, heated at  $6^\circ\text{C min}^{-1}$  lost a very small amount by  $110^\circ\text{C}$ , but started to lose weight rapidly at  $150^\circ\text{C}$  to a plateau corresponding to a loss of 14.0 mg. Above  $200^\circ\text{C}$ , further weight was lost and a final plateau obtained at a loss of 45.5 mg by  $700^\circ\text{C}$ . Suggest why

(a) the loss up to  $110^\circ\text{C}$  is small;

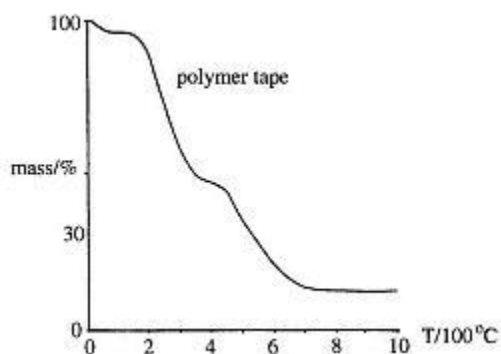
(b) the loss up to  $700^\circ\text{C}$  is in two stages and calculate the percentage by weight of coating material.

(3) A sample of white plastic tape was placed in a thermobalance and heated at  $10^\circ\text{C min}^{-1}$  in nitrogen to give the thermogravimetric curve below. By careful measurement identify

(a) the moisture content of the polymer tape;

(b) the filler content of the tape;

(c) the identity of the polymer from its decomposition temperature and the stages of the decomposition.



(4) Compare and contrast the techniques of DTA and DSC.

(5) Polyethylene terephthalate (9.94 mg) gave a peak of area  $116.3 \text{ cm}^2$  on melting on a DSC, whereas 5.89 mg of pure indium ( $\Delta H_{\text{fus}} = 28.45 \text{ J g}^{-1}$ ) gave a peak of  $40.0 \text{ cm}^2$ . Calculate the latent heat of fusion of this polyethylene terephthalate, and compare with the pure crystalline value  $\Delta H_{\text{fus}} = 117.57 \text{ J g}^{-1}$ . Comment on the answers.

### Further Reading

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