Chapter 4 Experimental techniques applied in this study

4.1 Thermogravimetry (TG)

Thermogravimetry is a group of techniques in which the mass of a sample is measured as a function of temperature or time, while subjected to a controlled heating programme in a specified atmosphere. The technique has a wide range of applications, of which some important ones are (Dodd *et al*, 1987; Haines, 1995):

- investigation of phase changes e.g. a liquid changes to a gas
- characterisation of materials
- to evaluate the thermal stability of materials
- to investigate thermal decomposition
- qualitative analysis
- quantitative analysis
- used in quality control to do purity assessment
- to investigate the chemical reactivity, e.g. the influence of addition of a catalyst
- kinetic studies

The sources of error during thermogravimetry and optimum operating conditions of the technique will be discussed in Chapter 4.3.6 and 4.3.7.

4.2 Differential Scanning Calorimetry (DSC)

DSC is a technique in which the difference in heat flow to a sample and to a reference is monitored against temperature or time while the temperature of the sample, in a specified atmosphere, is programmed (Haines, 1995).

Thermal events in the sample appear as deviations from the DSC baseline curve, in either endothermic or exothermic direction. Because of the absorption of more power by a sample,

endothermic responses are usually represented as positive (above the baseline). The melting of well-known material, such as indium, is used to calibrate the instruments.

Two types of DSC are recognised, namely power-compensated DSC and heat-flux DSC. In the first type, the sample and reference are heated by separate, individual heaters, and the temperature difference is kept close to zero while the difference in electrical power needed to maintain equal temperatures are measured (Haines, 1995). Heat-flux DSC was used during this study. The sample and reference are heated from the same source and the temperature difference between them is measured. This signal is then converted to a power difference.

4.2.1 Heat-flux DSC

In heat-flux DSC the thermocouples are positioned beneath the sample and reference pans. A shift in the baseline is not influenced by any property of the sample, but by a change in the specific heat capacity of the sample. It is also dependent on the characteristics of the sample holders. Therefore, the apparatus has to be calibrated by using known standard materials.

The area under the DSC peak is directly proportional to the heat of the reaction by the following equation (Haines, 1995):

$$\Delta H = K \int \Delta T \, dt = K \cdot (\text{peak area}) \qquad (4.1)$$

where ΔH = heat of the reaction

ΔT = temperature difference between the sample and the reference

t = time

K = the calibration constant that converts peak area into joules, and is a thermal factor that may vary with temperature

4.2.2 Calibration of the DSC apparatus

The DSC apparatus must be calibrated for calorimetric sensitivity. Usually the melting points of pure metals are used, and because the value of the calibration constant (K) is markedly dependent upon temperature, calibrations have to be carried out over the full operating range of the instrument. ICTAC (International Confederation for Thermal Analysis and Calorimetry) has approved a set of standard substances that can be used for the calibration (Haines, 1995). The calibration factor is specific to a particular instrument under one set of operating conditions, since the geometry and thermal conductivity of the sample and reference system contribute to the value of the calibration factor.

The integrated peak area of a pure substance may be used to calculate the calorimetric sensitivity constant:

$$K_T = \Delta H_s \cdot \frac{m_s}{A_s} \qquad (4.2)$$

where ΔH_s = enthalpy of fusion of the calibration substance
m_s = sample mass of the calibration substance
A_s = peak area
K_T = calorimetric sensitivity constant at temperature T

4.2.3 Applications of DSC

The DSC curve can be used to estimate the purity of samples. Melting endotherms are very sharp if the substance is pure, but are broader for impure substances. Physical changes and measurements can be investigated, such as melting, phase changes, enthalpies of vaporization and of sublimation, heat capacity, glass transitions and thermal conductivity. The path of chemical reactions such as dehydration, decompositions, polymer curing, glass formation and oxidative attack can also be followed (Brown, 1988; Charsley and Warrington, 1992; Dodd *et al*, 1987; Haines, 1995).

4.3 Simultaneous TG-DSC

Thermal methods sometimes require complementary techniques for a more comprehensive understanding of the process occurring. In simultaneous TG-DSC systems, the designs are based on a thermobalance which is modified to weigh both the sample and the reference and to measure the temperature of each. The sample and reference are contained in crucibles, which are located on a heat-flux DSC plate. Therefore, both techniques are sensed simultaneously. This technique saves time and also gives the results for two or more techniques under precisely the same experimental conditions. A shortcoming of this technique is that the sensitivity of both techniques is reduced on combination, because of compromises in instrumental design (Charsley and Warrington, 1992).

The instrument used during this study was the NETZSCH-STA 409 EP, which enables the simultaneous execution of Thermogravimetry (TG) and Heat-flux-Differential Scanning Calorimetry (DSC). The instrument can measure in a temperature range of 20°C up to 1400°C. Both measuring techniques are applied simultaneously and on the same sample. By using the software, developed by NETZSCH-Gerätebau GmbH, characteristic temperatures, enthalpy values, and mass changes were obtained. A simplified diagram of the NETZSCH-STA 409 EP is given in Figure 4.1.

4.3.1 The balance

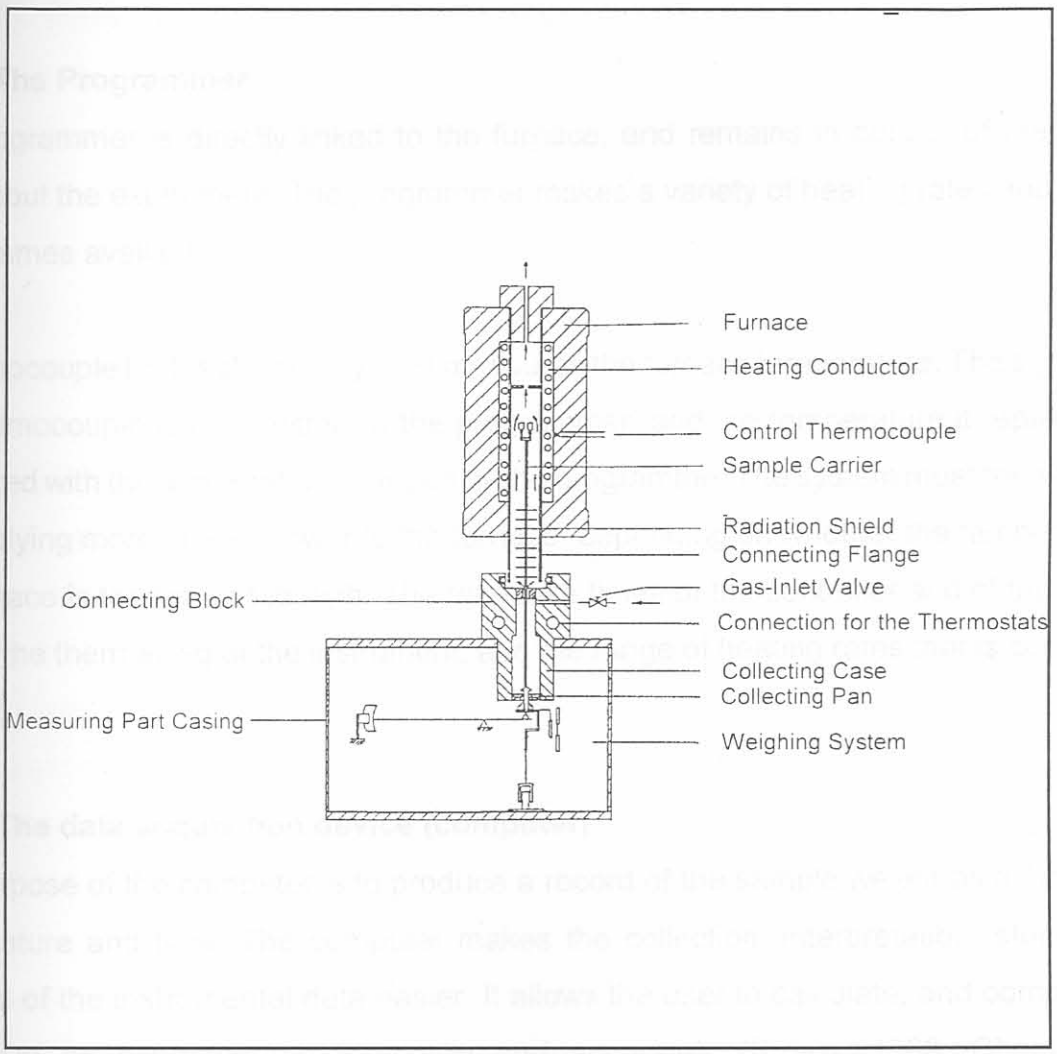
The STA 409 contains a highly sensitive analytical balance that works according to the principle of the substitution beam balance. The change in mass occurring during a reaction, causes deviation of the weighing beam, which is registered as a change in voltage. The presence of oxidising or corrosive gases near the balance mechanism is undesirable. Therefore, the balance enclosure is often purged with an inert gas.

4.3.2 Sample carrier system

The sample carrier system is connected to the balance. It contains the thermocouples (Pt10%Rh-Pt) to measure the temperature and the temperature difference between the sample and reference sides. The sample and reference materials are contained in

crucibles, located on and supported by a heat-flux DSC plate. Below the crucibles, the thermocouple wires of the temperature sensors go through the alumina support rod to the balance and detector systems.

Figure 4.1 The structure of the measuring part of the Netzsch-STA 409 EP (Netzsch-Gerätebau)



4.3.3 The furnace

Maximum temperatures of approximately 1400°C are produced by the tube furnace of the STA 409 EP, which is heated with a resistance coil. The furnace should be capable of reaching temperatures 100 to 200°C above the maximum desired working temperature. If operated in the presence of a corrosive atmosphere the linings of the furnace must consist

of a material that can resist chemical attack.

The uniform heating zone must be of reasonable length to provide a uniform sample temperature, and the furnace should not affect the balance mechanism through radiation or convection. Inclusion of radiation shields and convection baffles reduces transfer of heat to the balance mechanism.

4.3.4 The Programmer

The programmer is directly linked to the furnace, and remains in control of the furnace throughout the experiment. The programmer makes a variety of heating rates and thermal programmes available.

A thermocouple that is chemically inert measures the furnace temperature. The signal from the thermocouple is transmitted to the programmer, and the temperature it represents is compared with the temperature required by the programme. The system must then respond by supplying more or less power to the furnace, depending on whether the temperature of the furnace is too low or too high. The response times of the controller and of the furnace govern the thermal lag of the instrument, and the range of heating rates that is achievable.

4.3.5 The data acquisition device (computer)

The purpose of the computer is to produce a record of the sample weight as a function of temperature and time. The computer makes the collection, interpretation, storage and retrieval of the instrumental data easier. It allows the user to calculate, and compare, the results of an experiment more easily and accurately (Brown, 1988; Charsley and Warrington, 1992; Dodd *et al*, 1987; Haines, 1995; Wunderlich, 1990).

4.3.6 Sources of error during thermogravimetry

Errors in thermogravimetric measurements can lead to inaccuracies in the recorded temperature and mass data. Some sources of error are discussed below (Dodd *et al*, 1987).

The buoyancy effect of the sample container refers to the apparent mass gain that can occur when an empty, and thermally inert crucible is heated. This effect is due to thermomolecular flow that can occur when the balance is operating at low pressure. As the sample is heated, the density of the atmosphere around the sample decreases, and the upthrust, caused by the gas, will decrease. The crucible will therefore show an apparent gain in measured mass.

Running a "blank" buoyancy curve with an empty crucible can compensate for this effect over the significant temperature range. This curve is then subtracted from the experimental curve for a specific sample. The use of very small samples and crucibles will also reduce this effect.

Gas flowing over and around the sample container may cause turbulence and the heat from the oven can cause convection effects. This can also be reduced by smaller sample masses.

The actual temperature of the sample will usually lag behind the temperature recorded by the thermocouple. This thermal lag is related to several factors that include the time in which a weight change is recorded, the heating rate, the gas flow, the geometry of the sample container, and the thermal conductivity of the sample. The heat of the reaction will also affect the sample temperature. An endothermic reaction at a specific temperature will cause a larger thermal lag, while an exothermic reaction will have the opposite effect. However, these effects are of very small magnitude.

Other factors that must be considered to cause errors in thermogravimetry are:

- condensation on the balance suspension
- reaction between the sample and crucible
- random fluctuations of the balance system
- electrostatic effects on the balance mechanism
- induction effects from the furnace
- the environment of the thermobalance

Well-designed thermobalances usually exclude most of these factors causing errors.

4.3.7 Optimum operating conditions

Many factors affect the nature, accuracy, and precision of experimental results. Comparison of samples can only be made when their curves are run under the same conditions, or when differences are clearly stated.

Large sample masses cause poor resolution in thermogravimetric curves. This is due to the significant temperature gradient within a large sample and the greater difficulty of volatile products to escape from a large sample. These factors can lead to irreproducibility, and therefore the sample mass should be kept as small as possible, especially for kinetic studies. Sample masses of less than 50 mg are normally used.

The sample must preferably be in powdered form, and should be spread uniformly in the sample container. The particle size must also be considered, because the thermal properties of powders differ from those of the bulk material (Brown, 1988; Dodd *et al*, 1987; Haines, 1995).

Thermogravimetric measurements can be done in a static or dynamic atmosphere. The transfer of heat and chemistry of the sample will depend upon the surrounding atmosphere. Even if there is no reaction between the sample and the atmosphere, the heat transfer by the gas may affect the results. Changing the surrounding atmosphere can alter the course of a chemical reaction completely. Usually an inert gas is used, which quickly removes the gaseous products from the sample, but the gas may also be used as a reactant in the reaction.

A flowing gas atmosphere will also reduce condensation of reaction products on the cooler parts of the weighing mechanism. It will flush out corrosive products, reduce secondary reactions, and act as a coolant for the balance system.The flow rate of the gas must also be considered. A very low gas flow will not sweep away reaction products, or act as a heat transfer agent. A very high gas flow can interfere with the balance mechanism or cause turbulence effects (Haines, 1995).

The sample holder should not react chemically with the sample during the experiment. Changing from an aluminium crucible to silica, alumina or platinum may change the heat transfer, because of the different thermal conductivity of these materials. It can also influence the chemistry of a process, for example, if a reaction occurs that can be catalysed by platinum.

The shape of the crucible is important, since a shallow container will allow a more significant exchange of gas between the sample and its gaseous surroundings. A narrow, deep crucible may restrict heat flow (Brown, 1988; Dodd *et al*, 1987; Haines, 1995; Wunderlich, 1990).

Increasing heating rates result in an inhomogeneous temperature distribution in the sample. The thermal lag between the actual temperature of the sample and the recorded temperature will increase with increasing heating rate, and the resolution of the thermogravimetric curve will decrease. Working with the lowest heating rate that is possible for the specific circumstances is best (Brown, 1988; Charsley and Warrington, 1992; Dodd *et al*, 1987; Haines, 1995; Wunderlich, 1990).

4.4 X-ray Fluorescence analysis

4.4.1 Introduction

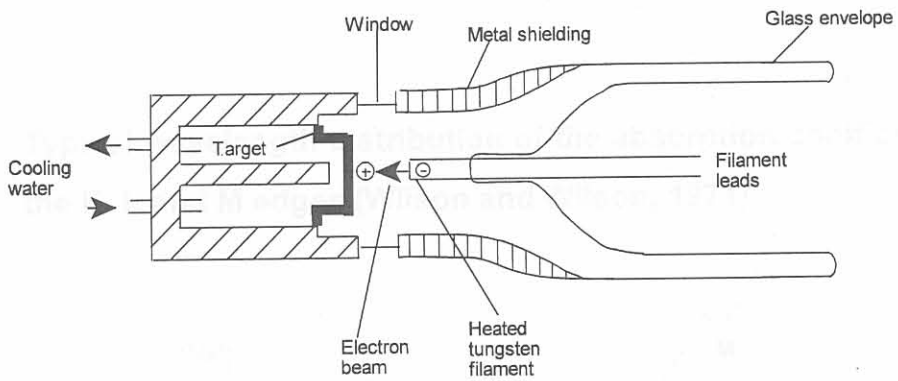
Since the discovery of X-rays in 1895, a variety of X-ray techniques have been developed. These include radiography, X-ray fluorescence analysis, X-ray crystallography, and radiotherapy.

In the devices used to apply these techniques, X-rays are being produced in X-ray tubes. Electrons are produced by an electrically heated tungsten filament, and are then accelerated towards the target by applying a large potential difference. The high speed electrons are stopped by the atoms of the target, resulting in X-rays being produced in all

directions from the surface of the target. Since X-rays are harmful, the tube is partly covered with a heavy absorbing metal such as lead. The X-rays then leave the tube through a window, consisting of a light metal such as aluminium or beryllium.

Only a fraction of the energy supplied to the tube is converted to X-rays, most is converted into heat. To prevent the target from melting, it is cooled by running water. The target material must be made of a high melting material which has good thermal conductivity and for the production of high-intensity X-rays, the target element should have a high atomic number. Pure transition metals such as molybdenum, wolfram, copper and chromium are typical target materials. Figure 4.2 shows a schematic diagram of an X-ray tube.

Figure 4.2 Schematic diagram of an X-ray tube (Whiston, 1987)



Characteristic X-rays are produced when high speed electrons remove inner K, L or M electrons from target atoms, and outer electrons fill the vacancies. The continuous spectrum arises from the conversion of the electron's kinetic energy to radiant energy on impact.

All matter absorbs X-ray to a certain extent. An X-ray beam of original intensity I_0 becomes reduced to intensity I on passing through a distance χ of absorbing medium of density ρ.

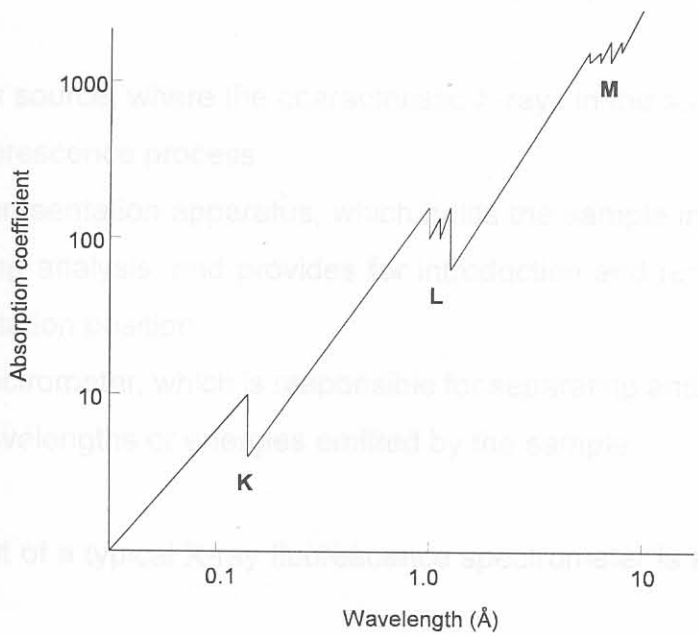
The intensities are related by the equation (Whiston, 1987):

$$I = I_0 \, e^{-\mu_m \rho \chi} \tag{4.3}$$

where μ_m is the mass absorption coefficient, which is characteristic of a particular medium.

The typical distribution of the mass absorption coefficient against wavelength is shown in Figure 4.3. Mass absorption generally increases with increasing wavelength, but in the graph of μ_m versus λ, a number of vertical discontinuities, called absorption edges, is observed. These correspond to the ionisation energies of the K, L and M electrons of the absorbing medium. The X-rays having wavelengths less than these absorption edges have sufficient energy to displace inner electrons resulting in the emission of characteristic radiation called X-ray fluorescence.

Figure 4.3 Typical wavelength distribution of the absorption coefficient, showing the K, L and M edges (Wilson and Wilson, 1971)



The planes of atoms in a crystal will only reflect an X-ray beam when the Bragg equation is fulfilled (Whiston, 1987, Wilson and Wilson, 1971):

$$2d \sin\theta = n\lambda \tag{4.4}$$

where d = the interplanar spacing
θ = the angle between the planes and the X-ray beam (Bragg angle)
λ = the X-ray wavelength
n = the order of reflection

4.4.2 Instrumentation

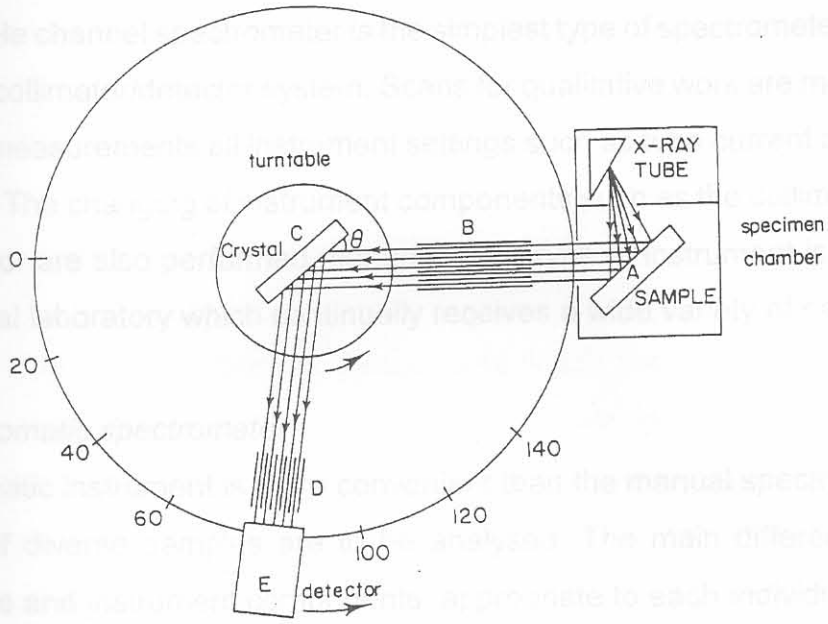
X-ray fluorescence is a rapid, non-destructive, qualitative and quantitative method of determining elements in solids and liquids. In principle, the technique is based on the measurement of wavelengths and intensities of X-rays emitted by a sample, when excited by the rays from a primary X-ray tube. Since the beam doesn't penetrate very far into the specimen, it is essentially a surface technique (Whiston, 1987).

An X-ray fluorescence spectrometer consists of three principal sections (Jenkins *et al*, 1981):

- the excitation source, where the characteristic X-rays in the sample are excited via the X-ray fluorescence process
- the sample presentation apparatus, which holds the sample in a precisely defined position during analysis, and provides for introduction and removal of the sample from the excitation position
- the X-ray spectrometer, which is responsible for separating and counting the X-rays of various wavelengths or energies emitted by the sample

The simplified layout of a typical X-ray fluorescence spectrometer is shown in Figure 4.4.

Figure 4.4 Simplified layout of a typical wavelength dispersive spectrometer (Whiston, 1987)



A primary X-ray beam irradiates the sample (A) causing it to fluoresce. Each element will emit its own characteristic X-radiation. Part of the radiation is collimated by a system of slits (B) onto an analysing crystal (C). Since a number of different crystals are necessary to cover the full wavelength range of the spectrometer, a multi-position crystal changer is usually incorporated. This usually consists of a turntable arrangement holding up to six crystals. The particular crystal in use is mounted on a turntable which can be rotated by a motor.

As the crystal rotates, so the angle (θ) presented to the fluorescent rays changes. Whenever the Bragg equation is fulfilled for a particular X-ray wavelength, this part of the beam is reflected by the crystal. The reflected beam passes through a set of collimating slits (D) and enters the detector (E). The detector and crystal table are connected in such a way that they always rotate together. Furthermore, they are geared so that when the crystal rotates through an angle θ, the detector rotates through 2θ. This results in the detector always being in the correct position to receive any rays reflected by the crystal.

There are four basic types of XRF instruments. These will be discussed shortly below.

(a) Manual spectrometer

The manual single channel spectrometer is the simplest type of spectrometer, and consists of a one crystal/collimator/detector system. Scans for qualitative work are motor driven, but for quantitative measurements all instrument settings such as tube current and voltage are made manually. The changing of instrument components such as the collimator, analysing crystal or detector are also performed manually. This type of instrument is sufficient for a general analytical laboratory which continually receives a wide variety of samples.

(b) Semi-automatic spectrometer

The semi-automatic instrument is more convenient than the manual spectrometer when a large number of diverse samples are to be analysed. The main difference is that the machine settings and instrument components, appropriate to each individual sample, are selected by a simple operation.

(c) Automatic sequential spectrometer

This instrument is adequate for routine analysis of large numbers of similar samples. The spectrometer is usually interfaced with a computer which has been programmed to control the entire sequence of the analysis. This involves control of samples, changing of settings and of instrument components applicable to each element of interest in each sample, moving the spectrometer from one 2θ setting to another, collection of intensity data, and calculation of element concentration.

(d) Simultaneous automatic spectrometer

This type of spectrometer is also suitable for the routine analysis of a large number of samples. The instrument consists of up to 26 single channel instruments situated around the X-ray tube and samples. Each channel is fixed at the 2θ angle of a specific element, and each channel is fitted with instrument components most suited for that element. The intensities are collected from each channel and fed to a computer for calculation of element concentration.

This type of instrument has several advantages when compared to the automatic sequential spectrometer. It has no moving parts and much time is saved by measuring the intensities simultaneously rather than sequentially. This makes the simultaneous spectrometer ideal for on-line analysis for production control. Another advantage lies in trace analysis, where intensities are likely to be very weak. Higher sensitivity can be obtained by having two or more output channels set on the same element line and combining their outputs.

The simultaneous spectrometer also has disadvantages when compared to a sequential spectrometer. The automatic spectrometer is more compact then the simultaneous instrument, and has fewer instrument components which means that it should be less expensive. The sequential spectrometer is more flexible in its use, since it can be programmed to detect any element, while simultaneous spectrometers are constructed to detect specific elements. Sequential instruments can be programmed to use machine parameters which are optimised for each element, with simultaneous instruments certain machine parameters are fixed and may not be optimum for all the elements being analysed.

4.4.3 Qualitative analysis by XRF

For qualitative analysis, the crystal is rotated so that all angles between about 15° and 145° are presented to the X-ray beam. Detected X-rays are amplified and recorded as a series of peaks. A scale of 2θ is automatically recorded, and elements are identified from their 2θ values in conjunction with an appropriate set of tables.

For a particular analysing crystal, the line-to-2θ tables list the wavelength and 2θ values of the characteristic elements that can be dispersed by the crystal. The data are listed in order of increasing atom number. 2θ-to-line tables list similar data, but in increasing magnitude of 2θ. The interpretation of an XRF trace involves the reading off the 2θ values of the peaks and then consulting 2θ-to-line tables, applicable to the analysing crystal used.

4.4.4 Quantitative analysis by XRF

For quantitative analysis, the crystal remains stationary, set at the appropriate angle to reflect a particular element's radiation. The recorded intensity is related to the element's concentration in the sample.

There is a usually not a linear relationship between analyte line intensity and concentration, because of matrix effects, which can arise from absorption and enhancement. Spectral interference can arise from overlap of analyte line with either a matrix line or an X-ray tube line. This may be overcome by using a different analyte line, by using a crystal with a higher dispersion, by using filters, or by reducing the voltage or current of the X-ray tube.

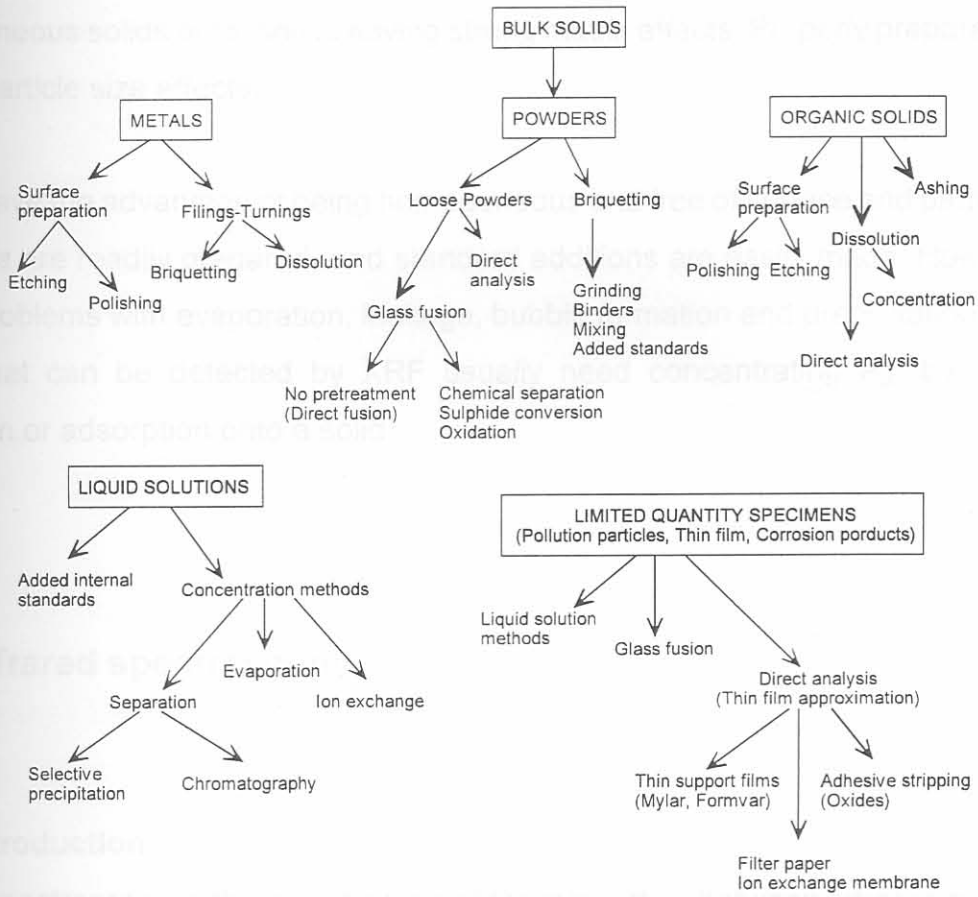
The three most common ways of overcoming matrix effects include the use of calibration curves, making standard additions, and correcting mathematically. Calibration curves are suitable to do routine analyses of samples where standards are readily available. Standard additions are applicable to infrequent analyses where standards are not available, while mathematical corrections are ideal for the routine analysis of large numbers of samples.

4.4.5 Sample preparation for XRF analysis

For qualitative analysis, the only prerequisite is usually that the sample fits into the sample holder. However, for quantitative work sample preparation may be necessary, particularly for solids where the analyte line intensity can be dependent on surface roughness, particle shape, particle size, size distribution and packing density (Jenkins, 1981 *et al*; Whiston, 1987).

The guiding principles for sample preparation techniques are reproducibility, accuracy, simplicity, low cost, and rapidity of preparation. A broad outline of different sample preparation procedures is shown in Figure 4.5. The details of some of these techniques are discussed below.

Figure 4.5 A summary of sample preparation procedures for XRF analysis (Jenkins *et al*, 1981)



Bulk solids such as metals and ceramics should preferably be in the form of a small cylinder about 5 cm in diameter. To eliminate the surface texture effects, one surface should be smoothed to a finish of about 50 µm. This can be achieved by making use of graded papers, machining, electropolishing and spark planing. The standards and unknown samples should have an identical surface finish. If standards are not available, the solid may be transformed into a powder or to a solution, to facilitate standard additions (Whiston, 1987).

To ensure homogeneity and to eliminate particle size effects, powdered samples are usually milled to a fineness of about 300 mesh. They may then be loosely packed into a cell, compacted into a pellet (with or without binder), or supported on a substrate such as filter paper, Scotch tape or Mylar film. Standards and unknowns should be prepared under

identical conditions.

Fusion with borax or with lithium tetraborate to produce a "glass" disc may be useful for heterogeneous solids or for solids having strong matrix effects. Properly prepared discs will give no particle size effects.

Liquids have the advantage of being homogeneous and free of surface and particle effects. Standards are readily prepared, and standard additions are easily made. However, there can be problems with evaporation, leakage, bubble formation and precipitation of analyte. Gases that can be detected by XRF usually need concentrating eg. by dissolution, absorption or adsorption onto a solid.

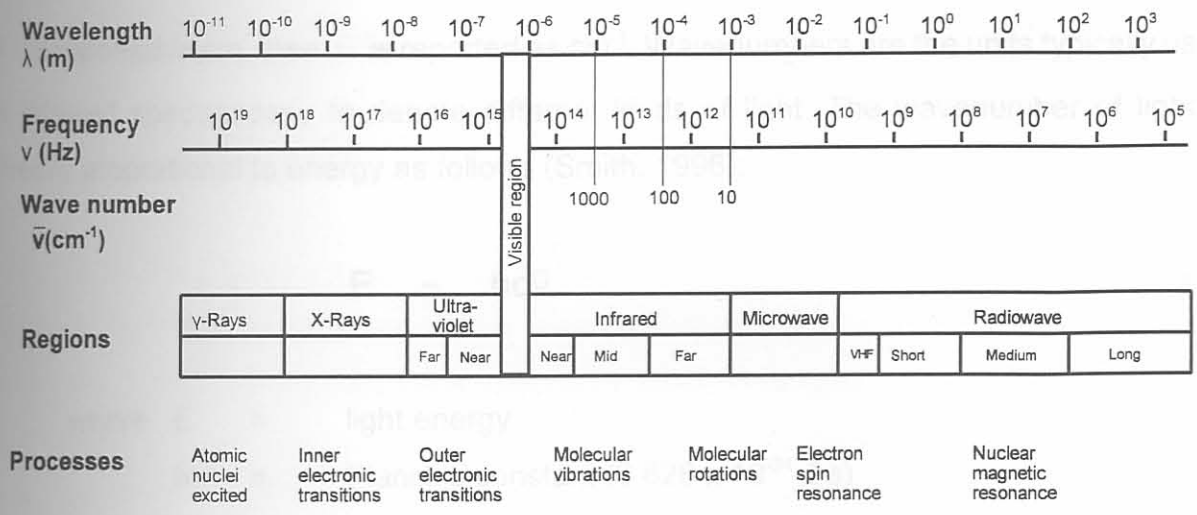
4.5 Infrared spectroscopy

4.5.1 Introduction

Infrared spectroscopy is the investigation of the interaction between infrared radiation and matter. When a substance is exposed to infrared radiation, the amount of radiation absorbed is different for components of the radiation having different wavenumbers, which means that the absorption is selective. The IR spectrum is obtained by recording passing radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in an absorption spectrum appears, corresponds to the frequency of a vibration of a part of a sample molecule (Stuart, 1996; Svehla, 1976).

When light constituted of components of various wavelengths is resolved according to wavelength with a monochromator, a spectrum of electromagnetic radiation is obtained. The division of the electromagnetic spectrum into its various regions is shown in Figure 4.6.

Figure 4.6 The electromagnetic spectrum



The electromagnetic spectrum and the varied interactions between these radiations and many forms of matter can either be considered in terms of classical or quantum theories. The nature of the various radiations shown in Figure 4.6 have been interpreted by Maxwell's classical theory of electro- and magnetodynamics, consequently the term of electromagnetic radiation.

According to this theory, light is composed of electric and magnetic waves. These two waves are in planes perpendicular to each other, and the light wave moves through space in a plane perpendicular to the planes containing the electric and magnetic waves. It is the electric part of light, called the electric vector, that interacts with molecules. The amplitude of the electric vector changes with time, and it has the form of a sine wave. The wavelength (λ) of the light wave is the distance between adjacent crests or throughs in the sine wave. The wavenumber ($\bar{\nu}$) of a light wave is the number of waves in a length of one centimetre, and is given by the following relationship (Smith, 1996; Stuart, 1996)

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \qquad (4.5)$$

where c = the speed of light (2.997925×10^8 m s^{-1})
ν = the frequency (number of cycles per second)

If λ is reported in cm, then $\bar{\nu}$ is reported as cm^{-1}. Wavenumbers are the units typically used in infrared spectroscopy to denote different kinds of light. The wavenumber of light is directly proportional to energy as follows (Smith, 1996):

$$E = hc\bar{\nu} \quad (4.6)$$

where E = light energy
h = Planck's constant (6.626×10^{-34} J s)
$\bar{\nu}$ = wavenumber

This indicates that high wavenumber light has more energy than low wavenumber light. Most FT-IR instruments operate in the wavenumber range between 4000 and 400 cm^{-1}, which is defined as mid-infrared radiation.

According to the quantum theory, processes of electronic change (including vibration and rotation) can be represented in terms of quantised discrete energy levels E_0, E_1, E_2 etc. Each atom or molecule in a system must exist in one or other of these levels. In a large group of molecules there will be a distribution of all atoms among these various energy levels. These energy levels are a function of the quantum number and a parameter associated with the particular atomic or molecular process associated with that state. Whenever a molecule interacts with radiation, a quantum of energy (or a photon) is either emitted or absorbed. In each case the energy of the quantum of radiation must exactly fit the energy gap $E_1 - E_0$, $E_2 - E_1$, etc. The energy of the quantum is related to the frequency by the following (Stuart, 1996):

$$\Delta E = h\nu \quad (4.7)$$

Therefore, the frequency of emission or absorption of radiation for a transition between the energy states E_0 and E_1 is given by the following relationship:

$$\nu = \frac{E_1 - E_0}{h} \tag{4.8}$$

When infrared radiation interacts with matter, it can be absorbed, causing the chemical bonds in the material to vibrate. The presence of chemical bonds in a material is a necessary condition for infrared absorbance to occur. Functional groups within molecules tend to absorb infrared radiation in the same wavenumber range, regardless of the structure of the rest of the molecule that the functional group is in. This means there is a correlation between the wavenumbers at which a molecule absorbs infrared radiation and its structure. This correlation allows the structure of unknown molecules to be identified from the molecule's infrared spectrum (Smith, 1996).

Molecules are considered as rigid ball-like atoms, connected by bonds with spring-like characteristics. The absorption of infrared radiation sets the molecule into vibrational or rotational motion, or a combination of the two. Similarly, emission of infrared radiation is accompanied by a decrease of the vibration or rotation. In order for the infrared radiation to be absorbed, the vibration frequency of the molecule must be identical to the frequency of radiation.

A molecule having *N* atoms can undergo $3N - 6$ fundamental modes of vibration, or $3N - 5$ if it is a linear molecule. Each of these fundamental modes has associated with it a ground-state energy:

$$E = \tfrac{1}{2} h\nu \tag{4.9}$$

This means that the absorption of energy is quantised. In addition, higher frequencies can be excited with energy

$$E = (n + \tfrac{1}{2})h\nu \quad n = 1, 2, 3, \ldots \tag{4.10}$$

The spectroscopist observes the frequencies of absorbed radiation and assigns the corresponding molecular vibrational frequencies to particular modes of oscillation. He can then use the known geometry and atomic masses with the observed vibrational frequencies to calculate the force constant (*k*), or stiffness, of the interatomic bonds. The reduced mass (μ) is defined as

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{4.11}$$

where m_1 and m_2 are the masses of the atoms at the end of the bond. The equation relating the force constant to the reduced mass and wavenumber values for bond vibrational frequencies is as follows (Stuart, 1996):

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{4.12}$$

where c is the speed of light.

The rotational energy levels of a molecule are also restricted to certain discrete values,

$$E = BJ(J + 1) \quad J = 0, 1, 2, \ldots \tag{4.13}$$

where *B* is a constant determined by the moment of inertia of the molecule about one of its axis, and *J* is the rotational quantum number. The spacing of these energy levels increases with increasing values of *J*. Each vibrational state of a gaseous molecule is accompanied by a set of rotational levels, which means that each vibrational band is a complex band containing many possible rotational transitions. The selection rules for rotational transitions depend on the geometry of the molecule and the particular mode in question (Stewart, 1970).

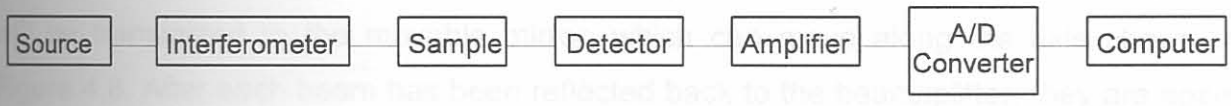
The infrared spectra of polyatomic molecules are quite complex, but the spectrum of a particular chemical bond is a unique characteristic of that compound. It reflects the geometry, bond strength, and atomic masses of the substance. This makes infrared spectroscopy important in the identification of unknown compounds.

4.5.2 Instrumentation for Fourier-Transform Infrared (FT-IR) spectroscopy

Fourier-transform infrared spectroscopy is based on the interference of radiation between two beams to yield an interferogram, which is a signal produced as a function of the change of pathlength between the two beams. The distance and frequency are interchangeable by the mathematical method of Fourier transformation.

The basic components of an FT-IR spectrometer are shown schematically in Figure 4.7. The radiation emerging from the source is passed to the sample through an interferometer, before reaching a detector. After high-frequency contributions have been eliminated by a filter, the signal is amplified and the data is converted to a digital form by an analog-to-digital converter. It is then transferred to the computer, for Fourier transformation to be carried out.

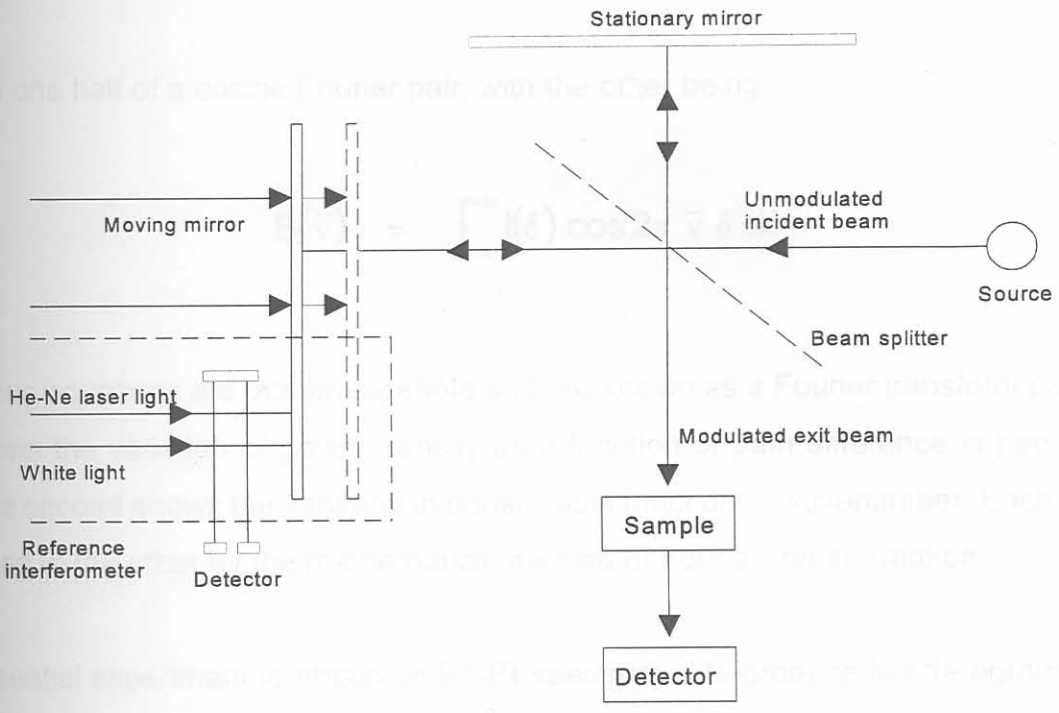
Figure 4.7 The basic components of a FT-IR spectrometer (Stuart, 1996)



The most conventional interferometer used is a Michelson interferometer. A simplified schematic layout is shown in Figure 4.8. It consists of two perpendicular plane mirrors, one of which travel in a direction perpendicular to the plane. A semi-reflecting film, the beamsplitter, crosses the planes of these two mirrors. The beamsplitter material has to be chosen according to the region to be examined. Materials such as germanium or iron oxide are coated on to an infrared-transparent substrate such as potassium bromide or caesium

iodide to produce beamsplitters for the mid- or near-infrared regions. Thin organic films, such as poly(ethylene terephthalate), are used in the far-infrared region.

Figure 4.8 A Michelson interferometer (Stuart, 1996)



If a collimated beam of monochromatic radiation of wavelength λ is passed into a perfect beam splitter, 50% of the incident radiation will be passed to the stationary mirror and 50% will be transmitted to the movable mirror, which can move along the axis shown in Figure 4.8. After each beam has been reflected back to the beamsplitter, they are again partially reflected and partially transmitted. Thus, 50% of the beam reflected from the stationary mirror is transmitted through the beamsplitter to sample and then to the detector, while the other 50% is reflected back in the direction of the source. The beam which emerges from the interferometer at 90° to the input beam is called the transmitted beam, and is the beam which is detected in FT-IR spectroscopy (Griffiths, 1975).

The intensity falling on the detector, I(δ), can be related to the spectral power density, given as $B(\bar{\nu})$, at a particular wavenumber ($\bar{\nu}$), as follows (Stuart, 1996):

$$I(\delta) = \int_0^{+\infty} B(\bar{\nu}) \cos 2\pi \, \bar{\nu} \, \delta \, d\bar{\nu} \qquad (4.14)$$

which is one half of a cosine Fourier pair, with the other being:

$$B(\bar{\nu}) = \int_{-\infty}^{+\infty} I(\delta) \cos 2\pi \, \bar{\nu} \, \delta \, d\delta \qquad (4.15)$$

These two equations are interchangeable and are known as a Fourier transform pair. The first shows the variation of power density as a function of path difference in pathlength, while the second shows the variation in density as a function of wavenumber. Each can be converted to the other by the mathematical method of Fourier transformation.

The essential experiment to obtain an FT-IR spectrum is to produce interferograms, both with and without a sample in the beam, and then transform these interferograms into spectra of the source with and without sample absorptions.

FT-IR spectrometers use a Nernst or Globar source for infrared emission in the mid-infrared region. The Globar source is constructed of silicon carbide, while the Nernst filament is a mixture of the oxides of zirconium, yttrium and erbium.

A detector must have adequate sensitivity to the radiation arriving from the sample over the whole spectral region required. There are two types of detectors which are generally used. The normal detector for routine use is a pyroelectric device, which incorporates deuterium tryglycine sulphate (DTGS) in a temperature-resistant alkali halide window. For more sensitive work, a mercury cadmium telluride (MCT) detector can be used, which requires that the detector has to be cooled by liquid nitrogen.

The moving mirror is the most crucial component of the interferometer, and produces an optical path difference between the two arms of the interferometer. It is either moved at a constant velocity, or is held at equidistant points for fixed short periods and is rapidly stepping between these points. It has to be accurately aligned and must be capable of scanning two distances so that the path difference corresponds to a known value. A number of factors associated with the moving mirror needs to be considered when calculating an infrared spectrum (Stuart, 1996).

4.5.3 Sampling

It is possible to analyse samples in liquid, solid or gaseous form by FT-IR. Gaseous samples are examined by using gas cells. Liquid samples can be analysed in fixed-pathlength sealed cells, which are particularly useful for volatile liquids. These cells cannot be taken apart for cleaning. Semi-permanent cells can also be used, and are demountable so that the windows can be cleaned. An important consideration in the choice of infrared cells is the type of window material. The material must be transparent to the incident infrared radiation, and therefore alkali halides are normally used (Stewart, 1970; Stuart, 1996).

Liquid films also provide a quick method for examining liquid samples. A drop of liquid is placed between two infrared plates, which are then mounted in a cell holder. However, a common problem encountered in obtaining good quality spectra from liquid films is sample volatility. The recorded spectrum progressively becomes weaker due to evaporation which takes place during the recording period.

There are three methods of examining solid samples in infrared spectroscopy, which are alkali halide discs, mulls and films. The use of alkali halide discs involves the mixing of a few milligrams of solid sample with 100 - 200 mg of a dry alkali halide powder (normally KBr). The mixture is then ground with a mortar and pestle and subjected to a pressure of approximately 1.58×10^5 kg cm^{-2}, in an evacuated die. This sinters the mixture and produces a clear transparent disc, which is used in the spectrometer (Stewart, 1970).

When using a mull for determining an infrared spectrum, about 50 mg of the solid sample is ground and then suspended in 1 - 2 drops of a mulling agent. This is followed by further grinding until a smooth paste is obtained. The most common mulling agent is Nujol (liquid paraffin).

Films can be produced by either solvent casting or by melt casting. In solvent casting the solid sample is dissolved in an appropriate solvent, at a concentration which depends on the required film thickness. The solution is then poured on to a levelled glass plate and spread to a uniform thickness. The solvent is evaporated in an oven, and once dry, the film can be stripped from the plate. Alternatively, it is possible to cast a film straight on to the infrared window to be used. Solid samples which melt at relatively low temperatures without decomposition can be prepared by melt casting. A film is prepared by hot-pressing the sample in a hydraulic press between heated metal plates (Stuart, 1996).

4.5.4 Interpretation of an infrared spectrum

In an infrared spectrum, two different types of absorption bands are present. The first type of band is attributable to distinct parts of a molecule, also called group frequencies. The group frequencies are localised at certain regions in the infrared spectrum, and are very useful for the identification of the functional groups of a molecule. The other type of bands are caused by vibrations of the molecule as a whole, and is referred to as skeletal modes. The skeletal frequencies are characteristic for a particular molecule, are not localised, and normally occur below 1500 cm^{-1} (the region which is also referred to as the fingerprint region) (van der Maas, 1969).

The interpretation of a spectrum will have to start with the identification of the localised group frequencies. A functional group can give rise to none, one, or more absorption bands, depending on the nature of the group. Group regions can overlap for different functional groups. Previously obtained data, which indicates the regions where a certain functional group will absorb radiation, are tabulated in tables and correlation charts. This information is used to interpret an obtained infrared spectrum. The intensities and shape of the bands can also provide additional information (George and McIntyre, 1987).

4.6 BET surface area analysis

Any solid can take up relatively large volumes of condensable gas, and this volume of gas taken up differs from solid to solid. Two important factors that play a role in the volume of gas adsorbed by a solid are the surface area and porosity (or pore volume) of the solid. This means that measurements of adsorption of gases or vapours can be made to obtain information regarding the surface area and pore structure of a solid.

The term adsorption implies the condensation of gases on free surfaces, in contradiction to gaseous absorption where the molecules of gas penetrate into the mass of the absorbing solid. Adsorption is internationally defined as the enrichment (i.e. positive adsorption or simply adsorption) or depletion (i.e. negative adsorption) of one or more components in an interfacial layer (Gregg and Sing, 1982).

The instrument used for the determination of surface area during this study was the Micromeritics FlowSorb 2300. This instrument is designed to rapidly measure the surface area on the molecular level of stable, granulated, and powdered materials. Surface area measurements can be accomplished either by a simplified, single point procedure or by the more conventional multipoint BET technique. The BET equation, that describes the adsorption of a gas upon a solid surface, is given below (Micromeritics Instruction manual, 1985):

$$\frac{\left(\frac{P}{P_o}\right)}{V\left[1-\left(\frac{P}{P_o}\right)\right]} = \frac{1}{V_m C} + \left(\frac{C-1}{V_m}\right)\left(\frac{P}{P_o}\right) \qquad (4.16)$$

where V = the volume (at standard temperature and pressure, STP) of gas adsorbed at pressure P

P_0 = the saturation pressure which is the vapour pressure of gas at the adsorbing temperature

V_m = the volume of gas (at STP) required to form an adsorbed monomolecular layer

C = a constant related to the energy of adsorption

The FlowSorb 2300 measures the surface area of a solid sample, by determining the quantity of a gas that adsorbs on a single layer of molecules on a sample. The surface area of the sample is calculated from this monolayer adsorbed gas volume by using the following equation:

$$S = \frac{V_m A N}{M} \tag{4.17}$$

where S = the surface area of the sample

V_m = the monolayer adsorbed gas volume at STP

A = Avogadro's number, which expresses the number of gas molecules in a mole of gas at STP

M = the molar volume of the gas

N = the area of each adsorbed gas molecule

This adsorption is done at or near the boiling point of the adsorbate gas. Under specific conditions, the area covered by each gas molecule is known within relatively narrow limits. This means that the area of the sample is directly calculated from the number of adsorbed molecules, which is derived from the gas quantity at the prescribed conditions, and the area occupied by each.

The FlowSorb2300 instrument permits the measurement of surface areas by the single point or multipoint procedures. Measurements for this study were performed using the single point determination method. In single point surface area determinations, the constant C of equation 4.16 is typically a relatively large number, i.e. C>>1. This reduces equation 4.16 to

$$\frac{\left(\frac{P}{P_0}\right)}{V\left[1-\left(\frac{P}{P_0}\right)\right]} = \frac{1}{V_m}\left[\left(\frac{1}{C}\right) + \left(\frac{P}{P_0}\right)\right] \tag{4.18}$$

If $P/P_0 >> 1/C$, then equation 4.18 can be represented by

$$\frac{\left(\frac{P}{P_0}\right)}{V\left[1-\left(\frac{P}{P_0}\right)\right]} = \frac{1}{V_m}\left(\frac{P}{P_0}\right) \tag{4.19}$$

which rearranges to

$$V_m = V\left[1-\frac{P}{P_0}\right] \tag{4.20}$$

Substituting equation 4.20 into equation 4.17 yields

$$S = \frac{VAN\left[1-\frac{P}{P_0}\right]}{M} \tag{4.21}$$

The surface area of the sample is then determined from equation 4.21, once the volume of gas adsorbed (V) is measured and appropriate values for the other terms are incorporated. For nitrogen gas adsorbed from a mixture of 30 % N_2 (mole percentage) and 70 % He using a liquid nitrogen bath, the respective values are obtained as set out below (Micromeritics Instruction manual, 1985):

- The volume (V) of gas with which the FlowSorb 2300 is calibrated is injected at room temperature and the current atmospheric pressure. This volume must be multiplied by the following ratio to convert it to standard conditions:

$$\frac{273.2\,K}{\text{Room temperature (K)}} \times \frac{\text{Atmospheric pressure (mmHg)}}{760\ \text{mmHg}} \tag{4.22}$$

- Avogadro's number (A) is 6.023×10^{23} molecules mol^{-1}
- The molar volume (M) of a gas at standard conditions is 22414 cm^3 mol^{-1}
- The accepted value for the area (N) of a solid surface occupied by an adsorbed nitrogen molecule is 16.2×10^{-20} m^2.
- Since the adsorption takes place at atmospheric pressure, the pressure (P) is obtained as

$$P = \frac{\%N_2}{100\%} \times \text{atmospheric pressure} \qquad (4.23)$$

- The saturation pressure of liquid nitrogen (P_0) is typically a small amount greater than atmospheric pressure, due to thermally induced circulation, dissolved oxygen, and other factors. With fresh, relatively pure liquid nitrogen, the saturation pressure is typically about 15 mmHg greater than atmospheric pressure.

When these values, for a 30% N_2 / 70% He mixture, adsorbed at liquid nitrogen temperature, when room temperature is 22°C and atmospheric pressure is 760 mmHg, are substituted into equation 4.21 a surface area of 2.84 x V is obtained. For calibration purposes, this means that a syringe injection of V = 1.00 cm^3 of nitrogen at 22 °C and 760 mmHg, should produce an indicated surface area of 2.84 m^2.

When the surface areas of hydrated cements are determined by the BET technique, different surface area values are obtained for different adsorbates used (Micromeritics Instruction manual, 1985). According to Brunauer, the co-developer of the BET-equation, the surface area measured by N_2-adsorption is inaccurate and suggests the use of H_2O-adsorption for hydrated cement samples. Only gypsum and phosphogypsum samples were characterised during this study, and measurements were compared relative to each other. Subsequently, nitrogen gas was chosen as absorbent.

4.7 Cement tests

4.7.1 Specific surface area and density

The fineness of cement is an important factor influencing the rate of hydration, since the hydration reactions occur at the interface of the cement particle with water. Ordinary Portland cement is usually ground to a surface area in the range 3000 - 3500 $cm^2\ g^{-1}$, but it should be kept in mind that the value obtained in the determination of surface area depends on the method used to measure it (Bye, 1983).

The weight specific surface area of cement (S_w) is usually determined by an air permeability method, on what is called a Lea and Nurse constant flow apparatus. The correlation between the specific area and the measured resistance to flow of a powder bed, for a specific surface in the range in which laminar flow occurs (250 - 500 $m^2\ kg^{-1}$), is given by the Carman-Kozeny equation (Bye, 1983):

$$S_w = \frac{N}{\rho(1-\varepsilon)} \frac{\varepsilon^3 A\, \Delta p}{\eta\, Q L} \tag{4.24}$$

where S_w = weight specific surface area
A = bed cross-sectional area
L = thickness of the bed
ϵ = porosity of the bed
η = the Stokes viscosity of air
Q = rate of air flow
ρ = density of the powder
Δp = the drop in pressure across the bed
N = a dimensionless constant depending on the chosen units

In the Lea and Nurse apparatus dry air is passed continuously at a constant pressure, first through a compacted cylindrical bed of cement (25 mm diameter, 10 mm deep) and then through a length of capillary tubing. A manometer is used to measure the drop in pressure

across the bed of cement (h_1). A second manometer measures the drop in pressure across the capillary, which acts as a flowmeter. For this apparatus, equation 4.24 becomes:

$$S_w = \frac{k}{\rho}\sqrt{\frac{h_1}{h_2}} \tag{4.25}$$

where $\frac{h_1}{h_2}$ = the average of the ratios of the two manometer readings at two air flow rates

k = a constant dependent on the dimensions of the apparatus

The density of Portland cement usually lies in the range of 3050 - 3250 kg m^{-3}, and is determined by the displacement of kerosine. A vacuum pump is used to ensure complete displacement of air. The mass of cement used in the apparatus is adjusted to produce a bed with a porosity of 0.475.

The specific surface area of cement can also be determined by a constant volume method developed in 1943 by Rigden and Blaine (Bye, 1983). This method is based on the fact that the time required to pass a fixed volume of air through a bed of cement with standard porosity, is related to the specific surface area of the cement by the following relationship:

$$S_w = K\sqrt{t} \tag{4.26}$$

where t is the time, and K is a constant for an apparatus determined by means of a cement with a known specific surface area.

The simplicity of constant-volume permeameters makes them suitable for use in the cement industry. They are normally permitted as complying to the standard, if calibrated against a Lea and Nurse apparatus.

One version of the constant-volume permeameter incorporates the use of an U-tube. Kerosine in one limb of the U-tube is raised to produce a head of about 100 mm. This is then allowed to fall, forcing air through the cement, which is compacted in a cell attached to the second limb. The time it takes for the meniscus to fall between two marks on the U-tube, which define the fixed volume, is noted and used to calculate the specific surface area.

4.7.2 Setting times

An essential property of cement is that it should exhibit setting when mixed with a limited quantity of water. Two setting times are described in all Standard procedures, namely an initial and a final set. There is no well-defined physical meaning of these terms, but the setting time of cement is usually described as the time at which a neat cement paste presents chosen resistance to the penetration of a needle (Bye, 1983; Hewlett, 1998c).

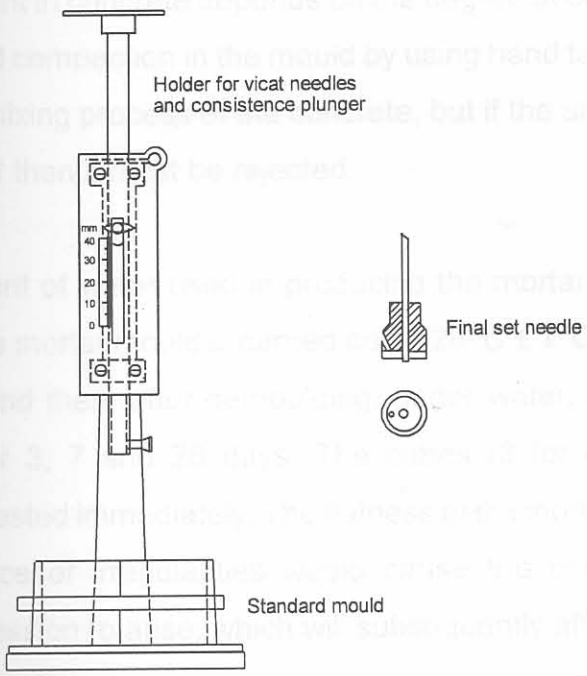
The main variables influencing penetration are the water content of the paste, the temperature, the load on the needle, the dimension of the needle, and the reactivity of the cement. The apparatus for the determination of setting times is shown in Figure 4.9. The needle, which has a diameter of 1.13 mm and a total load of 300 g, is named after Vicat (1828). It is released at the surface of the hydrating paste, at intervals, until it penetrates only to a point 5 ± 1 mm from the bottom of the standard mould. When the paste has attained this degree of stiffness it has reached initial set.

The needle is then replaced by cylindrical knife edge attachment for the final setting time determination. Final set is reached when the knife edge makes only a shallow impression on the surface of the paste but does not penetrate the 0.5 mm necessary to mark the surface.

The amount of water used in making the standard cement paste is determined by the standard consistence of the paste. This is achieved when a 10 mm diameter plunger, which is held in the apparatus used for the Vicat needle, can be forced under its own weight to penetrate to 5 ± 1 mm from the bottom of the mould. Trial and error methods determine the

correct amount of water to form this paste consistence.

Figure 4.9 Apparatus for the determination of setting times and standard consistence (Bye, 1983).



4.7.3 Compressive strength

Compressive strength is the most important material parameter used to characterize cement quality. Usually the term implies the crushing strength of concrete or mortar cubes cast in steel moulds, either 100 or 150 mm in length. The compressive strengths developed in these cubes, depend on the material used, the mix proportions, the efficiency with which the mix is compacted into the mould, and the temperature, humidity and time of curing. Materials and procedures are therefore described in detail in national standards, which enables inter-laboratory co-operative testing.

Concrete strength is related to the volumes of cement (C), water (W) and air (A) it contains by Feret's empirical law (Bye, 1983):

$$S = k\left(\frac{C}{C + W + A}\right)^2 \quad (4.27)$$

where k is a constant for the aggregates, cement and curing employed.

The volume of air present in concrete depends on the degree of compaction achieved, and the aim is to achieve full compaction in the mould by using hand tamping. Some air may be introduced during the mixing process of the concrete, but if the amount is abnormal with a particular batch of sand then it must be rejected.

The effect of the amount of water used in producing the mortar is significant, but easily controlled. Curing of the mortar mould is carried out at 20 °C ± 1 °C, in a high humidity room for the first 24 hours and then, after demoulding, under water. Compressive strength is usually measured after 3, 7 and 28 days. The cubes (3 for each curing period) are superficially dried and tested immediately. The flatness of the mortar cube face is important, because the occurrence of irregularities would cause the concentration of abnormal stresses during compression to arise, which will subsequently affect the results.

The procedures as set out in SABS EN 196-1:1996 (Determination of strength) and SABS EN 196-3:1996 (Determination of setting time and soundness) were followed as standard methods of cement testing during this study.