Chapter 2

Instrumentation Techniques

2.1 Introduction

The instrumentation techniques generally required for research in materials science are for the purpose of characterization of the materials and investigation of the relevant properties.

The materials synthesized for this study are meant to yield optical properties. These properties were investigated by UV/Visible as well as Fluorescence spectrometer. The characterization was done using usual techniques like X - ray diffraction and Scanning Electron Microscopy. Both the techniques are based on the phenomena of diffraction.

Diffraction is the general characteristics of all waves and can be defined as the modification of the behavior of light or the other waves by its interaction with an object. Diffraction occurs when a wave encounters a series of regularly spaced obstacles that (1) are capable of scattering the wave, and (2) have spacings that are comparable in magnitude to the wavelength. Furthermore, diffraction is a consequence of specific phase relationships established between two or more waves that have been scattered by the obstacles [1, 2].

Considering an individual atom, if the beam of X rays is incident on the atom, the electrons in the atom absorb the energy and then oscillate about their mean positions. When an electron decelerates in its oscillations, it emits energy in the form of X rays. This process of absorption and reemission of electromagnetic radiation is known as scattering. It the atoms are closely spaced, each of them contribute many scattered x-rays. The scattered waves from each atom interfere. If the waves are in phase constructive interference occurs. If the waves are 180° out of phase, then destructive interference occurs. A diffracted beam may be defined as a beam

composed of large number of superimposed scattered waves. For a measurable diffracted beam complete destructive interference does not take place. Thus diffracted beam is composed of a large number of scattered waves that mutually reinforce one another.

2.2 Diffraction from Crystalline Materials – Bragg's Law

X-rays are a form of electromagnetic radiation that have high energies and short wavelengths of the order of the atomic spacings for solids. When a beam of x-rays impinges on a solid material, a portion of this beam will be scattered in all directions by the electrons associated with each atom or ion that lies within the beam's path. The direction is governed by the wavelength (λ) of the incident radiation and the nature of the crystalline sample.

Each plane of atoms partially reflects the incident wave much like a half-silvered mirror. The x-rays are not really being reflected, they are being scattered but it is very convenient to think of them as reflected and they are often called as 'reflecting planes' and the diffracted beams the 'reflected beams'.

Consider the two parallel planes of atoms A–A′ and B–B′ in Figure 1, which are separated by the interplanar spacing *d*. Now assume that a parallel, monochromatic, and coherent (in-phase) beam of x-rays of wavelength λ is incident on these two planes at an angle Θ.

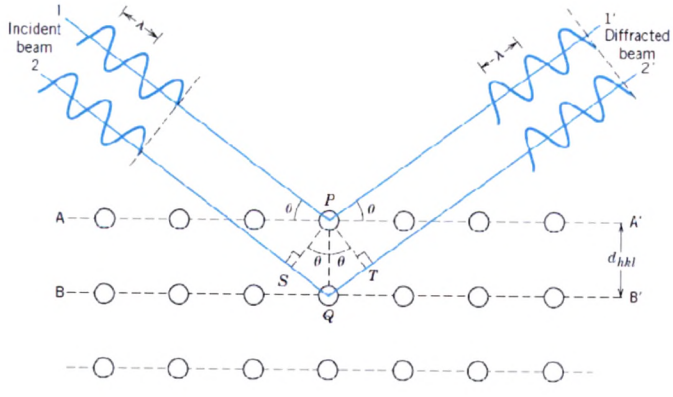


Figure 1

Two rays in this beam, labeled 1 and 2, are scattered by atoms *P* and *Q*. The scattered rays 1′ and 2′ occur also at an angle θ to the planes. The path length difference between wavefronts 1-1′ and 2 –2′ (i.e., *SQ* + *QT*) is equal to a whole number, *n*, of wavelengths. Therefore the path difference is

$$\delta = n\lambda$$

where n is an integer. Since line PT and PS are also wavefronts, we can write

$$\delta = SQ + QT = 2QT$$

from elementary trigonometry,

$$\delta = 2QT \sin\theta$$

and because PQ is the interplanar spacing d,

$$\delta = 2d \sin\theta$$

from above equations,

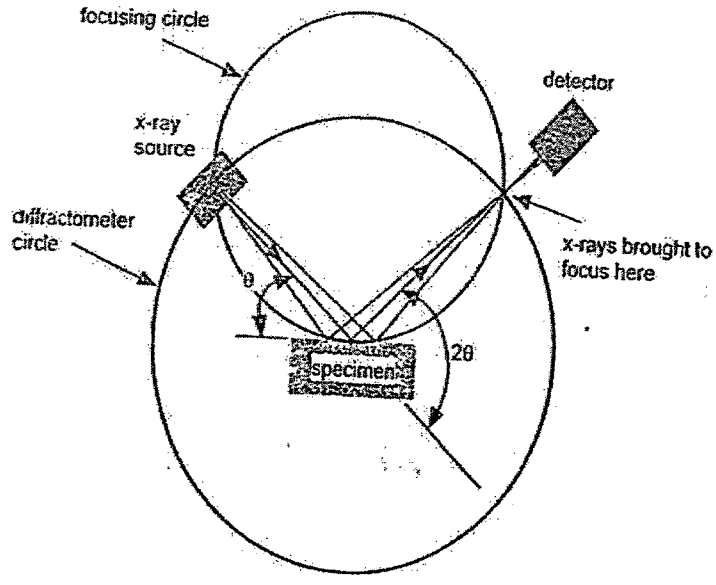
$$n\lambda = 2d \sin\theta$$

This equation is known as ***Bragg's Law.*** The parameter n is known as the order of reflection and is the path difference, in terms of number of wavelengths, between waves scattered by adjacent planes of atoms. A first order reflection occurs when n=1 and the scattered and incident waves have a path difference of one wavelength. When n>1, the reflections are called higher-order.

Practical X-Ray Diffraction

The three basic components of an x ray diffractometer are the x ray source, specimen, X ray detector and they all lie on the circumference of a circle, which is known as the focusing circle. The angle between the plane of the specimen and the x ray source is θ, the Bragg angle. The angle between the projection of the x ray source and the detector is 2θ. For this reason, the X ray diffraction patterns produced with this geometry are often known as θ-2θ scans. In the θ-2θ geometry the X ray source is fixed, and the detector moves through a range of angles. The radius of the focusing circle is not constant but increases as the angle 2θ decreases, which can be seen from the figure below. The 2θ measurement range is typically from 0° to about

170°.The choice of range depends upon the crystal structure of the material. For an unknown specimen a large range of angles is often used because the positions of the reflections are not known.



Geometry of an X ray diffractometer

Although the θ - 2θ geometry is the most common, there are other geometries. In the θ - θ geometry both the X ray source and the detector move in the vertical plane in the opposite directions above the center of the specimen. There are other specialized techniques such as ω scan and Φ scan but they are not widely used.

The *Diffractometer* circle is different from the focusing circle. The diffractometer circle is centered at the specimen, and both the x ray source and the detector lie on the circumference of the circle. The radius of the diffractometer circle is fixed. The diffractometer circle is also known as the *Goniometer* circle. The goniometer is the central component of an x ray diffractometer and contains the specimen holder. It has arms to which the x ray source and the detector are mounted. In most powder diffractometers, the goniometer is vertically mounted but in other diffractometers

for example those used to study thin films, the goniometer may be horizontally mounted.

A standard X ray diffraction pattern consists of a series of peaks whose intensity is plotted on y axis and the measured diffraction angle 2θ along x axis. These peaks are called reflections. Each reflection corresponds to x rays diffracted from specific set of planes in the specimen and these peaks are of different intensities. The intensity is proportional to the number of X ray photons of a particular energy that have been counted by the detector for each angle 2θ. The intensity is usually expressed in arbitrary units. The intensities of reflections depend on several factors, including structure factor, incident intensity, slit width and the value of current and voltage used in the X ray source. The recorded X ray diffraction pattern generally has a background which is subtracted to smoothen the peaks. The intensity scale is often adjusted so as to have a reasonable intensity for all the peaks since the most intense peak may have a much higher intensity than the other peaks.

The structure and lattice parameters of the material are determined by the positions of the X ray diffraction peaks in the pattern. As the symmetry of the crystal structure decreases, there is an increase in the number of the peaks, e.g X ray diffraction pattern of materials with cubic structures have few peaks but with hexagonal structures have more peaks. The intensity of the reflections in a single phase material provides information about the atomic positions in the crystal.

The ideal size of material for powder diffraction is usually 500 nm. If the crystallites are smaller, the number of parallel planes available is too small for a sharp diffraction maximum to be build up and the peaks broaden.

There can be further broadening of diffraction peaks arising on account of factors like **Instrumental Effects** which include imperfect focusing, unresolved α_1 and α_2 peaks or finite widths of α_1 and α_2 peaks in cases where the peaks are resolved and **Lattice Strain** due to variation in the lattice constants from one crystallite to another as well as structural faults. Due to the simultaneous effect of all these factors, the

peaks broaden significantly. The width of an individual peak, often measured as full width at half the maximum of the height, can be used to determine the crystallite size and can be used to ascertain the presence of lattice distortions in the crystal. To get the broadening only due to the crystallite size, the broadening due to instrument and lattice strain has to be subtracted. In order to estimate the magnitude of instrumental broadening the unknown specimen is mixed with some coarse grain or well annealed standard powder whose crystallite size is so large that it does not cause any broadening, e.g silicon powder with grain size of 10μm is ideal. Alternatively a powder of same composition can be used but in an annealed condition so that grain size is large and the lattice strain is removed.

The X ray diffraction of standard powder is recorded under instrumental condition identical to those of unknown specimen so that the peak broadening in unknown specimen and instrumental broadening in standard powder are measured at same angle. Proper care has to be taken to ensure that the instrumental broadening is measured at similar Bragg angles for both materials. It is observed that if the X-ray peak has width B_0 and the width due to instrumental effects is B_i, then the remaining width B_r due to the combined effects of crystallite size and lattice strain, assuming that the profile to be Gaussian is,

$$B_r^2 = B_0^2 - B_i^2 \quad (1)$$

According to Scherrer, the expression for broadening of XRD peaks, only due to small crystallite size, is given by

$$B_{crystallite} = \frac{k\lambda}{L\cos\theta} \quad (2)$$

where λ is the wavelength of the X-rays, θ is the Bragg angle, L is the 'average' crystallite size measured in a direction perpendicular to the surface of the specimen, and k is a constant. The broadening is evaluated by measuring width B in radians at intensity equal to half of the maximum intensity (Full Width at Half Maximum).

Above equation is called Debye Scherrer equation derived for Gaussian profiles and small cubic crystals. The value of k varies between 0.89 and 1.39 but is usually taken as 1.0, since the precision of crystallite size by this method is at best about ± 10%.

The broadening of the diffraction peaks due to the lattice strain in the material is represented by the relationship,

$$B_{strain} = \eta \tan\theta \quad (3)$$

where η is the strain in the material.

The width B_r is the sum of widths due to small crystallite sizes and lattice strains

$$B_r = B_{crystallite} + B_{strain} \quad (4)$$

From equations 2 and 3

$$B_r = \frac{k\lambda}{L\cos\theta} + \eta \tan\theta \quad (5)$$

Multiplying by cos θ we get,

$$B_r = \frac{k\lambda}{L} + \eta \sin\theta$$

The plot of $B_r \cos\theta$ versus sin θ gives a straight line with slope η and intercept $k\lambda/L$. Crystallite size without strain can be calculated from the intercept by using the appropriate values of K and λ.

For low values of 2θ each reflection appears as a single sharp peak. For larger values of 2θ each reflection consists of a pair of peaks, which corresponds to $K\alpha_1$ and $K\alpha_2$ wavelengths. A peak always contains α_1 and α_2 components. The resolution depends upon 2θ values, the scale on the x axis, and the resolution of the diffractometer. At lower values of 2θ the separation of the peaks is quite small but increases at larger 2θ values. For a known sample, suitable range of 2θ values are considered to obtain the diffraction pattern but for an unknown specimen full range of angles are to be covered to avoid missing any of the important reflection. To obtain higher signal to noise ratio and better resolution, the length of time taken to collect the data at each angle has to be reasonably long. The diffractometer has to be calibrated and aligned properly so that there are no errors in measurement like loss of intensity and resolution, increased background, incorrect profile, shapes, etc.

One of the most useful sources of information for crystal structure data is the powder diffraction file (PDF). It contains single phase X ray diffraction patterns in the form of tables on interplanar spacings (d) and corresponding relative intensities. It also contains information like physical and crystallographic properties of the material. There was a committee constituted in 1969 known as Joint Committee on Powder Diffraction Standard (JCPDS) to collect standard diffraction patterns of material as repository. Later it was renamed as International Center for Diffraction Data (ICDD) in 1978. Both the acronyms JCPDS and ICDD are used to refer these patterns. The diffraction pattern obtained from diffractometer is compared with the standard patterns in the JCPDS-ICDD data base for matching of patterns and material identification. This matching is important for nanocrystalline materials that may contain several crystallographic phases, including highly disordered or amorphous phases and for nanocrystals whose crystal structure may be different from that of corresponding bulk form due to surface effects.

The phase identification, crystal structure, lattice parameters and particle sizes are determined by the powder x-ray diffraction (XRD) technique using Bruker D8 advance diffractometer with Ni-filtered Cu Ku. (λ = 1.5406 °A) radiation. The fine powder is mounted on a plexi-glass holder, which does not show any x-ray diffraction peaks in the whole 2θ range. Powder is assumed to consist of randomly oriented grains and crystallites.

2.3 Scanning Electron Microscope

Structure of material can be viewed through optical microscope or by imaging of electrons passed through a thin specimen in the transmission electron microscope, or imaging by collecting electrons emitted from the surface of the material of interest in the scanning electron microscope [3, 4].

There are two important drawbacks of optical microscope namely resolution limit and small depth of focus. The resolution limit of an optical microscope is a consequence of the wavelength of visible light (about 0.5μm). Microstructural features smaller than 0.5 μm cannot be resolved in an optical microscope. If purple

or ultraviolet light is used than the wavelength can be shorter than 0.5 μm but the resolution only increases about a factor of 2 and observations are also difficult as human eye is not very sensitive to those wavelengths. The depth of focus is defined as difference in height of features that are simultaneously in focus in the image. For a typical objective lens, the depth of focus is only about 0.5 um. For observing rough objects and fractured surfaces the small depth of focus is a severe limitation.

Instead of using a light beam if a beam of electrons is focused on the sample the limitations of resolution and the depth of focus can be overcome. The wavelength of the electrons emitted from the electrons gun is about 0.05 nm, 10,000 times smaller than the wavelengths of visible light (about 500 nm.). The wavelength is small enough to resolve features all the way down to the atomic scale.

The Scanning Electron Microscope focuses an accelerated beam of electrons, emitted from a thermionic triode electron gun. The beam of ejected electrons is divergent and they get collimated into parallel stream by passing through electro optical lens and condenser magnetic lens. First it passes through electro optical lens and then it passes through condenser magnetic lens. The condenser magnetic lens controls the amount of current that passes down the rest of the column by focusing the electron beam to variable degrees. The sharper the focus, the less of the beam intercepted by an aperture located below the lenses and higher the current. In some SEM's there is second condenser lens that is used to provide a better focus for SEM work.

The beam incident on the specimen is very small and may be as little as 0.01 μm in diameter. A portion of the current leaving the sample is collected by the detector and conveyed to an amplifier. The output of the amplifier determines the potential of the modulating electrode of a cathode ray tube (CRT). Thus the current reaching the detector controls the brightness of the spot on the face of this tube. Current from the scanning generator (saw tooth generator) passes through pairs of scanning coils, causing the initial electron beam in the microscope and the spot on the face of the cathode ray tube to be deflected. Two such systems are used to produce deflection at right angles to each other; so that the electron beam focused

on the specimen and the spot on the CRT describe rectangular zigzag raster in synchronism. As the electron beam scans the surface of the specimen, changes in composition, texture or topography at the point where the electrons strike the specimen cause variation in the electron current reaching the detector and thus in the brightness of the Cathode Ray Tube spot. Thus the image of the specimen is built up on the Cathode Ray Tube screen.

The synchronism between the deflection of the electron probe over the specimen and the deflection of the electron beam in cathode ray tubes is achieved by connecting two sets of scanning coils effectively in series and supplying them from a signal generator for the X scan and a separate signal generator for the Y scan. The magnification of the microscope is the ratio of the length of the corresponding side of the raster scanned by the electron probe on the specimen. It is possible to change the magnification of the scanning electron microscope rapidly over the range from 20 to 5×10^4.

Electron Gun

Electron gun is a place where electrons come from to reach the electron microscope. There are two ways to eject electrons from their respective atoms. The first method is to give enough thermal energy to them so that they are driven off. The second is to put them in a strong enough electric field so that if they are too far from their atoms, they will be pulled off. The most commonly used electron gun is conventional triode electron gun. The electrons are generated as a result of thermionic emission when a high potential is applied to the electron gun. There are various types of electron guns like Tungsten, Lanthanum Hexaboride (LaB_6), Field Emission etc.

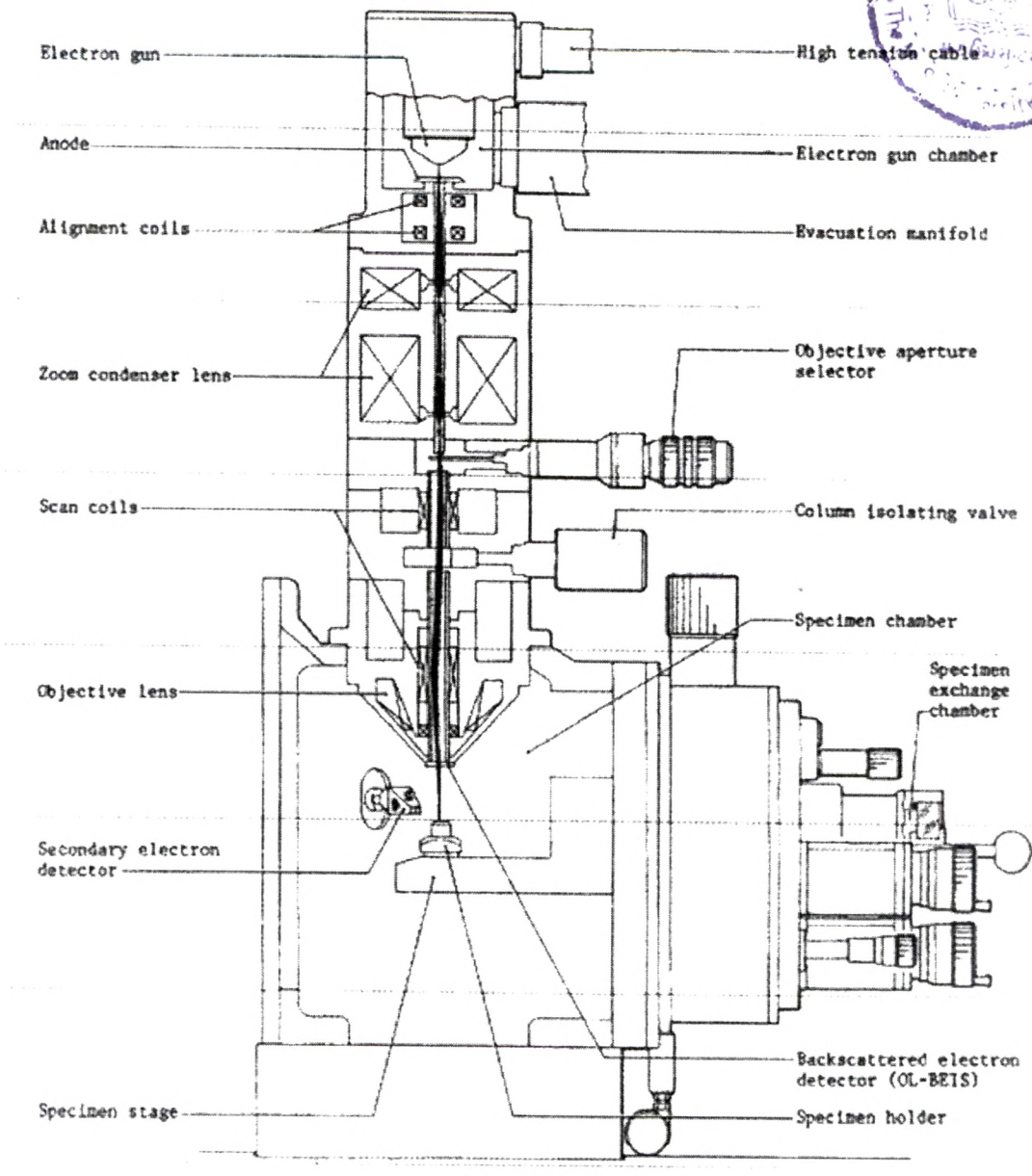


Figure 3

Interaction of Electron beam with matter

When the energetic electrons strike the surface of the sample, the interaction results in elastic and inelastic scattering [5]. Elastic scattering results in backscattered electrons and diffraction. Inelastic scattering results in generation of secondary electrons and X rays. The interaction also results in the emission of Auger electrons, Cathodoluminescence and Bremsstrahlung .

The energy distribution of **Secondary electrons** is typically less than 50 eV but strongly peaked around 10eV. They are outer shell electrons that have been produced as a result of inelastic scattering between the incident electrons and the sample. These electrons escape from the near surface of the sample where the spread of the incident beam in minimal. This allows images with high spatial resolution of the order of the incident beam, to be acquired. Changes in topography and composition of the material produces changes in signal level, making it a powerful imaging mode for analysis.

Backscattered electrons are primary beam electrons that have undergone one or more elastic collisions within the sample and eventually have bounced around to re emerge from the surface they came in. These electrons will also undergo several inelastic collisions during their time inside the solid and will typically have an energy that is lower than beam energy upon their escape. The Back scattered yield from a randomly oriented polycrystalline material tends to increase monotonically with atomic number Z. This forms the basis for differentiating between different phases, thus providing ideal starting point for further microanalysis. The backscattered signal is also sensitive to local topography, crystallography, as well as magnetic field structure of the material.

When an inner K shell electron is ejected and an electron from the L shell fills this vacancy, the released energy can eject an **Auger electron** from the L shell. The transition is termed as KLL transition. The energies of the Auger electron peaks allow all elements with exception of Hydrogen and Helium to be identified since minimum of three electrons are required for the emission process.

Cathodoluminescence is a condition where some material emits visible photons under the influence of the high energetic electron beam. When an incident electron inelastically scatters off the atom, electrons ejected from the filled valence band can be promoted to the conduction band leaving a hole in the valence band. The band gap energies are typically between 2 and 5 eV. Sensitivity to very small changes in the material composition leads to a difference in the cathodoluminescence. This technique thus provides for recording high spatial resolution images at different

wavelengths. It is a versatile technique for structural and optical characterization of thin films and bulk form.

When a high energy electron interacts with an atom, it may result in the ejection of an electron from an inner atomic shell. De-excitation can occur by an electron from an outer shell filling the vacancy. The characteristic energy released is called emission of **X-ray photons** with energy specific to that transition of the element. The detector that releases these characteristic X-rays are called Energy Dispersive Spectrometer and Wavelength Dispersive Spectrometer and attached to the microscope for doing chemical analysis. The continuum or **Bremsstrahlung** X- rays are formed from direct energy loss of the beam electrons as they are slowed in the sample. This results in counts in the x ray spectrum channels between zero energy upto an energy that corresponds to the value of incident electron beam energy.

Different detectors are used for detecting these different types of electrons. The nature of the image collected in Scanning electron microscope is also dependent on the detector used to collect them. At each location on the secondary electron image, the brightness is proportional to the intensity of secondary electrons ejected from the sample. For the secondary electron image to be useful, insight into how the sample characteristics affect the intensity of secondary electron emission is needed. There are few ways to discover this. Usually the processes are described as mechanisms that produce contrast.

1. **Surface Topography Contrast**

When the primary electrons impinge on the sample, they have such a high kinetic energy that they penetrate into the sample upto some distance, nearly a micrometer. As each electron penetrates into the solid sample, it gradually loses energy by various collisions, some of which result in ejection of secondary electrons from atoms of the solid. A few electrons are collected by the detector. The further a secondary electron is from the surface, the lower the probability that it will escape from the sample. Therefore when a primary electron impinges on the ridge or ledge, more secondary electrons escape from the sample and they appear as bright images. In contrast, valleys or grooves prevent the escape of some secondary

electrons that would be able to escape if the surface was flat and therefore, they appear as dark images.

2. Atomic Number Contrast

As the primary beam penetrates in to the sample, electrons interact with electrons associated with atoms in the sample. The higher the atomic number (Z) of the atoms in the sample, the greater number of collisions occurs per atom. Thus, samples with high Z result in generation of more secondary electrons near the surface where they can escape from the sample than samples with low Z.

3. Sample potential contrast

Differences in electric potential at various locations in an electronic circuit in operation produces contrast which is used for the analysis of the circuit. The positively charged secondary electrons emitted from the sample will be drawn back producing a dark image and negatively charged electrons are repelled from the sample producing a bright image.

Generation of electron beam requires vacuum. To attain desired vacuum levels in the system four types of vacuum pumps are commonly employed in Scanning electron microscope namely Mechanical Pump, Diffusion Pump, Turbo Pump and Ion Pump.

Most of the parts of the Scanning electron microscope are controlled through the control console

2.5 Specimen

The primary electron beam can be viewed as a current of electrons flowing into the sample. If the sample is as electrical conductor, the current flows through the sample to ground. If the sample is a poor conductor, negative charge builds up on the sample, causing the entire sample to appear bright in the secondary electron image. The contrast effect due to charging of the sample quickly overwhelms all of the other contrast producing effects, preventing a useful image of the sample from being formed. Therefore, it is not possible to observe nonconducting samples in the

Scanning Electron Microscope. Only conducting samples can be observed. To overcome this limitation, non conducting sample must be coated with a thin layer of conducting metal, usually gold.

2.6 Advanced Scanning Electron Microscopes

Conventional Scanning Electron Microscopy requires a relatively high vacuum in the specimen chamber to prevent atmospheric interference with primary or secondary electrons but an **Environmental Scanning Electron Microscope** can be operated with a low vacuum (up to 10 Torr of pressure, or one seventy- sixth of an atmosphere) .Though a certain degree of resolution is compromised, specimens can be investigated in their natural state or under natural environmental conditions without the need for conventional preparation techniques that may produce unwanted artifacts in the sample. Magnifications up to 50000 times with resolution guaranteed to 100 A° are possible in such environments.

Field emission Scanning Electron Microscope has a Field Emission Gun for generation of electron beams. The field emission source permits very high resolution imaging of coated or naturally conductive samples under normal high vacuum and high voltage conditions. Various detectors can be attached to this microscope for elemental analysis at any spot in the specimen.

For the present study JEOL make JSM 5610 LV Scanning Electron Microscope was used as shown in the **Figure 4** below for microstructural analysis.

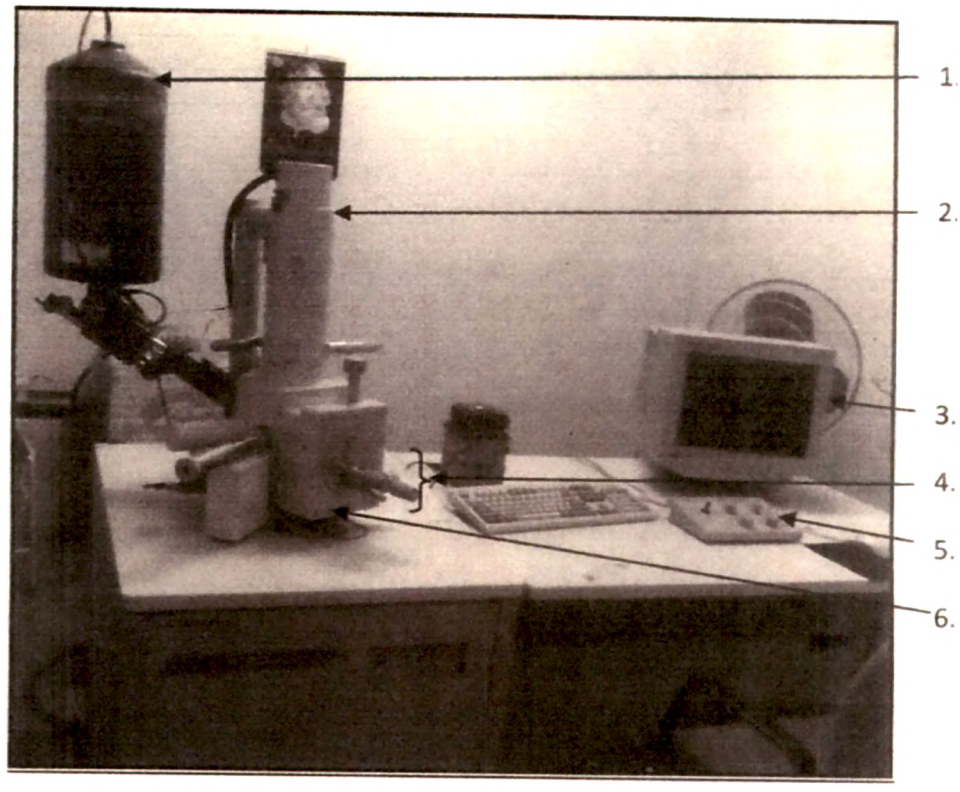


Fig. 4: Scanning Electron Microscope with EDS facility

(1) Liquid Nitrogen Chamber (2) Microscope column with electromagnetic lenses (3) Display unit (4) Knob for changing the position of the specimen (5) Focusing and magnifying unit (6) Specimen chamber

2.5 Fluorescence Spectroscopy

The fluorescence process is characterized by two different pr0cesses. A fluorescent molecule emits its *fluorescence spectrum* after it absorbs radiation anywhere within its *excitation spectrum*, which may differ from the usual absorption spectrum of the molecule as a result of instrumental artifacts [6].

Fluorescent species must be exposed to radiation in the portion of the spectrum where the molecule is capable of absorbing energy before fluorescence emission can occur. When a quanta of light impinges on a molecule, it is absorbed in about 10^{-15} sec. The radiation of a particular energy can be absorbed only by characteristic structures. The absorption transitions originate usually in the lowest vibrational level of the ground electronic state and one of the paired electrons is raised to upper

excited state S_1 or S_2.This state persists for a finite time of the order of 10^{-8} to 10^{-4} sec. During this time interval the absorbed energy is dissipated to the vibrational levels until the lowest vibrational level of the excited state is attained. If all the energy is not dissipated then after a short period of time which is characteristic of a molecule, the electron returns to the ground electronic level. The transition from the excited state to one of the vibrational within the ground state leads to a release of energy and gives rise to fluorescence emission. The probability for return of the electron to the ground electronic state is highest at this point. The fluorescence emission spectrum will appear on a low frequency side of the absorption band of longest wavelength and it might appear as a series of emission bands and peaks. The fluorescence emission spectrum must be determined before the wavelength for the measurement of the fluorescence can be selected. The excitation spectrum must also be determined. To obtain these spectra a fluorescence spectrometer or spectrofluorimeter is desirable.

Figure shows the schematic diagram of the optical system used in a spectrofluorimeter [7]. The source of the light is a 150 W high pressure xenon arc lamp. The ellipsoidal mirror collects radiation from this lamp and focuses an enlarged image of the arc upon the entrance slit of the excitation monochromator, completely filling the mirrors. Monochromator radiation of specific wavelength is selected by angular positioning of the grating. The desired bandpass is achieved by the selection of appropriate interchangeable slits for the entrance and exit positions of the monochromator. The radiant energy emerging from the exit slit of the excitation monochromator activates specific molecules within the sample, resulting in fluorescence emission. The emitted radiation is viewed by the analyzing monochromator, which permits only characteristic sample emission to reach the detector, blocking all undesired spectral regions. When fluorescent energy falls on the photomultiplier, the registered photocurrent can be indicated on the meter, recorder or oscilloscope. The spectrum can be manually or automatically scanned.

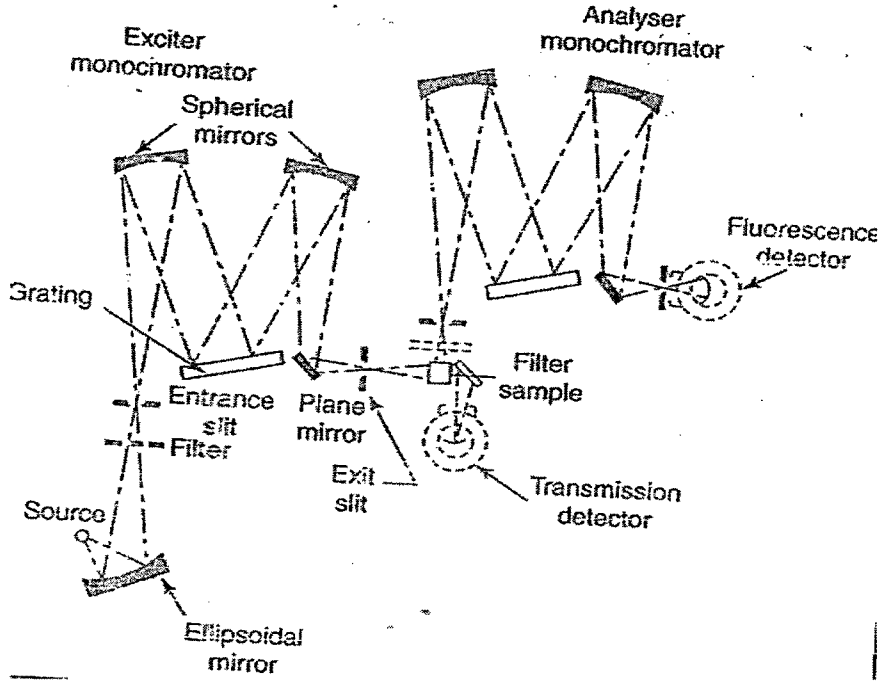


Figure 5 : Optical system of a typical Spectrofluorimeter

The spectrofluorimeters are usually accompanied by cryogenic accessories to cool the sample by means of an immersion probe, which is cooled by an easily replenished reservoir refrigerant like liquid Nitrogen.

Excitation Spectrum

The wavelength of excitation is varied by scanning the excitation monochromator for fixed emission wavelengths. By this means the upper energy levels of the luminescent centres (or ions) are revealed, even when these levels are non-radiatively relaxing to the lower most excitation level involved in radiative emission. By monitoring at different fixed emission wavelengths, complete knowledge can be derived about the upper energy levels involved directly or indirectly in the luminescence process. The excitation spectrum is a replica of the absorption spectrum of the same ion but the position of the energy levels in excitation spectrum is determined by monitoring the intensity of emission, not by the intensity of radiation passed through the sample as in absorption spectrum. Depending upon the absorption cross section of the excitation bands the intensity of the emission varies.

From the excitation spectrum the region of luminescence can be determined, as also the energy levels of the ions in the host lattice.

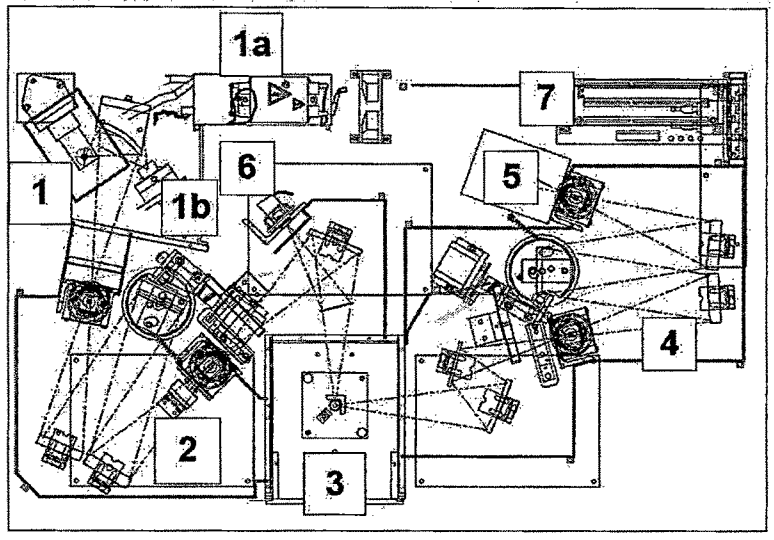
Emission Spectrum

The luminescent centre or the activator ion in a phosphor that has passed on to the excited state returns to the ground state through either radiationless transitions or by way of emission transitions. Emission transition is seen as a glow of the materials and registered in the form of a band in the luminescence spectrum. The intensity of emission is plotted as a function of wavelength by scanning the emission monochromator at fixed excitation wavelengths. The position of the band in the luminescence spectrum of the ion does not depend on the method of excitation. There can be several emission levels. Transitions from each one of them can not only be to the ground state, but also to the intermediate levels. The ground state can be split into sublevels and then transitions from each emission level will be to the ground state sublevels. This can result in the appearance of complex luminescence spectra consisting of many bands characteristic of trivalent rare earth ions.

In the present study, the photoluminescence excitation and emission spectrum of the phosphors have been measured using Horiba Jobin Yvon make Fluoromax-4 Spectrofluorometer [8] ***Figure 6***. The excitation source is 150-W ozone-free xenon arc-lamp as shown in. Light from the lamp is collected by a diamond-turned elliptical mirror, and then focused on the entrance slit of the excitation monochromator. A schematic layout is shown in ***Figure 7***. The lamp housing is separated from the excitation monochromator by a quartz window. This vents heat out of the instrument, and protects against the unlikely occurrence of lamp failure.

Figure 6

It contains Czerny-Turner monochromators for excitation and emission. The Czerny-Turner design uses all-reflective optics to maintain high resolution over the entire spectral range, and minimize spherical aberrations and re-diffraction. The essential part of a monochromator is a reflection grating. A grating disperses the incident light by means of its vertical grooves. A spectrum is obtained by rotating the gratings, and recording the intensity values at each wavelength. The gratings in the Fluoro-Max 4 contain 1200 grooves mm^{-1}, and are blazed at 330 nm (excitation) and 500 n m (emission). *Blazing* is etching the grooves at a particular angle, to optimize the grating's reflectivity in a particular spectral region. The wavelengths selected are optimal for excitation in the UV and visible, and for emission in the high-UV to near-IR.



1 Xenon arc-lamp and lamp housing
1a Xenon-lamp power supply
1b Xenon flash lamp (FluoroMax®-4P only)
2 Excitation monochromator
3 Sample compartment
4 Emission monochromator
5 Signal detector (photomultiplier tube and housing)
6 Reference detector (photodiode and current-acquisition module)
7 Instrument controller
Host computer (not on diagram)

Figure 7: Schematic layout of Horiba Jobin YVON spectrofluorometer.

Each grating is coated with MgF_2 for protection against oxidation. The system uses a direct drive for each grating, to scan the spectrum at rates up to 200 nm^{-1}, with accuracy better than 0.5 nm, and repeatability of 0.3 nm.

The entrance and exit ports of each monochromator have continuously adjustable slits controlled by FluorEssence Software. The width of the slits on the excitation monochromator determines the bandpass of light incident on the sample. The emission monochromator's slits control the intensity of the fluorescence signal recorded by the signal detector. The wider the slits are, more light falls on the sample and detector, but the resolution decreases. The narrower the slits are, the higher the resolution gets, but at the expense of signal. The bandpass is determined by the dispersion of the monochromator. The dispersion of FluoroMax-4 monochromators is 4.25 nm mm^{-1} for gratings with 1200 grooves mm^{-1}.

An excitation shutter is located just after the excitation monochromator's exit slit. The shutter protects samples from photobleaching or photodegradation from prolonged exposure to the light source. An emission shutter is an optional accessory, placed just before the emission monochromator's entrance, and protects the detector from bright light. A toroidal mirror focuses the beam from the excitation monochromator on the sample. About 8% of this excitation light is split off, using a beam-splitter, to the reference photodiode. Fluorescence from the sample is then collected and directed to the emission spectrometer. The sample compartment accommodates various optional accessories, as well as fiber-optic bundles to take the excitation beam to a remote sample and return the emission beam to the emission monochromator.

Fluoromax 4 contains two detectors viz. Signal detector and Reference detector. The signal detector is a photon counting detector. The reference detector monitors the xenon lamp, in order to correct for wavelength and time dependent output of the lamp. This detector is a UV-enhanced silicon photodiode, which is just before the sample compartment.

2.6 Ultra Violet/Visible Absorption Spectroscopy

The wavelength of light that a compound will absorb is characteristic of its chemical structure. Specific regions of the electromagnetic spectrum are absorbed by exciting specific types of molecular and atomic motion to higher energy levels. Absorption of microwave radiation is generally due to excitation of molecular rotational motion. Infrared absorption is associated with vibrational motions of molecules. Absorption of visible and ultraviolet (UV) radiation is associated with excitation of electrons, in both atoms and molecules, to higher energy states. All molecules will undergo electronic excitation following absorption of light, but for most molecules very high energy radiation (in the vacuum ultraviolet, <200 nm) is required.

percentage and referred to as % transmittance. Mathematically, absorbance is related to percentage transmittance T by the expression

$$A = \log_{10}(I_o/I) = \log_{10}(100/T) = KCL$$

where L is the length of the radiation path through the sample, C is the concentration of absorbing molecules in that path, and k is the extinction coefficient - a constant dependent only on the nature of the molecule and the wavelength of the radiation.

Instrumentation

The measurement of Absorption spectra is done on Absorption Spectrophotometers [10]. The components include a radiation source, a monochromator to select the desirable wavelength of radiation to be examined, a sample container and a detector for measuring the intensity of radiation after it passes through the sample. The components can be lined up in two basic optical systems: (1) single-beam optics and (2) double- beam optics.

The Single-Beam Optical System

A **Single-beam optical system** is shown in ***Figure 8*** Radiation from the light source passes through the sample. From here the light proceeds to monochromator. The monochromator disperses the radiation in the same manner as a prism. By using a slit system with the monochromator, only light of the desired wavelength is allowed to proceed along the light path. This light passes to the detector. The detector in turn measures the intensity of the light, and the signal is read out on a recorder.

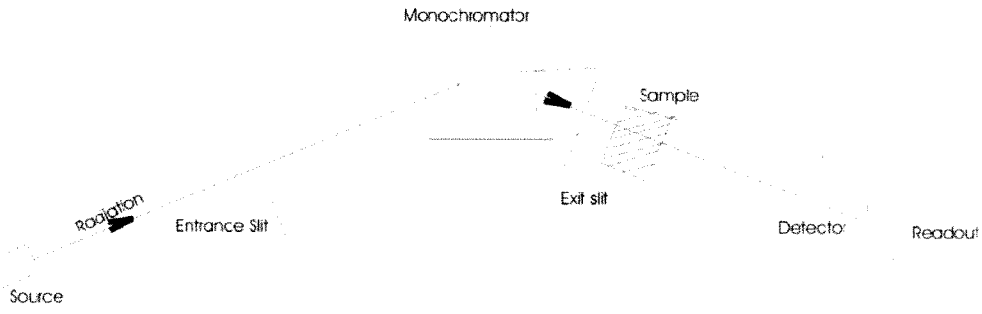


Figure 8

This system is subject to one major source of error. If the intensity of radiation from the source varies, then the entire signal drifts. The dual beam method is faster, and has the added advantage that lamp drift and other slow intensity fluctuations are properly accounted for in the calculation.

A schematic diagram of the **Double-beam optical system** is shown in ***Figure 9*** in this system. The light from the radiation source is split by a beam splitter and forms two paths, the reference path and the sample path. The beam splitting alternately directs the light from the radiation source along the reference path and then along the sample path. The light beams passing down these two paths are equal in intensity and pass alternately through sample and a reference. After passing through reference and sample, they are then recombined and continue through monochromator split system to the detector.

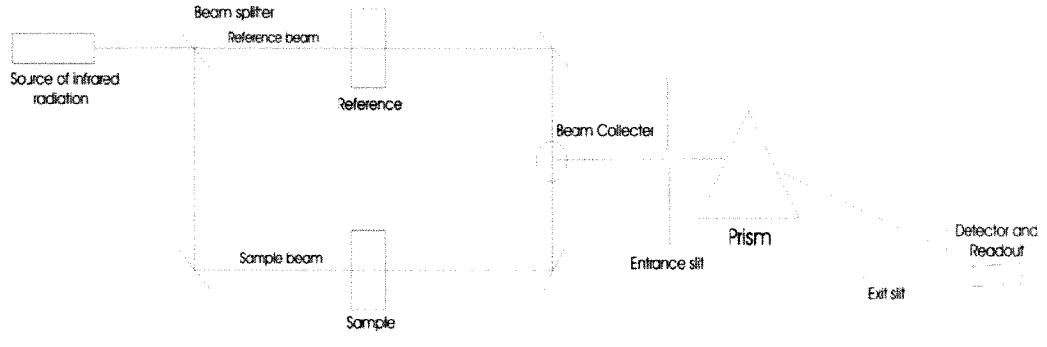


Figure 9

In practice, the reference beam either is not absorbed or is absorbed by a constant quantity by a standard reference cell. It is not possible to use a reference flame. The radiation in the sample beam however is absorbed by the atomized sample. When

the two beams are recombined, an oscillating signal is produced which falls on the detector.

If there is no absorption by the sample or by the reference, then the two beams recombine to form the original unsplit beam. This beam does not vary in intensity as the detector views alternately the reference beam and the sample beam. In this instance, the readout gives zero absorption.

In the present work, Ultraviolet/visible absorption spectra were taken on a Thermo Fisher Scientific Make Evolution 300/600 spectrophotometer as shown in ***Figure 10***. The light source is a combination of Tungsten halogen and Deuterium lamps.

With solid sample it is usually found that the material is in a condition unsuitable for direct spectrometry. The refractive index of the material is high and a large proportion of the radiation may be lost by random reflection or refraction at the surface or in the mass. The sample is made as a homogenous polished block or film or it is dissolved in a transparent solvent to eliminate these interfaces.

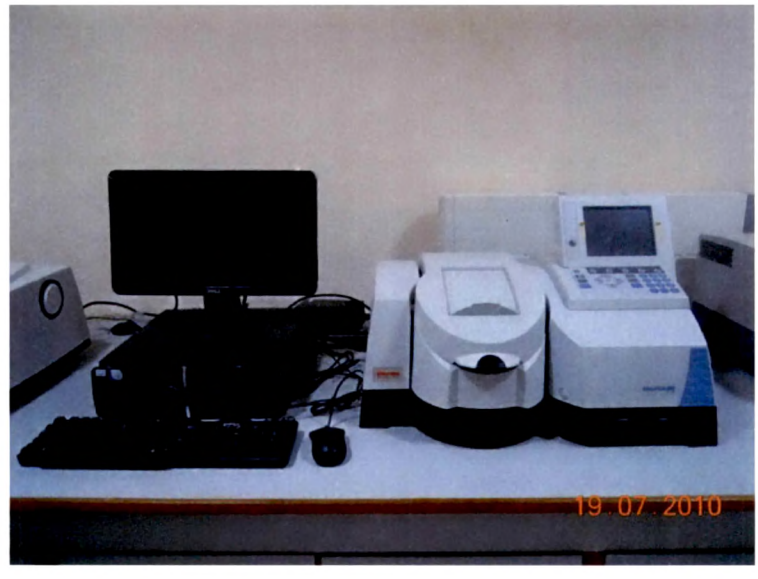


Figure 10

Liquids may be contained in a vessel made of transparent material such as silica, glass or plastic, known as a cell or cuvette. The faces of these cells through which the radiation passes are highly polished to keep reflection and scatter losses to a minimum. Gases may be contained in similar cells which are sealed or stoppered to make them gas tight. With the sample now ready for measurement, the Io (incident intensity) can be set by moving the sample out of the beam and letting the light fall directly on the detector. In modern instrumentation, *I*o setting is generally accomplished by an 'autozero' command. In practice, such a method does not account for the proportion of radiation which is reflected or scattered at the cell faces. It also does not account for the radiation which is absorbed by any solvent and thus does not effectively pass through the sample. Therefore it is usual to employ a reference or blank cell, identical to that containing the sample, but filled only with solvent and to measure the light transmitted by this reference as a true or practical *I*o. Thus, for a fixed path length, UV/VIS spectroscopy can be used to determine the concentration of the absorber in a solution.

References

1 X Ray Diffraction - a practical approach, C. Surnarayana, Grant Norton, Plenum press New York, 1998

2 P. Heroll, L. E. Alexander, X-ray Diflraction Procedures for Polycrystafline and Amorphous Materials John Wiley and Sons, New York, 1954

3 S.A Gangal, Physics Education, Vol 20 nos 1 – 2, 2003

4 M. H. Loretto, Electron Beam Analysis of Materials, Chapman and Hall Ltd., New York,1984

5 Deepak Rajput, S.K. Tiwari, National Workshop on different aspects of electron microscopy, March 29 -31,2006

6 Howart H williard, Lynne L Merritt Jr,John H Dean,Instrumental methods of analysis 4th edition, New Jersey,1965

7 Handbook of Analytical Instruments

8 Fluoromax 4 spectrofluorometer, Operation Manual part number 81110,Version 1.1

9 Shigeo Shionoya William M Yen, Phosphor Handbook, CRC press London,1999

10 James W Robinson, Atomic Absorption Spectroscopy second edition, New York, 1975