CHAPTER 1

SECTION 2

Characterization Techniques
1.2 Introduction:

This division describes the characterization methods employed in this thesis, including brief description of instrument involved and theoretical background of these techniques. The methods applied are UV-VIS spectroscopy, FTIR spectroscopy; powder XRD, DTA/TGA, Raman Spectroscopy, SEM-EDX, TEM-EDX-SAED, Fluorescence spectroscopy, weight loss technique and Electro-chemical method viz. Potentiodynamic polarization study etc.

1.2.1 UV-VIS spectroscopy:

UV-visible absorption spectroscopy is one of the most accepted methods in clinical and chemical laboratories. It is generally used for the quantitative determination of different organic and inorganic species in solution [1-3].

Ultraviolet (200-380 nm) and visible (380-780 nm) absorption spectra are obtained for a pure liquid compound or a compound after dissolving in an appropriate solvent. Spectra can also be obtained in solid and gaseous sample.

The significant thing to realize about the UV-Vis absorption spectra is that it involves transitions of electrons from ground state to the excited states. Valence shell electrons are responsible for this electronic transition. Molecules having π-electrons or non-bonding electrons (i.e., n-electrons) are able to absorb the energy in the form of ultraviolet or visible radiation to transit these valence electrons to higher energy i.e. anti-bonding molecular orbital. The easier to excite the electrons (i.e. lower energy gap between the HOMO and the LUMO), the lower energy radiation i.e., it will absorb longer wavelength of radiation and for higher energy gap between HOMO and LUMO, it will absorb shorter wavelength of radiation.

The instrument used for UV-VIS spectroscopy is called UV-VIS spectrophotometer. This instrument determines the intensity of incident (I₀) and transmitted beam of radiation (I) passing through the sample and their ratio (I/I₀) is termed as the transmittance (T). Transmittance is commonly expressed as percentage (%T). Absorbance is calculated as: Absorbance (A) = - log (T) [4].
The spectrophotometer consists of a light source, a diffraction grating in an amonochromator or a prism to separate the various wavelengths of light, a sample holder and a detector. Different radiation source is frequently used, such as, Tungsten filament (300-2500 nm), a deuterium arc lamp (190-400 nm), Xenon arc lamp (160-2,000 nm) etc. Very recently, light-emitting diodes (LED) are used as radiation source for visible ranges.

In our experiment, Optizen Pop UV-Vis spectrophotometer has been used (Figure 1.2.1).

![Photographic image of Optizen Pop UV-VIS spectrophotometer](image)

**Figure 1.2.1:** Photographic image of Optizen Pop UV-VIS spectrophotometer.

### 1.2.2 Fourier Transform Infrared (FT-IR) Spectroscopy:

Fourier Transform Infrared (FTIR) is the preferred technique of infrared spectroscopy [5-7]. In FTIR, IR radiation is used as the incident radiation. When IR radiation strikes on a sample, a part of the radiation is absorbed by the sample and rest of it is emerged through the sample. The resulting spectrum symbolizes the molecular absorption and transmission, which is the molecular fingerprint of the sample.

FTIR spectroscopy is useful for structural determination of IR active compounds. This is the molecular vibrational spectrum. The sample molecules selectively absorb IR radiation of definite wavelengths from the incident beam i.e. the mixture of different wavelength of radiation. Dipole moment of the molecule is altered after absorption. This causes the transform of vibrational energy levels of sample molecules promoting from ground to excited state. The absorption frequency depends on the energy difference between the vibrational energy levels. A
large gap between the energy levels needs high frequency of absorption radiation. The number of absorption peaks is proportional to the number of vibrational freedom of the molecule. Therefore, FTIR spectrum provides plentiful structural information of a molecule. A large number of molecules are infrared active except some homo-nuclear diatomic molecules, e.g., O$_2$, N$_2$ and Cl$_2$ because of no change dipole moment during vibration and rotation. Thus FT-IR spectroscopy is valuable to analyze many gases, liquids and solid compounds.

In our experiments the FT-IR spectrometer, which has been used, is shown in figure 1.2.2 (model no. 8400S, Shimadzu, Japan). The sample was tested after pulverizing it with well-desiccated KBr crystal. The spectrum was recorded with respect to the KBr

![FT-IR Spectrometer](image)

**Figure 1.2.2:** Photographic image of a FT-IR spectrometer, model no. 8400S, Shimadzu, (Japan).

### 1.2.3 Powder X-ray diffraction (XRD):

Powder X-ray diffraction (XRD) is a speedy analytical method frequently uses for phase detection of a crystalline solid material and able to afford information about unit cell parameters [10]. This technique is used not only to scrutinize phase information, but also to determine the structure of an unknown substance [8].
XRD technique is based on productive interference between monochromatic X-ray radiation and experimental solid crystalline substances [9-10]. X-rays are produced in a cathode ray tube. They are filtered to have monochromatic X-ray radiation, collimated to concentrate, and finally hit on the sample. The incident beam of X-rays with interaction with the studying material creates constructive interference when conditions satisfy Bragg's Law \( (n\lambda=2d \sin \theta) \). Where, \( \lambda \) = wavelength of incident radiation, \( \theta \) = diffraction angle after interaction, \( d \) = spacing between lattice planes of crystal and \( n = 1, 2, 3 \ldots \) This diffracted beam of X-rays are then detected and evaluated. XRD pattern also help to determine the particle size of the compound. The Scherrer equation, in XRD, is a formula that relates the size of sub-micrometre particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern [11]. The Scherrer equation can be written as:

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]

Where, \( D \) is the average size of the ordered (crystalline) domains; \( K \) is a dimensionless shape factor; with a value close to unity; \( \lambda \) is the X-ray wavelength; \( \beta \) is the line broadening at half the maximum intensity (FWHM); also sometimes denoted as \( 2\theta \); \( \theta \) is the Bragg angle.

In our experiments, Ultima IV Rigaku (Japan) powder X-ray diffractometer (Figure 1.2.3) has been used, where, Cu K\( \alpha \) (\( \lambda=1.5406 \) Å) has been performed as the X-ray originator.

**Figure 1.2.3:** Photographic image (partial) of an Ultima IV Rigaku (Japan) powder X-ray diffractometer.
1.2.4 Thermo Gravimetric Analysis (TGA):

Thermo Gravimetric Analysis (TGA) is a technique where the mass of a substance is monitored as a function of temperature or time, when the sample specimen is subjected to a controlled temperature programme under a specific atmospheric condition [12-13]. The mass of a solid material is measured with time during heating or cooling of the sample placed inside the furnace. The sample used here is usually remains in the solid state after degradation. TGA is extensively used to analysis the dehydration, disintegration, desorption, and oxidation processes.

A sample pan, made out of a heat conducting ceramic material and can sustain high temperature, is kept inside a furnace of the TGA machine. A precision balance is attached with the pan, which can calculate the weight of the empty pan as well as pan with sample during experiment. A gas pipe is enclosed from an outside gas cylinder with the furnace and a regulator fitted with the cylinder controls the gas flow to uphold the sample atmosphere out of moisture and air. This arrangement is connected with a programmable computer, which displays the entire measurements [14].

In our experiments, a TGA machine of Perkin Elmer, Sweden model number STA 6000 has been used (Figure 1.2.4).

Figure 1.2.4: Photographic image of a TGA machine of Perkin Elmer, Sweden model number STA 6000.
1.2.5 Raman Spectroscopy:

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source [15-16]. Inelastic scattering means that the frequency of photons in monochromatic light changes upon contact with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman Effect. This shift gives information about vibrational, rotational and other low frequency transitions in molecules. Raman spectroscopy can be used to study solid, liquid and gaseous samples.

A Raman system usually consists of four major components: 1. Excitation source (Laser). 2. Sample illumination system and light collection optics. 3. Wavelength selector (Filter or Spectrophotometer). 4. Detector. A sample is usually illuminated with a laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range. Scattered light is gathered with a lens and is sent through interference filter or spectrophotometer to obtain Raman spectrum of a sample. Raman spectroscopy is generally used in chemistry, since vibrational information is specific to the chemical bonds and symmetry of molecules. Consequently, it provides a fingerprint by which the molecule can be identified.

In our experiments, a Raman instrument of Microscope-BX41, TRIAX 550 model with 478 nm excitation source has been used (Figure 1.2.5).

Figure 1.2.5: Image of a Raman instrument of Microscope-BX41, TRIAX 550.
1.2.6 Scanning Electron Microscopy (SEM)-Energy Dispersive X-ray Spectroscopy (EDX):

Scanning electron microscopy (SEM) is a technique for high magnification imaging of the surface [17-18]. An energy dispersive x-ray detector connected with SEM instrument, used to conclude sample’s constituent elements with their atomic and weight percentage, is known as Energy Dispersive X-ray spectroscopy (EDX) [19-20]. The scanning electron microscope has been developed owing to the incapability of optical microscope for high-resolution imaging. The SEM can provide $10^5$ times higher magnified image than that of optical microscope. The key reason of high imaging capability is the use of shorter wavelength (electron wave) in SEM in comparison to optical microscope [21].

In a SEM, an electron beam is generated from a thermal emission source like a heated tungsten filament, or by a field emission cathode. The electron beam of energy ranging from 0.2 keV to 40 keV, is focused to a spot near about 0.4 nm to 5 nm in diameter after passing through a series of electromagnetic lenses. The electron beam scans in a raster fashion over the sample surface for imaging.

When the incident electron beam hits on the sample, the electrons from the atomic orbital of the sample eject as secondary electrons. This leaves thousands of the sample atoms with holes in the electron shells. When the holes are created in the inner shells, the atoms become unsteady. Electrons from higher energy shell drop into the vacant shell to stabilize the atoms. Consequently, the liberated energy radiates as x-rays from atoms. In EDX-detector, these X-rays are analyzed to find the sample’s constituent elements and measure its percentage.

In our experiments, a FESEM of ZEISSL, SUPRA 55 VP (Germany) (Figure 1.2.6) attached with EDX-detector has been used for SEM imaging and EDX analysis.
1.2.7 Transmission Electron Microscopy (TEM)-Energy Dispersive X-ray Spectroscopy (EDX)-Selected Area (Electron) Diffraction (SAED):

Transmission electron microscopes (TEM) can be regarded as complex analytical tools that supply information about the structure, crystallography and chemistry of materials. They may be basic instruments with a thermionic electron source that can provide limited information such as selected area diffraction (SAED) for crystallographic information, energy dispersive spectroscopy (EDX) etc. For most applications in materials science, a minimum of 200 kV accelerating voltage is required for sample penetration and analytical capability in the form of EDX [22-24].

In TEM, a beam is passed through a series of lenses to form a magnified image of a specimen in the area of the objective lens. This image may then be viewed on a fluorescent screen or Charge Couple Device camera. Unlike a light microscope, the TEM functions under vacuum because electrons are easily scattered at atmospheric pressure. The lenses are electromagnetic as opposed to glass, which is opaque to electrons. These lenses are subject to aberrations, which must be corrected electronically. Due to the difficulty of contemporary, analytical TEM most processes are computer controlled for ease of use as there are many unpredictable parameters depending upon the imaging and or analytical techniques being used. Moreover, the light microscope has a resolution limit in the order of 100 nm modern TEM is now capable of atomic imaging in the picometer range.
Chapter 1 Section 2: Characterization Techniques

Energy-dispersive X-ray spectroscopy (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. This spectrum can be performed inside TEM as like SEM-EDX [20].

Selected area (electron) diffraction (SAED) is a crystallographic experimental technique that can be performed inside a TEM [25]. SAED is used mainly in material science and solid-state physics, and is one of the most commonly used experimental techniques in those fields. SAED of nanoparticles or nanocrystals gives ring patterns equivalent to those from X-ray powder diffraction, and can be used to recognize texture and discriminate nanocrystalline from amorphous phases.

In our experiments, a TEM microscope of JEM 2100, JEOL (Japan), (Figure 1.2.7) attached with EDX-SAED detector has been used for TEM imaging, EDX and SAED analysis.

Figure 1.2.7: Photographic image of a TEM-EDX-SAED microscope of JEM 2100, JEOL (Japan).

1.2.8 Fluorescence Spectroscopy:

Fluorescence spectroscopy determines the intensity of photons emitted from a sample after it has absorbed photons. Most fluorescent molecules are aromatic. Fluorescence is a significant investigational tool in many areas of analytical science, due to its high sensitivity and selectivity.
It can be used to explore real-time structure and dynamics both in solution state and under microscopes, particularly for bio-molecular systems [26-27].

Fluorescence takes place when a fluorescent capable material (a fluorophore) is excited into the higher electronic states by absorbing an incident photon and cannot come back to the ground state except by emitting a photon. The emission generally occurs from the ground vibrational level of the excited electronic state and goes to an excited vibrational state of the ground electronic state. Thus fluorescence signals arise at longer wavelengths than absorbance. The energies and relative intensities of the fluorescence signals give information about structure and environments of the fluorophores. A fluorescence emission spectrum is recorded when the excitation wavelength of light is held stable and the emission beam is scanned as a function of wavelength.

In our experiments, a Fluorescence spectrum of LS 55, PerkinElmer (Japan), (Figure 1.2.8) has been used with 280 nm and 440 nm excitation wavelength.

Figure 1.2.8: Photographic image of a Fluorescence spectrum of LS 55, PerkinElmer (Japan).

1.2.9 Weight Loss Technique:

The Weight Loss technique is the best known and simplest of all corrosion monitoring techniques. The method involves exposing a specimen of material (the coupon) to a particular environment, and then removing it after a reasonable time interval for analysis. The basic measurement, which is found from corrosion coupons is weight loss; the weight loss happening
over the period of exposure being expressed as corrosion rate. The straightforwardness of the measurement offered by the corrosion coupon is such that the coupon technique forms the baseline method of measurement in many corrosion-monitoring programs [28].

Weight loss measurement is still the most widely used means of determining corrosion loss, despite being the oldest method currently in use. The technique requires no multifaceted equipment or procedures, merely an appropriately shaped coupon, a coupon holder, and a reliable means of removing corrosion product without disruption of the metal substrate. The technique is extremely versatile, since weight loss coupons can be fabricated from any commercially available alloy. A wide variety of corrosion phenomena may be studied using appropriate geometric designs, which includes, but is not limited to:

- Stress-assisted corrosion
- Galvanic corrosion
- Differential aeration
- Heat-affected zones

Weight loss determination has a number of attractive features that account for its sustained popularity. Advantages of weight loss coupons are that:

- The technique is applicable to all environments - gases, liquids, solids/particulate flow.
- Visual inspection can be undertaken.
- Corrosion deposits can be scrutinized.
- Weight loss can be readily determined and corrosion rate easily calculated.
- Localized corrosion can be identified and measured.
- Inhibitor performance can be easily assessed.
- No sophisticated instrumentation is required to obtain a result.
- A direct measurement is obtained, with no theoretical assumptions or approximations.
- It is appropriate to all corrosive environments, and provides information on all forms of corrosion.

In a typical monitoring program, coupons are exposed for three months duration before being removed for a laboratory analysis. This furnishes the basic corrosion rate measurements at
a frequency of four times per year. The weight loss resulting from any single coupon exposure yields the "average" value of corrosion occurring during that exposure. The disadvantage of this technique is that, if a corrosion upset occurs during the period of exposure, the coupon alone will not be able to identify the time of occurrence of the upset, and depending upon the peak value of the upset and its duration, may not even record a statistically significant increased weight loss.

Therefore, coupon monitoring is most helpful in environments where corrosion rates do not significantly change over long time periods. However, they can provide a useful correlation with other techniques such as Electro-chemical measurements.

In our experiments, Al coupons of Johnson, Matthey, UK, 99.9% pure has been used for weight loss investigation.

1.2.10 Electro-chemical method viz. Potentiodynamic Polarization technique:

Potentiodynamic polarization is an electrochemical method of recording electrochemical potential in independence of measuring time at specified current density [29]. Potentiostat is a tool in which the current is kept stable and potential is varied. There are typically three electrodes, which are employed in it comprising of working electrode, the counter electrode, and the reference electrode. The working electrode is the sample i.e. metal or alloys. The reference electrode supplies a stable “reference” against which the applied potential may be precisely measured. The counter electrode is used to afford the applied current, and as such should be composed of a highly corrosion resistant material, such as platinum or graphite. In this arrangement current is passed between working and counter electrode. The root of controlled current experiments is that a redox (electron transfer) reaction must take place at the surface of the working electrode in order to hold up the applied current.

Corrosion, an electrochemical phenomenon, can be investigated by variety of electrochemical methods [30-32]. Among these, Potentiodynamic polarization technique is the most commonly used for the study of the action of corrosion as well as corrosion inhibition process in variety of environments [33-36].
The study of an electrode reaction of the corrosion can be achieved by determining current as a function of potential since the anodic and cathodic reaction are no longer balanced when polarization happens and a net current will flow from the electronic circuit to metal sample. In corrosion reaction, the oxidation and reduction reactions take place at the electrode surface and the potential of the electrodes are no longer at the equilibrium potential (open circuit potential) during polarization.

Potential-current (E-logi) diagrams are known as polarization diagrams or Tafel plots i.e. the Tafel equation gives the relation between current and potential that is, the current is frequently related exponentially to the activation over-potential ($\eta_A$).

The equation is: 
\[ \eta_A = a + b \log i \]

Where ‘i’ is the current density and ‘a’ and ‘b’ are the Tafel constants, which fluctuate with the nature of the electrode process and the solution.

The current-potential curves are called polarization curves where the potential is on x-axis and the logarithm of the current is on y-axis (figure 1.2.9). The use of a logarithm is necessary because of the broad range of current values that must be exhibited during a corrosion experiment. The value of either the anodic or cathodic current at the open circuit potential ($E_{ocp}$) is called the corrosion current ($i_{corr}$). The equilibrium potential reached by the metal in the absence of electrical connections to the metal is called the open circuit potential ($E_{ocp}$) and the term corrosion potential ($E_{corr}$) is the potential in an electrochemical experiment at which no current flows, which is measured by a numerical fit of current versus potential data. In general, the values for $E_{ocp}$ and $E_{corr}$ will be identical.
Figure 1.2.9: Schematic polarization curve or Tafel extrapolation showing the current density can be obtained with the intercept.

The Tafel equations for both the anodic and cathodic reactions in a corrosion system can be merged together to create the Butler-Volmer equation,

\[ i = i_{\text{corr}} \left\{ \exp(2.303(E - E_{\text{corr}})/b_a) - \exp(2.303(E-E_{\text{corr}})/b_c) \right\} \]

where, \( i \) = the measured cell current in amperes
\( i_{\text{corr}} \) = the corrosion current in amperes
\( E \) = the electrode potential in volts
\( E_{\text{corr}} \) = the corrosion potential in volts
\( b_a \) = the anodic Beta Tafel constant in milli volts/decade
\( b_c \) = the cathodic Beta Tafel constant in milli volts/decade

At \( E_{\text{corr}} \), each exponential term is equal to one. Therefore, \( i = 0 \). Near to \( E_{\text{corr}} \), both exponential terms contribute to the overall current. Finally, as the potential is shifted far from \( E_{\text{corr}} \), one exponential term governs and the other term can be ignored. When this happens, the plot of log \( i \) versus \( E \) becomes a straight line. In practice, a lot of corrosion systems are kinetically controlled and thus follow the above equation. A plot of log \( i \) versus \( E \) is found to be linear on the both sides of \( E_{\text{corr}} \), which is the indicative of the kinetic control for the system. However, in most cases, non-linearities in the Tafel plot were established. This may be owing to some factors such as:
Oxide formation that may or may not lead to passivation and that can alter the surface of the sample. The actual surface and the altered surface may have dissimilar values for the Tafel constants in the equation.

A mixed control process where more than one cathodic and anodic reaction arises concurrently that may make difficult the model.

Analysis of Tafel plot is executed by extrapolating the linear portion of the plot of a log $i$ versus $E$, to their intersection with $E_{\text{corr}}$. The value of either the anodic or the cathodic current at the intersection is the $i_{\text{corr}}$. The examination of inhibited action may be carried out separately on either of these partial processes by comparing the electrochemical parameters in the presence and absence of an inhibitor in a particular electrolyte solution.

In our experiments, the Electrochemical characterizations such as Potentiodynamic polarization study has been carried out using a three electrodes set-up, viz. Al rod having 3.5 cm$^2$ surface area from Johnson, Matthey, (UK, 99.9%) as working electrode, platinum foil (1 cm$^2$) as counter electrode, and a Saturated Calomel Electrode (SCE) as reference electrode. A potentiostat/galvanostat, model VersaStatTM II (Princeton Applied Research, USA) instrument (Figure 1.2.10) has been used for the electrochemical measurements and whole measurements have been performed over a potential range versus SCE at a certain scan rate.

**Figure 1.2.10:** Photographic image of a potentiostat/galvanostat, model VersaStatTM II (Princeton Applied Research, USA).
1.2.11 References:

Chapter 1 Section 2: Characterization Techniques


