

## *MATERIALS AND METHODS*

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### **3. MATERIALS AND METHODS**

The present investigation has been under taken to study the inhibiting efficiency of some derivatives of Benzotriazole on the corrosion of Brass in NaCl media. Selection of sample, Preparation of the specimen, Synthesis of organic inhibitors, Test medium, Techniques used are discussed in details in this chapter.

#### **SAMPLE SELECTION**

Brass is usually the first-choice material for many of the components made in the general electrical and all precision engineering industries. Brass is specified because of the unique combination of properties that make it indispensable when a long, cost-effective service life is required. This combination is matched by in no other material. Brass being a material of choice in various industries encounters severe corrosion during dezincification pickling rotary valves, electroplating, and heat exchanger tubes.

Copper and its alloys are widely used in industry because of their excellent electric thermal conductivity. Brass has been widely used as tubing material for condensers and heat exchangers in various cooling water system brass has been extensively used under different conditions in chemical and allied industries for handling alkalis, acids and salt solutions. Widespread use in cooling water system and its corrosion studies are of immense interest.

#### **SELECTION OF THE MEDIA**

Subscale attack can be commonly observed in alloy substrates in halide-containing environments. As far as a halide is concerned, NaCl is an important corrosion constituent that attacks the components of gas turbines in marine environments, accelerating oxidation of the alloy. The NaCl accelerated oxidation is generally considered the result of the formation of volatile species beneath the oxide scale. Copper and its alloys are applied extensively in marine environments due to their high corrosion resistance in sea water. In addition, copper dissolution in chloride solutions is very important in the electro polishing, electro machining industries and

cooling water system. Due to these reasons attention has focused on the behaviour of brass in chloride solutions. Hence 3% NaCl was selected to study the inhibition effect of derivatives of benzotriazole on brass.

## **INHIBITORS**

To inhibit corrosion small amount of corrosion inhibitors can be added to affected areas and process streams to reduce corrosion rate to acceptable values. In general corrosion inhibitors incorporate themselves in to corrosion product films in such a way as to increase the films capacity to prevent corrosion. The most efficient inhibitors used in industry are organic compounds having heterogeneous atoms like sulphur, oxygen, nitrogen and the compounds with multiple bonds through which they are adsorbed on the metal surface thus assist in inhibition of corrosion and its behave like an effective inhibitor in an industrial application. The polar nature of some molecules also promotes adsorption of the corrosion inhibitor on the metal surface. This films act as barrier is erroneous. The rate of adsorption onto the surface is dependent on the nature of the molecule as well as the concentration of the inhibitor. In the present study the choice of inhibitor is the benzotriazole derivatives, due to the effective inhibiting character of the heterocyclic compounds towards corrosion.

Corrosion inhibitors, widely used in heat exchange equipment, water supply systems, oil and gas processing, marine transport, power facilities and machine manufacture and storage, have found many newer applications, particularly in rocket technology. They have also been introduced into other classical protective media, such as oils, greases, polymeric coatings, cooling agents and brake fluids. Presents the theoretical bases of the use of anticorrosive inhibitors to protect metals, analyzing passivation of the metal surface and the effect of reaction kinetics, describes the protective properties of various inhibitors in neutral electrolyte. A special investigation is devoted to inhibitors used in the NaCl medium of brass.

## **PRE TREATMENT OF BRASS**

A large sheet of brass was pressed cut into rectangular coupons of area  $1 \times 5 \text{cm}^2$ . They were mechanically polished with EASY OFF BANG and wash with distilled water and dried thoroughly before all studies

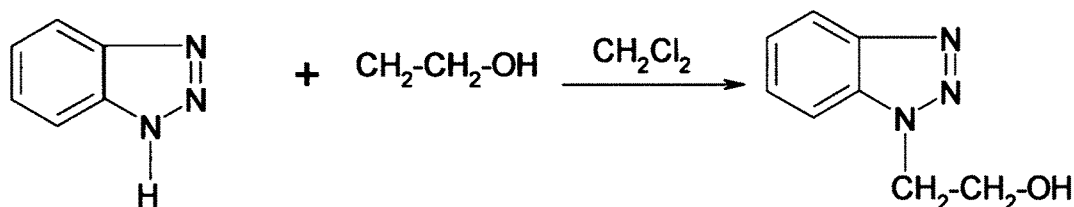
### Composition of brass:

ELEMENT	COMPOSITION
1) Copper	63.63%
2) Zinc	37.88%
3) Nickel	0.047%
4) Lead	0.251%
5) Tin	0.105%
6) Manganese	0.053%
7) Iron	0.035%
8) Phosphorus	0.001%

## PREPARATION OF ORGANIC INHIBITOR

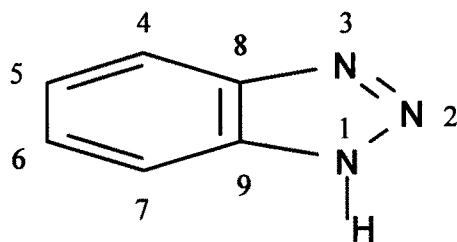
### a) Preparation of 2 - hydroxyl ethyl benzotriazole

To a solution of Benzotriazole (11.9g), in NaOH solution (4.8g in 70ml H<sub>2</sub>O) added 2- chloroethanol (6.7ml). The reaction mixture is heated for 100°C for 2 hours in a round bottomed flask fitted with a water condenser. It is cooled at room temperature and extracted with dichloromethane. The contents are dried over sodium sulphate and the solvent is evaporated. The residue is purified by recrystallization.



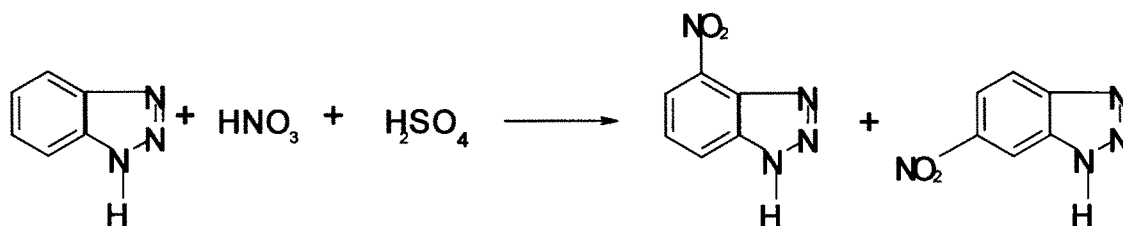
The solvent reagents are used for the synthesis can be purified by standard methods. The thin layer chromatography is used to check the completion of the reaction. A mixture of benzene and ethyl acetate (1:1) was used as developing solvent for 2-hydroxy ethyl Benzotriazole. And the spots were detected with Iodine chamber. Nitration and bromination occur with heteroaromatic organic compounds via an electrophilic substitution mechanism involving the attachment of the nitronium ion (nitryl) on the electron rich benzotriazole ring. In Bromination Br<sup>+</sup> ion is attach in the electron rich benzotriazole ring.

Possible position for attack is 4 and 6 for electrophilic attack



### b) Preparation of nitro benzotriazole

1.346 ml of concentrate  $\text{HNO}_3$  is taken in a 100ml round bottomed flask and added in portions with shaking 1.538ml of concentrated  $\text{H}_2\text{SO}_4$  acid in an efficient fume cupboard. The mixture is kept in ice. A thermometer is placed in the acid mixture. 1g of benzotriazole is introduced. A reflux condenser is fitted in the flask and heated it in a water bath maintained at  $60^\circ\text{C}$  for 40-45 minutes. The flask is removed and poured the contents of the flask into about 100ml of cold water in a beaker. Stirred the mixture well in order to wash out as much acid as possible from the nitro benzotriazole and allowed to stand and filtered. The products are filtered through a small fluted filter paper and dried. A portion of the product obtained is recrystallised with benzene.

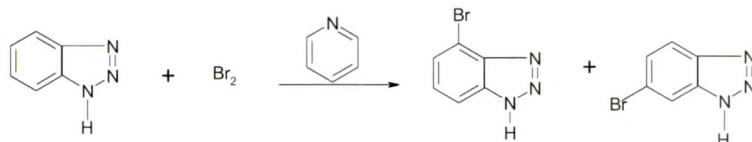


The reaction completion is checked using thin layer chromatographic technique. The eluting solvent mixture combination used is 1:1 benzene, ethyl acetate with 2 drops of alcohol. The spot recognition is viewed using iodine chamber.

### c) Preparation of bromo benzotriazole

1g of benzotriazole and 0.1ml of dry pyridine (dried over potassium hydroxide pellets) is taken in a 100ml round bottomed flask. A reflux condenser is attached to the flask and fitted a device for absorbing the hydrogen bromide gas subsequently evolved. The flask is immersed in a bath of cold water, partially supported upon a tripod and gauze carefully. 4ml of bromine is added through the condenser and immediately

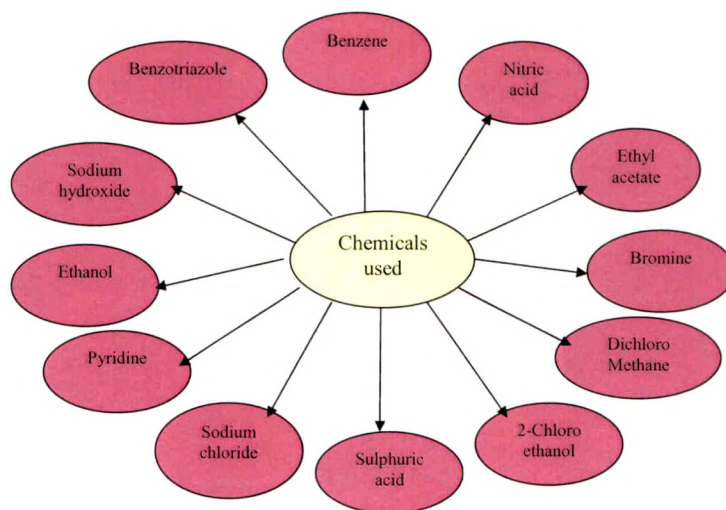
inserted the absorption device into the upper end of the condenser. A vigorous reaction soon occurs and HBr evolved is absorbed by the H<sub>2</sub>O in the beaker. The reaction is carried out in a water bath at a temperature of 25- 30°C for 1 hour. Finally the temperature is raised up to 65-70°C for further 45 minutes. The solid obtained is filtered and dried. A portion of the product obtained is recrystallised with benzene.



The reaction completion is verified using thin layer chromatographic technique. The eluting solvent mixture is ethyl acetate, benzene in ratio of 5:0.5. The spot recognition is viewed using iodine chamber.

### PREPARATION OF INHIBITORS

About 1 g of the dried sample is weighed and dissolved using minimum ethanol. Complete solubility is obtained by keeping it in the sonicating bath for 10 minutes. It is then made upto 1000ml using distilled water which gives the concentration of 1000ppm.



## OPTICAL MICROSCOPE



SOLARTRON (1280B)

CYCLIC  
VOLTAMMETRY

OPTICAL ELECTRON  
SPECTROSCOPY

DIGITAL BALANCE

THERMOSTAT

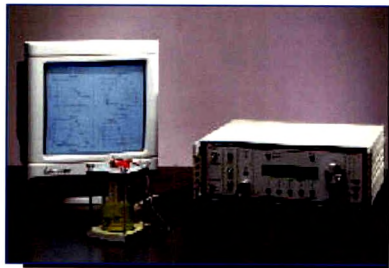
FT-IR spectrometer

SONICATING BATH  
(DIGITAL)

HEATING MANTLE

OVEN

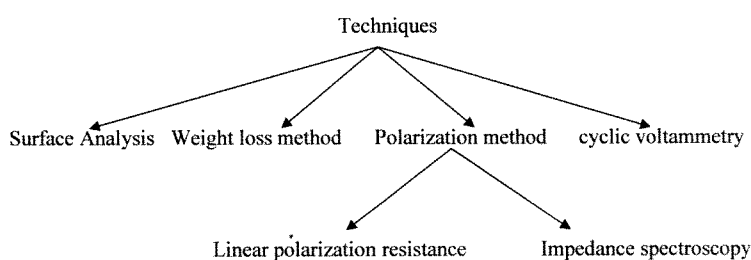
WATER BATH



## CYCLIC VOLTAMMETRY

## TECHNIQUES

The efficiency of the inhibitor under study are evaluated using the following techniques



## WEIGHT LOSS METHOD

It is one of the oldest techniques of monitoring corrosion and is carried out by exposing the weighed metal coupons in the test media for a predetermined period of time. It is then removed and weighed the weight loss obtained for the coupons are then measured. In this present work, pre weighed coupons were immersed in triplicate glass hook into a beaker containing 100ml of acid with and without inhibitor for a particular period of time(3days, 5 days,15 days and 25 days). Afterwards, the coupons were rinsed with distilled water and adherent corrosion products were removed by dissolving in 1M H<sub>2</sub>SO<sub>4</sub> for 10 min. Then the coupons were rinsed with water, cleaned with acetone and dried. Triplicate test were conducted for each experiment and percentage of inhibition efficiency over the exposure period was calculated. The average weight losses of the coupons were recorded.

The experiments were performed by varying the parameters such as

Concentration	:	100ppm-450ppm
Time	:	3, 5, 7, and 25 days
Temperature	:	313 K, 323 K, 333K, 343K, 353K.



## **DETERMINATION OF CORROSION RATE**

The weight loss of a corrosion coupon after exposure to a corrosive environment, expressed as mils (thousandths of an inch) per year penetration corrosion rate is calculated assuming uniform corrosion over the entire surface of the coupon.

$$\text{Corrosion rate} = \frac{534 \times W}{DAT}$$

Where A - Area of coupon (sq in)

D - Metal density of coupon (g/cm<sup>2</sup>)

T - Time of exposure in corrosive environment (days)

## **DETERMINATION OF INHIBITOR EFFICIENCY**

The inhibition efficiencies (IE %) are calculated by the formula

$$IE = \frac{W - W_0}{W}$$

W and W<sub>0</sub> are the weight losses of Brass in the presence and absence of inhibitor respectively.

## **DETERMINATION OF SURFACE COVERAGE (θ)**

The degree of surface coverage (θ) was calculated from the measurement result at various concentrations using the formula.

$$\theta = \frac{W_0 - W}{W}$$

Where, W<sub>0</sub> - Weight loss without inhibitor.

W - Weight loss with inhibitor

The surface coverage values (θ) were then tested graphically for fitting into a suitable adsorption isotherms.

## ADSORPTION ISOTHERMS

The adsorption of the inhibitor may determine the structural change of the double layer thus reducing the rate of electro chemical partial reaction. The knowledge of the adsorption behavior of the inhibitor is important for the definition of its active mechanism various adsorption isotherms.

Langmuir : plot of  $\log (\theta / 1-\theta)$  Vs  $\log C$

Temkin :  $\theta$  Vs  $\log C$

- Where  $\theta$  - Surface coverage  
C - Concentration of inhibitor (%)  
IE - Inhibitor efficiency (%)  
I - Inhibitor concentration in the bulk of the solution

Organic molecules having polar atoms or groups which are adsorbed on the metal surface such adsorbed species may interact by mutual attraction or repulsion. The adsorption isotherms supports that the inhibition of corrosion by the inhibitors is due to their adsorption on the metal surface.

## KINETIC AND THERMODYNAMIC PARAMETERS

### DETERMINATION OF CHANGE IN FREE ENERGY OF ADSORPTION ( $\Delta G$ )

$$-\Delta G = 2.303 \times R \times T (1.74 + \log \theta / (1 - \theta) - \log C)$$

- Where R - 8.314 Joules/ mol  
T - Temperature  
C - Concentration of inhibitor

The change in free energy of adsorption for different temperature at various concentrations of the inhibitor was calculated by using the above the above equation

## **DETERMINATION OF CHANGE OF ENTHALPY ( $\Delta H$ ) AND ENTROPY CHANGE ( $\Delta S$ ) OF ADSORPTION**

The change in enthalpy and change in entropy of adsorption for different concentrations at various temperatures were determined by plotting  $-\Delta G$  Vs Temperature (T) in Kelvin. (According to Gibb's Helmholtz equation.)

$$\Delta G = \Delta H - T\Delta S$$

Where  $\Delta G$  - Change in free energy of adsorption

$\Delta H$  - Change in enthalpy

$\Delta S$  - Change in entropy.

The intercept obtained from the graph shows the change in enthalpy ( $\Delta H$  J/mol) and the slope gives the change in entropy ( $\Delta S$  in J/mol)

## **ELECTROCHEMICAL METHOD**

### **1. POTENTIODYNAMIC POLARIZATION METHOD**

Electrochemical experiments were carried out in a conventional three electrodes at room temperature with a platinum counter electrode and a saturated calomel electrode (SCE) as reference and the brass sample as working electrode (WE). All electrochemical experiment was performed with solatron1280B. The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -1V to 1V with scan rate of  $5 \text{ mVs}^{-1}$ .

### **TAFEL PLOT TECHNIQUES**

In the Tafel plot technique a controlled potential scan can be applied extending in both the anodic and the cathodic direction of corrosion potential for a few hundred mill volts. The linear regions of the plot (applied potential Vs log current) are projected to intercept. This define corrosion current ( $I_{\text{corr}}$ ) and the corrosion potential( $E_{\text{corr}}$ ) and the slope of the linear region is the Tafel slopes (ba & bc). The corrosion rate in mpy can be calculated using the equation

$$\text{Corrosion rate (mpy)} = 0.13 \times I_{\text{corr}} \text{ E W/d}$$

Where  $I_{\text{corr}}$  - The corrosion current density ( $\mu\text{ cm}^{-2}$ )

EW - The equivalent weight of the corroding material

D - The density of the metal /alloy in  $\text{g cm}^{-3}$

IE was calculated by applying the formula

$$\text{IE} = \frac{I_{\text{corr}}(\text{blank}) - I_{\text{corr}}(\text{inhibited})}{I_{\text{corr}}(\text{blank})} \times 100$$

$$\text{IE} = \frac{R_p(\text{inhibited}) - R_p(\text{blank})}{R_p(\text{inhibited})} \times 100$$

Where  $R_p(\text{inhibited})$  and  $R_p(\text{blank})$  are linear polarization resistance in the presence and absence of the inhibitor respectively.

## 2. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPIC TECHNIQUES

Electrochemical impedance spectroscopy techniques were carried out in a frequency range of 10 KHz to 100 MHz at open circuit potential in the presence and absence of the inhibitors.

The inhibition efficiency can be calculated using the equation

$$\text{IE} = \frac{\text{CR}(\text{blank}) - \text{CR}(\text{inhibited})}{\text{CR}(\text{blank})} \times 100$$

Where CR = corrosion rate

$$\text{IE} = \frac{R_{\text{ct}}(\text{inhibited}) - R_{\text{ct}}(\text{blank})}{R_{\text{ct}}(\text{inhibited})} \times 100$$

Where  $R_{\text{ct}}(\text{inhibited})$  and  $R_{\text{ct}}(\text{blank})$  are charge transfer resistance in the presence and absence of the inhibitor respectively.

$$\theta = 1 - \frac{C_{dl}(\text{inhibited})}{C_{dl}(\text{blank})}$$

Where  $C_{dl}(\text{inhibited})$  and  $C_{dl}(\text{blank})$  are double layer capacitance in the presence and absence of the inhibitor respectively.

## CYCLIC VOLTAMMETRY

Cyclic voltammetry (CV) is one of the most frequently used electrochemical methods because of its relative simplicity and its high information content. The waveform of the voltage applied to the working electrode versus the reference electrode is triangular shaped. Since this voltage varies linearly with time, the slope is referred to as the scan rate (mV/s). On the reverse scan, oxidation takes place, during the forward scan, it undergoes reduction reaction. The peak shape of the oxidative and reverse current-potential (I-E) curve is typical for an electrode reaction in which the rate is governed by diffusion to a planar electrode surface. That is, the rate of the electron transfer step is relatively fast compared to that of diffusion. One of the workhorses of electrochemical measurements is cyclic voltammetry, an electrochemical technique that is capable of providing a wealth of information about an electrochemical system. Information related to analytic concentration, electrode reaction kinetics, and diffusional contributions is all contained in a cyclic voltammogram. Experiments described in this investigation should use a platinum electrode, working electrode and reference electrode. Following parameters are adjusted during the study.

### I. Electrode preparation

The response of a species at an electrode surface is strongly dependent on how the electrode has been prepared prior to running the experiment. Typically, electrodes are polished and rinsed before the start of the experiment.

### II. Scan rate dependence

The response observed during a voltammetry experiment depends strongly on the rate that material approaches the electrode surface.

### III. Concentration dependence

The concentration of electro active species present in a solution also plays a major role in determining the response observed in a voltammetric experiment.

Cyclic voltammetry experiments were performed in a typical single compartment three electrode cell using frequency analyzer solatron 1280B. Cyclic voltammogram study was carried out using the following steps.

1. Brass will act as working electrode.
2. Immerse the working, reference, and platinum electrodes in a 100 ml beaker (cell) containing 3% NaCl solutions and inhibitors.
3. Perform a cyclic voltammetry experiment using the following conditions.

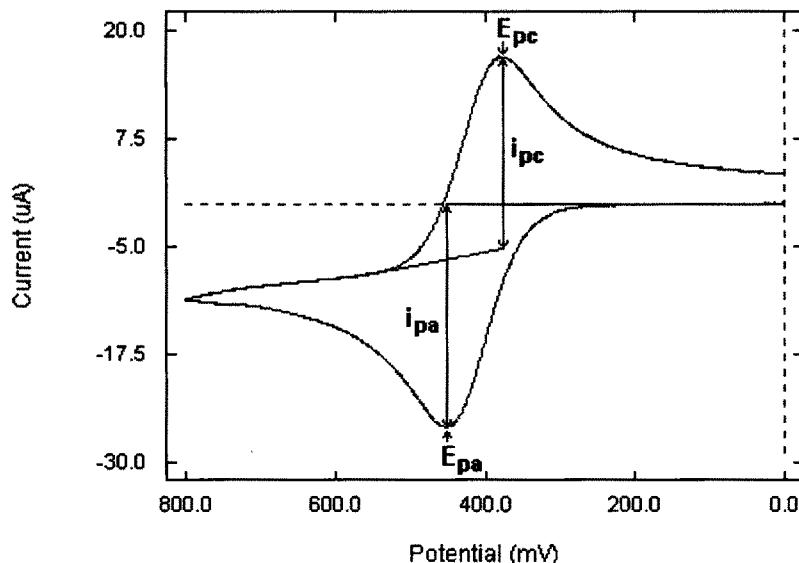
<b>Initial E</b>	-0.75
<b>High E</b>	1
<b>Scan Rate</b>	10 mV/s
<b>Number of Segments</b>	3
<b>Sensitive</b>	10 mV

4. Disconnect and remove the electrodes from the cell, and rinse them with deionized water.
5. Immerse the working, reference, and platinum electrodes in a cell Perform a cyclic voltammetry experiment using the same conditions with different inhibitors such as HEBTA, NBTA and BBTA.

### Study of reactions mechanisms using cyclic voltammetry

The last aspect of CV that we will discuss is its ability to provide information about the Chemistry of redox couples. This is perhaps the most attractive feature of this

technique. For example, if a redox couple undergoes two sequential electron-transfer reactions, two peaks in the voltammogram, one for reduction and other for oxidation



## Electrode reactions and electrode capacitance

Electrochemical system that includes electron transfer along with its equivalent circuit.

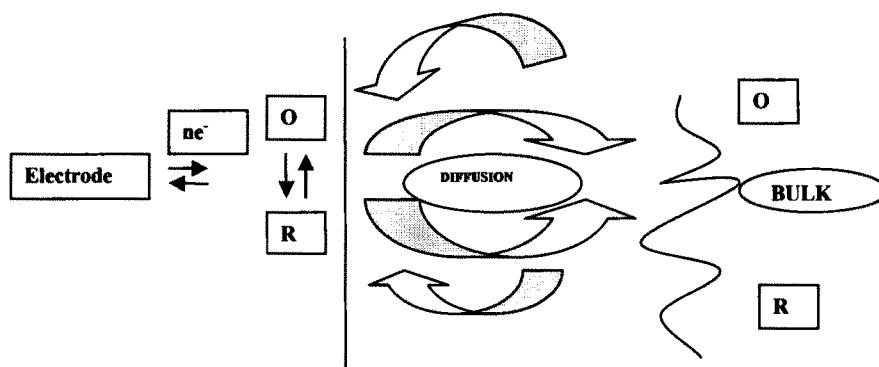


Figure-1

Figure 1 describes the process that occurs in simple electrode reactions. In the case of reduction, a species (O) capable of receiving an electron from the electrode diffuses to the surface, receives an electron and diffuses away from the surface. Current at the surface is generated by the transfer of electrons from the electrode to the redox species. In solution current is carried by migration of ions.

## **SURFACE ANALYSIS TECHNIQUES**

Surface analysis refers to the region between the outermost atomic layer of the solid and a depth of about 2 microns below this outermost layer. Surface analysis is important in thin films for a variety of applications in failure analysis of mechanical parts, in corrosion, in catalysis, in thermonuclear reactors, etc.

Microscopy is any technique for producing visible images of structures or details too small to otherwise be seen by the human eye, using a microscope or other magnification too. It is often used more specifically as a technique of using a microscope. Hence there are three main branches of microscopy, optical, electron and scanning probe microscopy. Optical and electron microscopy involves the diffraction, reflection, or refraction of radiation incident upon the subject of study, and the subsequent collection of this scattered radiation in order to build up an image. This process may be carried out by wide field irradiation of the sample (for example standard light microscopy and transmission electron microscopy) or by scanning electron microscopy. Scanning probe microscopy involves the interaction of a scanning probe with the surface or object of interest. The development of microscopy revolutionized biology and remains an essential tool in that science, along with many others.

### **OPTICAL MICROSCOPY**

Optical or light microscopy involves passing visible light transmitted through or reflected from the sample through a single or multiple lenses to allow a magnified view of the sample. The resulting image can be detected directly by the eye imaged on a photographic plate or captured digitally. The single lens with its attachments, or the system of lenses and imaging equipment, along with the appropriate lighting equipment, sample stage and support, makes up the light microscope.

Most modern instruments provide simple solutions for micro- photography and image recording electronically. As resolution depend on the wavelength of the light. (Image analyzer-Nikon EPIPHOT-DX)



## **REGIONS OF THE IR SPECTRUM**

Over time organic chemists have recorded and catalogued the types and locations of IR absorptions produced by a wide variety of chemical bonds in various chemical environments. The qualitative aspects of IR spectroscopy are one of the most powerful attributes of this diverse and versatile analytical technique. IR spectrum can be used as a finger print for identification of unknown compounds. As a general rule, the most important factors determining where a chemical bond will absorb are the bond order and the types of atoms joined by the bond. Conjugation and nearby atoms shift the frequency to a lesser degree. Therefore the same or similar functional groups in different molecules will typically absorb within the same, specific frequency ranges

FT-IR 8400S model shimadzer instruments were used for recording IR spectrum. The spectrum of HEBTA, NBTA and BBTA were recorded using KBr pellet method.