ABSTRACT

The growing importance and usefulness of electrochemical techniques, their high accuracy and precision of analytical determination, makes these techniques highly dependable for qualitative and quantitative determination of a large number of organic and inorganic compounds in single/oligo systems.

Polarography is a versatile electrochemical technique that makes use of dropping mercury electrode. The unique nature of mercury to form amalgam with many metals, its large hydrogen over potential, continuous renewal of electrode surface area and ability to acquire applied potential instantaneously renders it most useful in analytical studies.

The information which can be drawn from a polarographic wave are identification of the compound, concentration of all the electroactive species present, number of electrons involved in the electrode process, reversibility of the reaction and many more.

Polarography is a convenient technique for measuring electrode potential and for studying electrode reactions. It has therefore large number of applications to inorganic and organic compounds, determination of dissolved oxygen, studies on metal:ligand complex, equilibria, studies on plant products, pharmaceuticals etc.

Looking at the applicability and versatility of polarography, the author has applied this technique to study the behaviour of many organic compounds having various reducible functional groups. The technique was applied to their determination in various samples of industrial products, plant products and biological fluids.
The present thesis entitled 'Electrochemical studies on some organic compounds' incorporates a systematic electrochemical (Direct Current Polarographic and Differential Pulse Polarographic) behaviour of some organic compounds having carbonyl, carboxylic, amino, amide, sulphydryl groups, with their complete analysis. Some unsaturated compounds were also undertaken for the present study. These compounds have been determined in suitable natural origin materials (plant products, body fluids), pharmaceuticals and industrial products (perfumes).

The thesis has been presented in four chapters:

Chapter I: The first chapter of the thesis consists of introductory portion of the subject. The electro-chemical behaviour of organic compounds has been discussed paying special attention to their reduction on DME surface. Electrochemical reduction of an organic compound involves the net transfer of electrons from the electrode to the electroactive substance with a rupture of a chemical bond. A single organic electrode reaction must involve the transfer of one electron, if a free radical is produced or of two electrons, if a bond is completely severed.

A brief introduction to polarography and voltammetry, describing the theory and technique has also been discussed in the chapter.

The theory, instrumentation and applications of polarography and the main factors which play important role in obtaining a well defined wave has been discussed. The various types of currents contributing to the polarographic wave have been discussed in brief.
The compounds which are not directly reduced at the DME surface can be analysed indirectly by a polarographic wave known as catalytic wave. It is the result of hydrogen evolution and it is produced because the molecule contains a labile hydrogen ion.

Besides, this the aim and scope of the present work have also been discussed in the chapter.

Chapter-II: Chapter II talks about the polarographic behaviour of compounds containing sulfhydryl and ketocarboxylic groups. For this purpose, cystine and pyruvic acid have been studied and their determination in biological fluid i.e., blood samples has been carried out and reported in the chapter.

The chapter has been presented in four parts. Part II A speaks about cystine and pyruvic acid. The disulfide cystine in an amino acid which forms an important structural unit of protein. It plays an important role in determining the gross shape of the molecule and serves as a cross link between protein chains. It is an important constituent of insulin. Pyruvic acid is a very important ketocarboxylic acid because it takes part in various metabolic activities of the plant and animal bodies. Pyruvic acid is the main product of glycolysis in tissues where oxygen supply is sufficient. On the other hand in tissues where oxygen supply is insufficient, pyruvic acid is reduced to lactic acid. Accumulation of pyruvic acid indicates the vitamin B₁ deficiency which may lead to heart failure.
A brief discussion about the structure, chemical and physical properties of these compounds has been made in this part of the chapter. Special attention is paid over their importance in biological systems.

In part II B an up to date relevant literature regarding the topic undertaken has been reported.

Part II C contains a detailed description of the experimental part of the work. A general description of the instruments, instrumental parameter, the chemicals used and the procedure adopted has been given. The optimum conditions to get well defined polarographic waves of cystine and pyruvic acid have been reported. Cystine and pyruvic acid have been determined in blood samples of healthy individuals. Their cystine and pyruvic acid content has been compared with blood samples of person suffering from various diseases like cancer, ulcer and heart ailments.

Result and discussion part of the chapter has been incorporated in part II D. It is found that cystine produces a catalytic hydrogen wave with $E_{1/2} / E_p = -1.65 \text{ V} / -1.70 \text{ V} \text{ vs SCE}$ in Brdicka cobaltous$_2$ solution (i.e. 0.1M NH$_4$Cl, 0.1M NH$_4$OH and 1mM CoCl$_2$) at pH 8.5. The cystine content of the blood of healthy individual was found to be 0.016 mg per ml where as it increased by 0.9 mg/ml in blood of cancer patients and 0.76 mg/ml in blood of ulcer patients.

Pyruvic acid produced a well defined reversible polarographic reduction wave with $E_{1/2}/E_p = -0.90 \text{ V} / -1.08 \text{ V} \text{ vs SCE}$ at pH 3.1 in 0.1M NH$_4$Cl and 0.05M NH$_4$OH. The pyruvic acid content of blood of healthy individuals is 0.028 mg/ml where as it
increased up to 3.84 mg/ml in blood of patient suffering from heart diseases. However, it was found to get lowered up to 1.62 mg/ml after angioplasty.

**Chapter III**: Chapter III comprised of the polarographic behaviour of some organic compounds having carbonyl, amide and amino groups and also some compounds having carbon - carbon double bond. Vitamin B₁, B₂, B₆ and vitamin C, acetophenone and benzophenone have been analysed. Their determination in samples of industrial products has been carried out.

Chapter III has been presented in four parts. Part III A gives an introduction to the compounds under study. Vitamin B₁ (Thiamin) was the first water soluble vitamin to be discovered by Funk in 1912. Vitamin B₁ functions in metabolism, as the coenzyme, thiamin pyrophosphate. A deficiency of this vitamin leads to loss of appetite, nervous disorder and increased level of blood and urine pyruvate. The human disease resulting from a lack of vitamin B₁ is called Beri-Beri. The vitamin is found in whole cereals, pork, kidney and yeast. Its requirement for human is 1.4 mg per day.

Vitamin B₂ (Riboflavin) is the heat stable water soluble compound. Lack of the substance is marked by impaired growth and acrodyinia. Its deficiency causes pellagra. The disease is characterised by lesions on the lips. Some good natural sources of B₂ are liver, kidney and heart. Its daily requirement is 3 mg for an adult.

Vitamin B₆ (Pyridoxin) was first identified by Gyorgy in 1934. A deficiency of the vitamin usually results in some form of dermatities and a specific anemia. Good sources of the vitamin are liver, meat, milk and cereal grains. There is no established human requirement but a dietary allowance of 2 mg per day is recommended.
Vitamin C (ascorbic acid) was first isolated by Szent-Gyorgyi in 1928. This is required in the diet of primates to promote normal connective tissue synthesis. Absence of the vitamin results in disease called Scurvy, which is characterized by abnormal bone and dental developments and poor wound healing. Ascorbic acid is found in high concentration in citrus fruits.

Benzophenone is a ketone having soft rose like fragrance and therefore used to impart a longer lasting sweet odour to several types of perfumes. It is also used as a fixative because it lowers the rate of evaporation of perfume constituents.

Acetophenone is a liquid ketone which has a persistent and powerful odour. This is taken advantage of by perfumers in the preparation of many types of perfumes.

Part III B reports an up to date relevant literature on the subject undertaken.

Part III C describes the experimental part of the chapter. The instrumental parameters, chemicals used and the procedure applied, have been discussed in this part. The preparation of analyte and optimum conditions for the well defined polarographic waves have been defined. The effect of pH and concentration on the polarographic wave have been studied. The determination of vitamins in a multivitamin capsule was carried out.

Acetophenons and Benzophenone were determined in various perfume samples. The names of these industrial samples (i.e. the multivitamin capsule and the perfumes) have not been disclosed due to secrecy purpose.
Part III D encorporates the results and discussion of the above experiments. Vitamin B₁ produces a well defined reversible reduction wave in 0.1 M KCl at pH 5.2 with $E_{1/2} / E_p = -1.2V / -1.30V$ vs SCE.

Vitamin B₂ produces a double wave with $E_{1/2} = -0.13V$ and $-0.34V$ vs SCE in BR buffer at pH 1.8. The first wave is adsorption prewave. However, the determination of riboflavin was carried out at pH 6.5. The wave at this pH with $E_{1/2} / E_p = -1.1V / -1.2V$ was proportional to the concentration of vitamin in the solution. Vitamin B₆ produced well defined reversible reduction wave in BR buffer at pH 6.5 with $E_{1/2} / E_p = -1.7V / -1.68V$ vs SCE. The reduction wave of ascorbic acid was obtained in BR buffer at pH 6.5 with $E_{1/2} / E_p = -0.090V / -0.10V$ vs SCE.

The height of reduction waves of all the vitamins was proportional to the concentration of the compounds in the solution. The concentration of vitamins was determined in a multivitamin capsule. It was found that the concentration of vitamin B₁, B₂, B₆ and C was 9.96 mg, 9.92 mg 3.01 mg and 150.1 mg respectively per 240 mg of the capsule powder.

Acetophenone and Benzophenone produced well defined reversible reduction waves over a wide range of pH. However, the determination was carried out in 0.05 M LiCl at pH 2.9. The $E_{1/2} / E_p$ of the wave of Aceptophenon was $-1.5V / -1.6V$ vs SCE and of Benzophenone was $-1.1V / -1.14V$ vs SCE. The determination of Acetophenone and Benzophenons was carried out in various perfume samples. The concentration of Acetophenome and Benzophenone in sample 1 was 3.99 and 3.02 mg/ml respectively. In sample 2 the concentration of Acetophenone was nil where as
Benzophenone was 1.96 mg/ml. In sample 3 concentration of Acetophenone was 10.0 mg/ml and Benzophenone was 2.44 mg/ml.

The results of vitamins and acetophenone and benzophenone content of capsule and perfume samples respectively were in good agreement with the reported by the manufacturer.

Chapter-IV: Chapter IV deals with the polarographic behaviour of compounds containing carbonyl group i.e. carvone. Its determination was carried out in samples of plant products i.e., essential oils of cumin seeds and caraway seeds. This chapter has been presented in four parts.

Part IV A gives an introductory idea of carvone. Carvone is a liquid ketone soluble in a mixture of alcohol and water. It is optically active and occurs in both d and l forms. It is the chief odour bearer of caraway and dill oils. It is used in flavoring perfumery, liquors and soaps.

In Part IV B, a relevant up to date literature of the subject undertaken has been reported.

Part IV C describes the experimental part of the work reported in the chapter. It discusses the chemicals used, the methods of preparing various solutions, preparation of analyte etc. The method of extraction of essential oils from various plants has been described.

The optimum conditions necessary for obtaining a well defined polarographic wave has been described. The determination of carvone in cumin and caraway seeds have been carried out.
Part IV D is the result and discussion part of the chapter. Carvone produces a well defined reduction wave over a wide range of pH with $E_{1/2} / E_p = -1.64 / -1.70$ V vs SCE in 0.2M LiCl. However a well defined wave was obtained at pH 7.3. Hence all the determinations were carried out at this pH. It was found that carvone content in cumin oil was 15% and in caraway oil it was 52.8%.

On the basis of the above studies it could be concluded that polarographic / voltammetric methods are very sensitive, accurate and reliable and can be used for the analysis of organic compounds in samples obtained from industrial, pharmaceutical and biological origin. The method can be recommended for pathological labs for diagnostic purposes.