

ELECTROCHEMICAL DEVICES FOR TRACE ANALYSIS AND POLLUTION CONTROL

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A broad classification of electroanalytical methods into equilibrium potential measurements and impedance measurements is presented. The ion selective electrode approach in the former and polarographic, voltammetric and stripping analysis methods in the latter are the more popular methods and are discussed in greater detail than the other methods. The application of electroanalytical chemistry in Marine Electrochemistry are then traced. Some special advantages of voltammetric method of analysis when compared to atomic absorption spectroscopy are brought out. Anodic Stripping Voltammetry and O_2 sensors are also discussed in some detail.

Key words: Electrochemical devices, trace analysis, anodic stripping voltammetry, ion selective electrodes, marine electrochemistry

INTRODUCTION

The basis of all the electroanalytical techniques is the device that consists of at least two conducting electrodes dipped in a conducting solution which represents a chemical transducer the electrochemical cell. There are a number of concentration dependent physical characteristics possessed by the electrochemical cell that offer themselves as probes for concentration measurements in the so called electroanalytical techniques. An almost bewildering array of these techniques with many more added new ones continuously to the existing ones confront any beginner who may choose to apply them often to the point of creating great confusion. It would be the endeavour of this article therefore to present a proper perspective of these techniques including the modern trends to the reader that helps in the grasp of the important underlying principles of these apparently different techniques in a simple and classified manner and illustrate their particular utility in trace analysis and pollution control.

CLASSIFICATION OF METHODS

Two basic aspects of the electrochemical cells characterise and lend themselves to the various experimental observables of interest in electroanalysis. They are: (i) the equilibrium potential which is a thermodynamic property of the cell and (ii) the cell impedance which is a kinetic property of the cell. The equilibrium potential originates primarily in potential differences between electrodes and solution, developed at participating redox couples and/or by potential developed at membrane/solution junctions (such as in glass electrode) by ion exchange or transport phenomenon. The second factor impedance, governed by the kinetic factor is determined by rate processes such as mass transfer, charge transfer, chemical reaction rates which are associated with the electrochemical reactions at the electrodes. It would be convenient to further subdivide the cell impedance into bulk impedance and the interfacial impedance recognizing that essentially the ohmic resistance that is responsible for retarding migration of ions through the solution constitutes the bulk impedance and the rate process occurring in the course of charge transfer at the electrode-solution interface constitute interfacial impedance. Further two distinct parts of the interfacial impedance viz. the double layer impedance and the faradaic

impedance can be recognized. The electrical double layer existing at the electrode solution interface acts like a capacitor, and permits current flow by virtual charge transfer associated with charging and discharging of the double layer. On the other hand the faradaic impedance accommodates current flow by the actual charge transfer associated with electrolysis. The magnitude of the faradaic impedance is dependent on the rate processes such as diffusion, charge transfer and coupled chemical reactions etc. Incidentally, the interfacial impedance cannot be represented in terms of simple circuit elements but is found to possess properties attributable to a complex collection of resistors, capacitors and diodes, the linear characteristics of the faradaic impedance being represented by a transmission line. Finally, it should be recognized that the two components of the impedance referred to above - the double layer impedance and faradaic impedance - are parallel which implies that one can 'short-out' the other under appropriate conditions.

All electrochemical methods can, therefore, be characterized according to which component(s) of the cell impedance is (are) the controlling factor(s) and whether the equilibrium cell potential manifests itself in the readout.

With the above background we shall examine the various techniques briefly with special reference to the emerging trends.

Methods based on equilibrium cell potentials

Potentiometric measurements with zero impressed current are the best known electroanalytical techniques and receive adequate treatment in most of the text books. The main basic relation employed for concentration measurements is the Nernst equation which connects the concentration of the species in solution with the measured cell (constituted by the measuring electrode and a reference electrode) potential. The cell potential may be employed as a direct monitor of the ion activity or to indicate the end point in a titration.

The popularity of this method currently is due to the fact that a large number of Ion Selective Electrodes (similar to glass electrode for sensing H^+ ions in solution) have been developed in recent years. They are electrodes based on solid membrane, and liquid membrane sensors. A variety of matrices like PVC cellulose acetate

etc. have also been developed as supports for the sensing compounds. In addition, sensors for a large number of organic compounds, biological compounds and sensors for gases all based on the Ion Selective Electrode principles or slight modifications thereof, have emerged in recent times. Typically the range of these ion selective electrodes (or sensors) cover metal ions (Pb^{+2} , Cd^{+2} , Hg^{+2} , Na^{+} , K^{+} , Ca^{+2} , Cu^{+2} , Ag^{+}) anions (CN^{-} , F^{-} , Cl^{-} , Br^{-} , I^{-} , CNS^{-} , S^{2-} , BF_4^{-} , ClO_4^{-} , NO_3^{-}) organics/biological compounds (amino acids, glucose, urea), different gases (NH_3 , SO_2 , CO_2) etc. The list above is only representative and encompasses a wider variety and a larger number of compounds. The applications of these electrodes are catalogued in many standard monographs and other research journals dealing with this topic. Suffices to record here that practically there is no field of activity in industrial analysis such as metallurgical, chemical, food processing, nuclear materials to quote only a few - which is not benefited by the application of these electrodes.

Methods based on ohmic impedance of the cell

The technique of conductivity measurement that utilizes the bulk ohmic impedance property of the cell is a classical one and proved useful particularly as an end point detection method in titrations involving ionic materials. However, it is good to remember that any ionic species contributes to conductivity and hence conductivity measurements have poor selectivity. It is also important to recall that precautions such as use of platinized platinum electrodes and correction for cell capacitance give recognition to the existence and possible undesirable influence of interfacial impedance.

Methods based on Faradaic impedance

A large number of techniques constitute this group much to the annoyance of a beginner (and sometimes even to a seasoned electroanalytical chemist!) who get lost in picking up the right one to carry out the assay on hand. At the outset it may be remarked that this situation has risen due to the simple fact that the required Faradaic impedance of the cell can be obtained experimentally by a variety of measuring techniques. These different techniques therefore differ basically in their electrical input (to the cell) characteristics [potential or current (time variant or time invariant)] and the measurement of corresponding output. Another important factor that contributed to the multiplicity of this type of techniques particularly in recent years is the realization that elimination or correction for the parallel double layer impedance discussed earlier from the total impedance of the cell to arrive at the pure faradaic impedance enhances the sensitivity of the technique several fold.

Beginning with the simple and conventional classical d.c. polarography in which a d.c. potential is applied to a dropping mercury electrode and the resulting electrolysis current measured, the procedure being repeated over a range of potentials covering the depolarization range of a number of metallic or other species (inorganic or organic) to record the d.c. polarogram that gives information on the nature (identity) of the species present in solution (from the half wave potential of the polarographic wave) and its concentration (usually applicable over 10^{-3} - $10^{-5}M$) (from the

magnitude of the diffusion current of the wave), we have a host of variants of this technique. However, all such modified techniques including the most modern and sophisticated techniques are akin to the d.c. polarographic method differing only in the mode of application of the potential and measurement of current, the motivations for doing so having been described already. The list of such techniques covers the following typical ones: a.c. polarography with (i) harmonics measurement and (ii) phase sensitive detection, pulse and differential pulse polarographic methods, square wave polarography, linear sweep voltammetry and oscillographic polarography. Incidentally the term polarography connotes generally the polarization studies carried out on mercury working electrode (Dropping Mercury, Hanging Mercury Drop Electrode) while voltammetry is generally reserved for the description of work carried out on solid working electrodes (such as platinum, carbon etc.)

The sensitivity attained with some of the above mentioned techniques (resulting from the effective removal of the contribution of the double layer impedance) enables the direct analysis of the depolarizers at a level of $10^{-7} M$ - $10^{-8} M$ in solution. However, the popularity of the above electroanalytical techniques has grown several fold giving them an honoured place on par with the Atomic Absorption Spectroscopy in recent years mainly because of their proven utility in the stripping analysis of amalgamable metals at ppb-sub ppb levels. The use of pulse anodic stripping voltammetry and Differential Pulse Anodic Stripping Voltammetry techniques for the simultaneous determination of heavy metals ions such as lead, copper, cadmium and zinc in a variety of samples including environmental samples is well established in recent years. The current efforts are in the direction of making the analysis times much shorter by employing computerized experimentation and innovative programmed potential-time inputs. Typical experiments would involve hooking up the cell to an on-line and interactive experimental set up so that preprogrammed electroanalyses can be performed under a variety of experimental conditions and optimized input-output conditions arrived, data analysed and the required analytical data printed out.

Methods based on double layer impedance

The capacitance of the double layer although depends on the nature and concentration of ions in solution cannot be used as a probe for concentration measurements as it is not very sensitive to the same. However, in the case of certain organic compounds which are surface active (the surfactants), the capacity changes abnormally over a potential range on a mercury electrode. One notices a concomitant current flow in an a.c. polarography experiment as a result of the above capacity change whose magnitude gives an indication of the concentration of the surfactant in solution. The term 'tensammetry' is employed for this technique which has a large clientele among surfactant researchers.

Electroanalytical instrumentation

The advent of operational amplifiers and microprocessors has changed the entire approach to electroanalytical instrumentation. Current concepts of this subject have very little in common with

the classical approach which is discrete technique based. The latest realization on this subject is that the superior versatility and performance of the Op amp approach is such that if one buys a small analogue computer a high quality instrument for any electroanalytical experiment can be easily constructed. There are standard text books now available on the use of Op amp circuitry to electroanalytical instrumentation. A variety of excellent commercial instruments based on this approach are also readily available.

Typical applications in marine electrochemistry

Determination of trace elements in sea water is important from the view points of (i) assessing their natural levels and (ii) monitoring marine pollution. It is now well established that a number of electroanalytical techniques are ideally suited for the above. Several electroanalytical techniques such as potentiometry, conductometry, polarography and voltammetry are known to be in vogue in solving a variety of marine electrochemical problems for several decades. However, it is only in recent times the potentialities offered by some of these techniques particularly in trace analysis are fully realized. The simplicity of the experimental set up, its modest cost, adaptability to on board (of ship) measurements, and finally their intrinsic capability to distinguish the different species of the same element, all helped in making these techniques the chosen ones for critical evaluation of not only the trace levels of different species in sea water but also in monitoring marine pollution.

Trace analysis of marine samples using electroanalytical methods has been most successful for the determination of heavy metals and iodine. A large number of methodologies and techniques have been evolved over years for dealing with samples of inshore origin as well as offshore. Again the offshore samples analysis was carried on board a ship, sampling being done to typically cover the surface waters as well as waters at different depths of the sea. In what follows we shall highlight some of the important techniques with the details of the methodologies evolved.

Single sweep polarography

This is one of the earliest electroanalytical methods that was applied to analyse a number of metals in sea water directly without any prior treatment of the sea water and employing the standard addition technique. Using a dropping mercury electrode and applying a potential sweep of a few hundred mV per second to cover a wide range of cathodic potentials (say upto -1.9 volts) the sweep polarograms recorded oscillographically quickly yield information on the different depolarizing metal ions present in sea water. No additional supporting electrolyte need be added as the dissolved salts present in the natural sample serve as a suitable background electrolyte.

Exhaustive studies have been made on board the ship as well as in laboratory making use of marine samples collected at different locations and at different depths (upto several thousand meters deep under surface of ocean) and the results compared with those obtained by Atomic Absorption Spectroscopy. Relative merits of the techniques Linear Sweep Polarography and AAS, Specially for on board applications have been critically examined. The samples after initial scrutiny directly on the sample (without

pretreatment), a lot of additional information can be simply obtained by running further LSV's on the sample after adding suitable reagents (to provide for complex formation of the different metal ions such as Cu^{+1} , Ca^{II} , Pb^{II} , As^{III} , Sb^{III} , Sb^V , Se^{IV} , Mn^{II} , Zn^{II} , Ni^{II} , Cr^{III} and Cr^{VI} . The complex species found by the above treatment will have different reduction potentials and help in identifying and measuring the concentration of a particular trace element in sea water. By this procedure lot more additional valuable trace element data per sample is obtained without significant increase in operator time. Thus by modifying the background from the predominantly near neutral chloride medium of natural sea water to an alkaline medium involving sodium or ammonium hydroxide or complex thiocyanate, tartrate medium etc it has been possible to estimate different metal ions typically at 5-500 parts per billion range. Other typical examples to illustrate the utility of the LSV in determining different valence states of elements involve: (i) the determination of Cr in sea water. The chromium (III) species gives a well defined polarogram in the presence of KCNS and acetic acid while Cr (VI) does not respond in the medium. On the other hand Cr (VI) species can be measured in NaOH medium where Cr (III) does not respond. (ii) The determination of arsenic present as As^{III} and As^V is possible by first running LSV directly on sea sample followed by running the same experiment on treated (with acid HClO_4 and pyrogallol) sample that yields the data as As^V content. And (iii) determination of iodide/iodate ratio in sea water at parts per billion range is feasible only by LSV technique. After the direct determination of iodate in natural sea water from its reduction wave height, the sample can be treated with chlorine to convert the iodide to iodate and again the LSV run on the sample to obtain the total iodate content. From the difference in the two sets of LSV data iodide present in the sea water is easily obtained.

The single sweep polarographic technique (with sensitivity of about 5×10^{-9} g/ml) is ideally suited for continuous analysis on board the ship with modest investment costs and operator time. Of course the precautions with regard to the usage of a Quartz electrochemical cell, use of ultrapure reagents and extra pure mercury (for d.m.e) and use of fresh sea samples (as storage in plastic or polythelene bottles changes the activity of the trace metals) are to be strictly adhered to for obtaining the reproducible data and achieving the desired precision. While good agreement could be obtained for the trace analysis data for the metals among LSV and AAS techniques, LSV additionally provides information on the individual valence states of the metals thereby giving idea on the nature of species of the metals - an aspect very relevant and important for the environmental pollution (discussed further under ASV procedures). Secondly LSV can provide direct information on trace anions nonmetallic species which are not amenable for AAS analysis.

Anodic Stripping Voltammetry (ASV) of trace metals in sea water:

ASV has gained popularity as the most sensitive electroanalytical tool today and is useful for the trace analysis of metals that amalgamate reversibly with mercury. The higher sensitivity of ASV compared to all the rest of the known electroanalytical techniques is due to the incorporation of a prior concentration (pre-electrolysis)

step wherein the amalgamable trace metal ions in sea water are reduced to the corresponding metal atoms and allowed to amalgamate with the mercury working electrode. In the next stage these amalgams are oxidized using suitable stripping techniques - a large number of them are available - the magnitudes of the stripping signals being indicative of the concentration of the metal under a given set of experimental conditions. It is here that a wide choice of electroanalytical techniques is available for the stripping. It may be remarked that the multiplicity of electroanalytical techniques offers a wide variety in stripping experimentation. The techniques differ in the details employed for the stripping signal format and have their main thrust on removing the contributions of the double layer to the measured signal to enhance the sensitivity of the detection and determination.

The nature of trace metals in natural samples

Trace substances in natural waters such as sea water exist in a variety of forms which had to be defined experimentally. For trace metals in sea water marine chemists have begun to recognize that the various chemical forms or species must be part of a continuum which eventually come to equilibrium, even though, very little can be said about the time scales required to reach equilibrium. The work involving ASV attempts to clarify the situation mainly by adopting the following (i) the study of the shift in trace metal peak potentials and (ii) the study of changes in metal peak heights or peak areas under different experimental conditions. The techniques based on peak potential shifts depend upon the degree of reactivity of the oxidized metal with ligands in the reaction layer. They can describe the species undergoing the reduction only indirectly and are therefore more suitable for model studies and for the determination of stability constants in known media. In the case of peak current measurement techniques, they include pH and complexometric titrations in which natural ligands are titrated with metal ions or alternatively ions are titrated with ligands. All of these depend on being able to discriminate between the 'free' uncomplexed metal and the 'bound' form.

Details of the above approaches have been worked out by different workers and described in the literature, for example, for the speciation of Cu, Cd, Pb, Zn in sea water.

Dissolved oxygen monitors

Among other applications of electroanalytical methods in trace analysis, determination of dissolved oxygen by amperometry with solid electrodes figured most in literature. The two general principles which are exploited to measure dissolved oxygen are: (i) the current density at suitable galvanic elements can be made proportional to the dissolved oxygen concentration in the electrolyte and (ii) a suitable potential can be applied externally to a working electrode and a nonpolarizable anode giving a current which is proportional to the dissolved oxygen current. Platinum, gold or amalgamated gold can be used as cathodes and zinc, iron or lead as the material for the anode. If a large anode is externally

connected to the cathode by a low resistance connection and the resistance of the electrolyte is kept small, the cathode potential is governed by the nonpolarizable anode. Usually the anode compartment is separated from the electrolyte compartment by a diaphragm. As the electrochemical determination of the dissolved oxygen in the electrolyte depends on the determination of the diffusion or boundary current, the electrolyte must be stirred with constant velocity or the cathode must be mounted in a flow-through system. There will be a direct correlation between the electrochemical reduction of oxygen and the measured current if the following conditions are satisfied:

- (1) The cathode potential should not be so negative that hydrogen ions are reduced to hydrogen.
- (2) The potential of the working cathode should be kept constant. This is the case if the anode remains nonpolarized during the measurements
- (3) Ions with a deposition potential less than or equal to that of the reduction of oxygen should not be present in the electrolyte
- (4) The pH of the electrolyte should be constant during the measurement
- (5) The geometry of the electrode must be such as to ensure a linear relationship between measured current and the dissolved oxygen content
- (6) Measurements are to be carried out at constant temperatures
- (7) The electrochemical measurements should be cross checked periodically with the standard Winkler titration for dissolved oxygen.

Large amount of literature is available on the description and performance characteristics of dissolved oxygen monitors that are available commercially.

Recommended References for further Reading

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