

A Review of Polarographic Techniques

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Abstract

The polarographic method has been associated with many successful achievements in many branches of physical and analytical chemistry, particularly in electrochemistry. *Polarography* and *voltammetry* are the names of analytical methods based on current potential measurements in electrochemical cells. With continuous development in technique limit of determination gradually decreases from 10^{-5} M (Classical Polarography) to 10^{-7} M (Differential Pulse Polarography) to 10^{-11} M (Adsorptive Stripping Voltammetry). A large number of pharmaceuticals can be reduced or oxidized in the available potential range and their waves can be used in their determination. It seems that often the therapeutical activity is paralleled by electrochemical reactivity.

Key Words- D.C. Polarography, Differential Pulse Polarography, Adsorptive Stripping Voltammetry.

Introduction

Polarography has come into existence on Friday 10th February 1922 afternoon when Jaroslav Heyrovský measured current-voltage curves in electrolysis of few aqueous solutions with dropping mercury electrode. Such curves appeared to be precisely reproducible, which was a challenge for further exact research. That happened at the Chemical Institute of the Philosophical Faculty of the Charles University in Prague. In the same year Heyrovský became reader and director of the newly established Department of Physical Chemistry. The term “polarography” was coined some two years later, when the polarization curves were recorded automatically by an instrument called “polarograph”.

In 1925 a special issue of the Dutch journal “*Recueil des Travaux Chimiques des Pays-Bas*” brought already a series of 11 papers by Heyrovský, his students and co-workers, under the title “Researches with the dropping mercury cathode, Parts I – XI”. Of the series authors five were Czech and five were of foreign origin. Among the foreigners was the Japanese Masuzo Shikata, who designed the first polarograph together with Heyrovský and who then introduced polarography in Japan.

Polarographs were commercially produced first in Prague in 1929, in the thirties various European as well as American companies joined in making polarographic instruments.

In 1929 under the editorship of Votoček and Heyrovský the monthly journal “*Collection of Czechoslovak Chemical Communications*” was initiated, publishing Czech and Slovak chemical papers in foreign languages, and thereby most of the results of the Prague polarographic school. Polarography was becoming known and used in chemical research and in analytical applications. Heyrovský’s institute was visited by chemists who wanted to learn how to work with the dropping mercury electrode. For longer stays G. Semerano from Italy, W. Kemula from Poland, E. Varasova from Russia, E. Verdier from France and O.H. Mueller from USA came to Prague.

In 1934 Heyrovsky’s assistant Dionýz Ilkovič derived a theoretical equation for diffusion-controlled polarographic current, which put polarography on exact quantitative basis. The Heyrovský-Ilkovič equation then formulated the theoretical shape of polarographic reversible “wave”, i.e., a curve displaying the simple case of electrolytic reduction or oxidation on the dropping mercury electrode, introducing a “half-wave potential”, the value characterizing the electro-active substance qualitatively.

The first textbook on polarography appeared in 1932 in Italian by G. Semerano, Heyrovský's book was published in Czech in 1933. In 1932 the well known German scientist Wilhelm Boettger of Leipzig University visited Heyrovský's laboratory and then he included Heyrovský's chapter on polarography in the second volume of his "*Physikalische Methoden der analytischen Chemie*", which appeared in 1936. The first proposal for the Nobel Prize in chemistry for Jaroslav Heyrovský was submitted to Stockholm by Wilhelm Boettger in 1934.

During his foreign tours Heyrovský lectured on polarography in 1926 in France, in 1933 in USA and in 1934 in USSR.

In Germany an active polarographic group was established at the Bonn University by M. V. Stackelberg, in Austria the pioneer of polarography became H. Hohn at the University of Vienna.

On 9th March 1938 Jean Perrin, F. G. Donnan and Jaroslav Heyrovský were nominated honorary members of the "*Verein Österreichischer Chemiker*"¹.

Furthermore, History of the development of the polarographic method from the birth of Professor Heyrovsky in 1890 until the Nobel Prize award in 1959 was recently described in detail².

The polarographic method has been associated with many successful achievements in many branches of physical and analytical chemistry, particularly in electrochemistry. Following the construction of the polarograph (with the excellent properties of Kucera's dropping mercury electrode³ incorporated) by Heyrovský and Shikata⁴, recording the current—voltage curves has become much simplified contributing thereby to the rapid development of the polarographic method. To date over 20000 papers have been published in this discipline and further applications of the method continue to be investigated. The major practical application of polarographic technique is in analytical chemistry since it makes possible, in a simplified way, the detection and estimation of elements and compounds when present in very small concentrations⁵.

Polarography and *voltammetry* are the names of analytical methods based on current potential measurements in electrochemical cells. The analytical signal is the current – normally a faradaic current – which flows through the cell during the reaction of the analyte at the working electrode with a small surface. The analyte may be a cation, an anion or a molecule. The founder of this method, Jaroslav Heyrovský, introduced the dropping mercury electrode as the working electrode. The electrode consists of a thick-walled glass capillary from which the mercury drops into the sample solution under the pressure of a column of mercury. In his paper *Electrolysis with the dropping mercury cathode* (1922) he called the recorded current-potential curves polarograms and introduced the term *polarography*.

The term *voltammetry* results from *volt-am(père)-metry* and should not be confused with voltammetry – written with one *m* – which is described by IUPAC (International Union of Pure and Applied Chemistry) as being a *controlled-current potentiometric titration*. The terms polarography and voltammetry are frequently used in the reverse sense or are used inaccurately. According to the IUPAC rules, the term *polarography* should always be used when the current-potential curve is recorded by using a liquid working electrode whose surface can be renewed periodically or continuously (e.g. by drops). This includes the classical dropping mercury drop electrode (DME) and the subsequently developed static mercury drop electrode.

Voltammetry includes all methods in which the current-potential measurements are made at stationary and fixed working electrodes (irrespective of their material composition). These include the hanging mercury drop electrode (HMDE), the thin mercury film electrode (TMFE), glassy carbon electrodes (GCE) and carbon paste electrodes (CPE). Working electrodes made of noble metals (e.g. gold or platinum) are used less frequently. Various methods are assigned to the terms polarography and voltammetry; these differ in the measuring technique and the type of electric potential used to excite the determination process.

Polarography is the branch of voltammetry in which a dropping mercury electrode is used as the indicator electrode. It is the electroanalytical technique that deals with the effect of the potential of an electrode in an electrolysis cell on the current that flows through it. The electrode whose potential is varied is called the indicator electrode voltammetric indicator electrodes may be made from quite a large number of materials say for instance mercury, platinum, gold and graphite, having varying shapes and construction. They may be stationary or in motion and the solutions in which these are used may be stationary or quiet⁶.

In the 1950s and 1960s Direct Current polarography was one of the five most frequently used methods in analysis and in investigations of solution chemistry, of both inorganic and organic species. Since that time it has been replaced in determination of heavy metal ions by techniques based on atomic absorption. In investigations of solution chemistry of organic compounds polarography competes with the more widely used spectrophotometry. In organic analyses now predominates mostly the use of separation technique, such as various forms of chromatography and electrophoresis. The DC polarography (DCP) is a physico-chemical technique, based on recording and measurement of current- voltage curves, obtained with a dropping mercury electrode. The quantities measured most frequently on such current-voltage curves are limiting currents and halfwave potentials. The rate of the reduction or oxidation varies with applied potential. For reductions the rate increases with increasingly negative potentials, for oxidation with increasingly positive potentials⁷.

The main contribution of Professor J. Heyrovský was the recognition of the importance of Voltage and its control, the opportunities offered by measurement of limiting current and the possibility to extend electrochemical studies to irreversible systems⁸.

With continuous development in technique limit of determination gradually decreases from 10^{-5} M (Classical Polarography⁹) to 10^{-7} M (Differential Pulse Polarography¹⁰) to 10^{-11} M (Adsorptive Stripping Voltammetry¹¹).

Various types of mercury electrodes developed and used till date are: classical dropping mercury electrode¹²⁻¹³, mercury streaming electrode¹⁴, hanging mercury drop electrode¹⁵, static mercury drop electrode¹⁶, mercury film electrode¹⁷, mercury amalgam electrode¹⁸, chemically modified mercury electrode¹⁹, controlled growth mercury electrode²⁰ etc. Measuring techniques of polarography also has been developed through various stages like: classical DC Polarography²¹, oscillopolarography²², AC Polarography²³, normal pulse polarography²⁴, differential pulse polarography²⁵, voltammetry²⁶, cyclic voltammetry²⁷, anodic stripping voltammetry²⁸, adsorptive stripping voltammetry²⁹, convolution techniques³⁰ and elimination methods³¹.

Advantages of electroanalytical methods:

(a) Electroanalytical methods have certain advantages over other analytical methods. Electrochemical analysis allows for the determination of different oxidation states of an element in a solution, not just the total concentration of the element.

(b) Electroanalytical techniques are capable of producing exceptionally low detection limits and an abundance of characterization information including chemical kinetics information. They are also useful in studies of equilibria, much more than HPLC or GC which often can perturb equilibria in the reaction mixture.

(c) Speed of Electroanalytical methods is important. An analysis can be routinely carried out in less than 4 min, if necessary within fractions of a second. As it is time saving this made electroanalytical methods of choice when analyzing large number of samples.

(d) Electroanalytical methods offer high sensitivity, e.g. differential pulse and square wave polarography have often lower limits at 10^{-8} M, whereas stripping techniques enable determinations up to 10^{-10} M or even 10^{-11} M.

(e) In polarography it is possible to carry out determination directly in the mixture without pre-separations.

(f) The other important advantage of this method is its low cost. The cost of instrumentation for electrochemistry is usually very small in comparison of instrumentation used for HPLC, GC or AAS. Further chemicals used in electroanalysis are also not very costly; for example, high purity solvents are not needed. These factors are of particular importance in developing countries.

(g) Electroanalytical methods can be used both in basic and applied research as well as in routine, practical analysis.

Advantages of Direct Current Polarography:

The DC polarography (DCP) is a physico-chemical technique, based on recording and measurement of current- voltage curves, obtained with a dropping mercury electrode. The quantities measured most frequently

on such current-voltage curves are limiting currents and half wave potentials. The rate of the reduction or oxidation varies with applied potential. For reductions the rate increases with increasingly negative potentials, for oxidation with increasingly positive potentials.

With the increase of the potential in negative direction, the region of potential is reached, where the rate of the electroreduction becomes faster than the transport of the reducible species to the electrode. As a result, the current due to electron uptakes by the reducible species reaches a limiting value and does not increase with a further increase of the negative potential. Its value remains practically constant until a more negative potential is reached at which another reduction process takes place. The transport controlling the limiting current is, in most instances, diffusion of the electroactive species to the electrode, but can also be limited by a rate of a chemical reaction (including catalyzed processes), which occurs in the vicinity of the electrode surface. Alternatively, the limiting current can be affected by adsorption phenomena. Currents due to reduction processes are denoted cathodic.

The situation of electro-oxidations, manifested by anodic currents, is similar, just the processes and currents involved are a mirror image of cathodic ones. The rate of oxidations, involving a loss of one or more electrons by the oxidized species, increases with increasingly positive potentials. After a potential is reached, when the transport of the species to be oxidized becomes the slow step, the anodic current (flowing in the opposite direction than that observed for reductions) reaches a limiting value.

In most cases, the transport processes observed for oxidations are also diffusion controlled. Nevertheless, in some instances it is the rate of a chemical reaction occurring in the vicinity of the electrode surface that becomes the rate limiting step. Kinetic anodic waves result.

When anodic processes are due to the formation of slightly soluble mercury species, anodic waves are often controlled by adsorption.

Measured limiting currents are often a simple function of concentration of the electroactive species. Measurements of limiting currents can be thus used for determination of the concentration of the reducible or oxidizable species. Such measurements can also allow the following and interpretation of rates of chemical reactions, detect adsorption phenomena and enable to distinguish between some types of adsorption.

The possibility to record limiting currents, together with the fact that each drop of the mercury electrode begins with a fresh, clean, well defined surface results in the main advantage of the use of the dropping mercury electrode (DME) – the possibility to obtain well reproducible results, not only with the same apparatus and in the same laboratories, but between different laboratories using different types of equipment.

The accuracy of measurements of limiting currents obtained with DME is typically of the order of $\pm 3\%$ in various types of samples. If needed, with greater care, this can be reduced to $\pm 1\%$. The peak currents obtained for example in linear sweep voltammetry (LSV), cyclic voltammetry (CV) or pulse techniques (like DPP) or square wave techniques (SWP, SWV) in real life samples, like food, natural products, blood or tissues are commonly determined to ± 2 to $\pm 5\%$. Lower reproducibility is frequently observed, when *i*-E curves are recorded with stationary mercury electrodes (such as hanging drop or pool), and even more frequently when electrodes from other metals and materials are used.

Hence the possibility to obtain and measure limiting currents is the main advantage in the use of DME in DCP. Limiting currents can be obtained also with some other techniques, such a normal pulse polarography or rotating disk electrodes.

In some instances, in particular when investigating adsorption phenomena, the timing of the contact of the electrode (the new drop) with the solution is better defined than that during the immersion of a stationary electrode (such as solid or hanging mercury drop) into the solution. For the latter electrodes the period between immersion and the beginning of measurement is often not well defined.

Another advantage of the use of the DME is the high hydrogen overvoltage of mercury in aqueous solutions. This allows following of electroreductions at potentials which are more negative than those that can be reached when other electrode materials are used as cathodes. For example, relative to the platinum electrode, the hydrogen evolution on mercury occurs at about $-1.0V$ within the range of which many metal ions are

reduced on the surface. Wide range of potentials from +0.4 V to about -3.0 V enables following reductions of a wide variety of both organic³² and of inorganic³³ species.

Further advantage of polarography is the possibility to apply it not only in investigations in homogeneous solutions, but also in heterogeneous suspensions. In some instances it is possible to determine both inorganic and organic species present in dispersions of inorganic or organic materials or colloidal solutions.

Mercury can be easily purified as it is a liquid with an atomically smooth surface.

From the theoretical point of view it is of interest that polarography enables examination of equilibria established in chemical reactions, based both on shifts of half wave potentials and on variations of limiting currents with the composition of the examined solution. The same applies to the use of polarography in a study of fast and slower reactions³⁴.

Advantages of dropping mercury electrode

(a) Each drop behaves in exactly same way as preceding one and current measured by galvanometer is accurately reproducible from drop to drop. This is because successive drops are born into solution of identical time, grow at a same rate and reach at the maximum size. Consequently, the currents are reproducible from one drop to next.

(b) The large hydrogen over voltage on mercury the working range is +0.4 to -2.0 V vs. S.C.E.

(c) The current is so small that change in concentration during electrolysis is negligible and thus same solution can be electrolyzed repeatedly.

(d) Small dimension of D.M.E. enable to carry out electrolysis of small volumes as small as 1 ml to 0.5 ml.

(e) The D.M.E. is ideally polarizable i.e. potential follow instantaneous the change of applied voltage.

(f) Several components in the mixture can be detected and estimated simultaneously provided their $E_{1/2}$ values differ by 0.3 volt or more.

(g) Solid products cannot accumulate on the electrode surface, changing its properties as it is possible with solid electrode.

(h) It is much less sensitive to mechanical disturbance than stationary electrode.

Limitations of DC Polarography (DCP)

To be followed by polarography, the investigated species must be electroactive. This means that it can be reduced or oxidized on DME within the available potential range.

Great majority of inorganic cations, acids, or anions can be reduced or oxidized at the DME, but the main area of analytical and theoretical applications of DCP in investigation of inorganic species involves the reduction of cations of heavy metals.

The situation is markedly different when considering oxidative processes. Due to an electro-oxidation of metallic mercury at about +0.4 V, it is possible to follow by DCP only the most easily oxidized species.

Classical polarography fails when solutions are more dilute than 10^{-6} M. At concentration lower than this, the diffusion current is of the same magnitude or even smaller than the contribution that residual currents make to total current.

The classical polarography provides the successful resolution of the waves, in the analysis of mixture only when there is at least difference of 0.1 V in the half wave potentials of compounds responsible for the waves. If the difference is less than this value, overlapping of waves is obtained.

The use of mercury in laboratories is prohibited in some countries. To a chemist it seems natural that, experiments dealing with metallic mercury must be carried out with care.

Principle of technique

In polarography, the electric potential (i.e. voltage) of a growing mercury drop in an electrolyte containing an electroactive species is varied as a function of time and the resulting current due to the electrochemical reaction is measured.

The shape of a Polarogram depends on the method and the type of periodic potential that is applied. For example, in simple DC polarography, the potential applied is a linearly varying voltage called *ramp* and the resulting current response is sigmoidal in shape. The resulting current response in each of the cases has been derived and can be related to the concentration of the species.

Successful Recent Applications of Polarography

These are as follow-

Pharmaceuticals

A large number of pharmaceuticals can be reduced or oxidized in the available potential range and their waves can be used in their determination. It seems that often the therapeutical activity is paralleled by electrochemical reactivity.

Some drugs can be determined using polarography directly, without separation, in some physiological liquids, for example in blood, lymph and saliva. Numerous examples of such applications have been reported early³⁵. In some cases, nevertheless, simple separation procedures, such as extraction, have to be used. In numerous cases of this type the uses of polarography would result in procedures which are as selective, but faster and less expensive to use than applications of the most widely used chromatographic methods.

The situation is different, when the content of the drug is to be determined in matrices, in which the drug is the only electroactive species. Such situation is often faced in analyses of tablets, solutions like eye drops or those used for injections, but also in analyses of some creams and ointments. In such cases the solution to be analyzed should contain the electroactive species at concentrations varying between 1×10^{-3} and 1×10^{-5} M. In such solutions DC polarography is the preferable technique of choice. The method is sufficiently sensitive and measurements of limiting currents are less affected than those of peak currents, used in other electroanalytical procedures, by the presence of electroinactive components of the sample. Presence of components in the sample, like that of starches, of some polymers or long-chain saturated compounds, has little effect on limiting currents, but can affect peak currents, as obtained in differential pulse or square wave variants.

To use polarographic methods for analyses of such simple matrices yields results often much faster, with a better accuracy and without using organic solvents. Pharmaceutical companies will use, whenever possible, officially approved methods of analysis. In the past, some polarographic analytical procedures were listed in numerous Pharmacopoeias.

It should be a goal of electroanalytical chemists around the world to have them listed again. The lower costs, faster results and the possibility for quickly detecting mishandlings by technicians, are powerful arguments.

Analyses of Heterogeneous Systems

Two successful recent applications of the following of processes taking place in non-homogeneous systems are the interactions of heavy metal ions with bile salts³⁶⁻⁴³ and the investigations in suspensions of lignin⁴⁴.

The binding of some heavy metal ions⁴⁵⁻⁴⁷, nitrosamines⁴⁸, bile salts⁴⁹ various pesticides⁵⁰⁻⁵² and lignin⁵³⁻⁵⁵ have been studied.

Basic Studies

Polarography proved to be useful for determination of oxidation states of metals, both in the ionic form and in complexes. Both the equilibria of labile complexes and properties of substitution inert complexes as well as characteristics of metal organic compounds may be investigated by DC polarography (DCP). Structure-reactivity relationships for such species can be established.

In investigations of organic compounds, polarography enables distinguishing the degree of the role of conjugation, of effects of ring size, of substituent effects in Linear Free Energy Relationships⁵⁶ and other structure reactivity relationships.

Rapidly Established Equilibria

Polarography is also a useful tool in investigations of solution chemistry, in particular of equilibria and kinetics. Thus for rapidly established equilibria, both acid-base and of formation of complexes, involving reducible heavy metal ions and a variety of ligands, the equilibrium constants can be determined based on shifts of potentials, using graphs in which these measured quantities are plotted as a function of pH or of a logarithm of ligand concentration. In some instances this enables determination of values of equilibrium constants of reactions involving organic compounds that would be difficult to obtain by other techniques.

Similarly, from the shifts of half-wave potentials of the reduction of metal ions, it is possible to obtain information about stability constants of formation of some labile complexes. Polarographic investigations also enabled detection of some unusual species formed in acid base equilibria, for example of the diprotonated forms of hydrazones⁵⁷⁻⁵⁸ and oximes⁵⁹⁻⁶⁰.

DC polarography is well, for investigation of chemical equilibria preceding the electron transfer systems and for identification of relatively stable intermediates in consecutive electroreductions. **Slowly Established Equilibria**

When equilibria are established slowly, as compared to the rate of the electrode process, the equilibrium constants can be determined based on measurements of limiting currents. The rates of dissociation of OH, SH or NH₃⁺ type acids are too fast to be followed in this way, but some equilibria involving cleavage of the C–H bond are established relatively slowly and can be investigated based on the dependence of the limiting current of the conjugate acid on pH. This approach was possible in establishing the acid-base properties of 3-thianaphthenone⁶¹, ethyl benzoylacetate⁶², ethyl benzoylbenzoates⁶³, ω-cyanoacetophenone⁶⁴ and 1-phenyl-1,3-butanedione⁶⁵.

Kinetics of Fast Reactions

The currents controlled by the rate of a chemical reaction are called kinetic and are observed particularly for compounds undergoing chemical reactions belonging to two large groups: some acid-base equilibria and some hydration-dehydration processes.

Investigations of acid-base equilibria by means of DC polarography are possible, because the reductions of conjugate acids invariably take place at potentials more positive than those of the conjugate base. On i-E curves of such reducible acids, obtained at varying pH-values, it is possible to observe waves of the acid form decreasing with increasing pH and the waves of the corresponding base increasing at more negative potentials with the total limiting current remaining constant. When the wave of the acid form becomes smaller than about 25% of the diffusion limiting current, it becomes controlled purely by the rate of protonation of the base and a kinetic current results. The value of the pH, at which the reduction wave of the acid reaches 50% of the diffusion current, is denoted pK', which is larger than pKa of the acid obtained for example by spectrophotometry. From values of pK' and pKa it is possible to calculate the rate constant of the reaction: base + H⁺ = acid. In this way the rate constants of protonations of anions of some α-ketoacids or maleic and fumaric acids⁶⁶ have been determined.

Bulk Reactions

Polarography can also be used as an analytical tool in the study of kinetics of reactions, where $\tau_{1/2} > 0.5$ min, often as a complementary method to spectrophotometry.

For reactions with half-lives $\tau_{1/2}$ between about 0.5 min and 5.0 min it is possible to record the current continuously as a function of time at a constant potential, corresponding usually to the limiting current. For reactions with $\tau_{1/2} > 5$ min the segments of the i-E curve, where changes of waves occur with time, are recorded after chosen time intervals. On such curves the limited currents at individual times are plotted as a function of time or as a function of a log t. Such approach is possible when dealing with simple zero, first or second order reactions. Some examples of such successful applications of polarography are hydrolyses⁶⁷⁻⁷⁵, nucleophilic additions⁷⁶⁻⁸² etc.

Furthermore, Polarography can be extensively applied in the field of metallurgy, geology and archaeology⁸³, polymer chemistry⁸⁴, colloids and surface active substances⁸⁵, food chemistry⁸⁶, petroleum and fuel analysis⁸⁷, trace analysis⁸⁸, rare earth analysis complex studies⁸⁹.

MODIFIED POLAROGRAPHIC METHODS

The various modifications of classical polarography are as follows:

(i) Oscillographic Polarography

A type of voltammetry using a dropping mercury electrode with oscillographic scanning of the applied potential, used to measure the concentration of electroactive species in solutions. This technique is now being widely used specially in the study of the organic compounds. Much work has been done on the theoretical and practical developments in this technique⁹⁰. This technique has further been subdivided into single sweep and multi-sweep polarography. A review has been published on this topic in the monographs of "Electroanalytical Chemistry" edited by A.J. Bard⁹¹.

(ii) Rapid Scan Polarography

In this technique applied potential is swept rapidly through a range up to 2 volt during part of life time of a single mercury drop. Typically the voltage sweeps occurs during last 2 seconds of the life time of a mercury drop which has a drop time of about 6 seconds. The resultant current-voltage curve has a peak shape.

The resultant peak current is greater than the diffusion current recorded with D.C. polarograph by a factor of ten or even more. The method thus shows enhanced sensitivity and it can be used to make measurements with solutions having concentration 10^{-6} to 10^{-7} M and with a resolution of the order of 0.05 V.

The D.M.E. can be replaced by S.M.D.E. (static mercury drop electrode) and it is possible to use platinum, graphite or glassy carbon electrode, in which procedure is termed voltammetry rather than polarography.

(iii) Square Wave Polarography

High sensitivity and low detection limit (about 10^{-7} M) are obtained with this technique. In this technique the entire potential sequence is applied during the life-time of a single drop. The polarogram is obtained in a few seconds, compared to much longer times with the other techniques. The potential sequence is applied several seconds after the drop birth, in order to take advantage of a larger surface area of the mercury drop.

Barker gave a brief account of this technique in a monograph '*Progress in Polarography*' edited by Zuman and Kolthoff⁹².

(iv) Sinusoidal A.C. Polarography

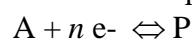
Breyer and Baur have given extensive review of this technique⁹³. In this kind of polarography a constant sine wave a.c. potential of few millivolts is superimposed upon the usual d.c. potential sweep. This technique may be used to study the nature of surface active substances, which produces capacity change at interfaces.

(v) Linear Sweep Voltammetry

Linear sweep voltammetry (LSV) is performed by applying a linear potential ramp in the same manner as DCP. However, with LSV the potential scan rate is usually much faster than with DCP. When the reduction potential of the analyte is approached, the current begins to flow. The current increases in response to the increasing potential.

However, as the reduction proceeds, a diffusion layer is formed and the rate of the electrode reduction becomes diffusion limited. At this point the current slowly declines. The result is the asymmetric peak-shaped I-E curve is scanned linearly to higher values as a function of time in linear sweep voltammetry.

A linear sweep voltammogram (Fig. 2.1) for the following reduction of "A" into a product "P" is shown



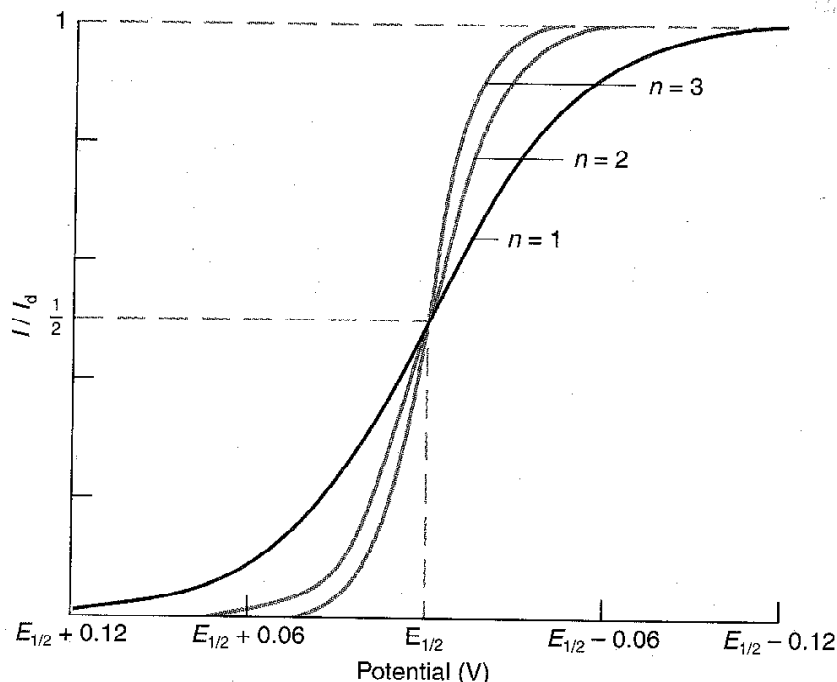


Fig. 2.1 A linear sweep voltammogram

(vi) Cyclic Voltammetry

Cyclic voltammetry (CV) is a type of potentiodynamic electrochemical measurement. In a cyclic voltammetry experiment the working electrode potential is ramped linearly versus time like linear sweep voltammetry. Cyclic voltammetry takes the experiment a step further than linear sweep voltammetry which ends when it reaches a set potential. When cyclic voltammetry reaches a set potential, the working electrode's potential ramp is inverted. This inversion can happen multiple times during a single experiment. The current at the working electrode is plotted versus the applied voltage to give the cyclic voltammogram (Fig. 2.2). Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution⁹⁴⁻⁹⁶.

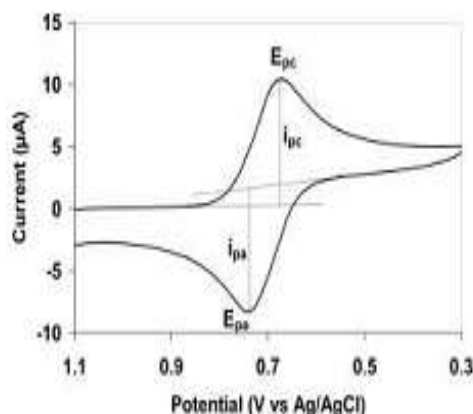


Fig. 2.2 Typical cyclic voltammogram where i_{pc} and i_{pa} show the peak cathodic and anodic current respectively for a reversible reaction.

THE DIRECT CURRENT POLAROGRAPHY : SIMPLE CONCEPTS

Applications of DC polarography are based on the measurement and interpretation of current potential (i-E) curves as recorded at a dropping mercury electrode (Fig. 2.3). The variation of current with a

continuously changing potential can be measured instrumentally to give DC polarogram. The potential axis is defined with respect to a reference electrode, traditionally a saturated calomel reference electrode (S.C.E). In the presence of substance which undergo reduction or oxidation at a dropping mercury electrode, an increase in cathodic (positive) or anodic (negative) current vs potential plot subsequent to this potential range, a region is reached where the current is independent of potential and has a limiting value. The sigmoidal shaped i vs E curve is called a polarographic wave.

The difference between the limiting current and the residual current is called the wave height; usually it depends on the concentration of the electroactive substance in solution. Most analytical applications of both organic and inorganic polarography are based on the increase in wave height with concentration.

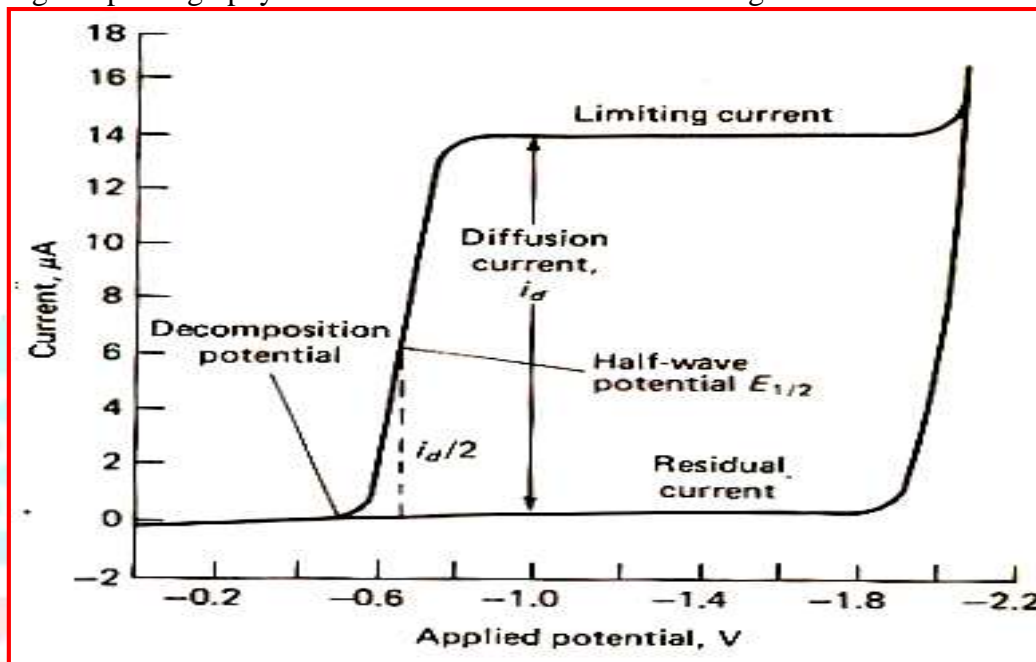


Fig. 2.3 Typical DC Polarogram

Another important parameter is the half wave potential $E_{1/2}$, that is, the potential on a polarographic curve at which the current reaches half of its limiting value. Although, the wave height depends on concentration, $E_{1/2}$ is almost independent of the concentration of electroactive species.

The $E_{1/2}$ value is a characteristic of the compound undergoing reduction or oxidation. Because $E_{1/2}$ depends on the nature of the electrolyzed substance and therefore the composition of the solution, etc., it is a quantity that can be used for qualitative characterization of a substance.

The slope of the wave is also an important ingredient in the overall characteristic or classification of a polarogram. (Fig. 2.4)

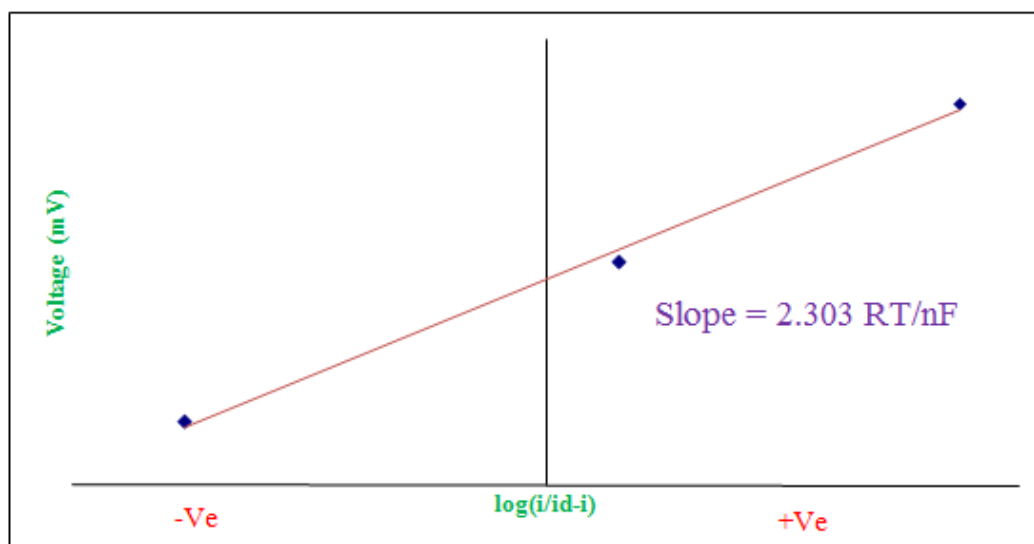


Fig. 2.4 plot E vs. $\log(i/i_d - i)$

From the Fig. 2.4, the nature of electrode process (For $2e^-$ transfer) define as-

If the slope of the graph E v/s $\log i / (i_d - i)$ is 1– 30 mV then the electrode process is reversible. When the value of slope is 30 – 45 mV, the electrode process is quasireversible. If the value of slope is more than the electrode process is 45 Irreversible.

Delahay⁹⁷ was the show that if standard rate constant (k_s) $\geq 2 \times 10^{-2} \text{ cm sec}^{-1}$, DC electrode process can be considered reversible for a drop time of approximately 3 sec. If the magnitudes of k_f and k_b are comparable and k_s lies within the limit $2 \times 10^{-2} \geq k_s \geq 5 \times 10^{-5} \text{ cm sec}^{-1}$, DC polarographic waves⁹⁸ are sometimes called quasi-reversible (drop time $\gg 3 \text{ sec}$). For a totally irreversible electron process the backward reaction can be neglected. Such a condition corresponds to a value of $k_s \leq 5 \times 10^{-5}$ in DC polarography.

Electrode reactions in which a reversible electron transfer step is preceded or followed by slow chemical transformation are called as quasireversible electrode reaction.

The $E_{1/2}$ value of an irreversible reduction wave is therefore considerably more negative than the half-wave potential ($E_{1/2}$) of a reversible reduction wave.

Faradaic and Non Faradaic current

The current flow to and from electrodes is the results of Faradaic and Non-Faradaic processes. These processes can occur alone or simultaneously. A Faradaic process involves the transfer of electrons across the electrode-electrolyte interface. A Non-Faradaic process involves charging of the interface (double layer), much like that of capacitor, without the transfer of electrons. Charge Transfer Electrodes: electrodes at which Faradaic process occur. Electrons are either gained or given up depending on their energy.

By driving the potential of the electrode more negative, the energy of the electrons in the electrode increases thereby given the electrons sufficient energy to occupy vacant states on the species in the electrolyte.

By driving the potential more positive, the electrons in the electrode loose energy, thereby making it possible for electrons from species in the electrolyte to lower their energy by transferring to the electrode.

Pulse Polarography

Pulse polarographic techniques are voltammetric measurements which are variants of the polarographic measurement which try to minimize the background *capacitive* contribution to the current by eliminating the continuously varying potential ramp, and replacing it with a series of potential steps of short duration. The application of a pulse technique to polarography results in a further improvement in polarographic performance, the new instrument being capable of detecting reversibly reduced species at

concentrations as low as 10^{-8} M, and irreversibly reduced species at 5×10^{-8} M. The new instrument also yields both derivative and normal polarograms of much improved types⁹⁹.

In pulse polarography, only a single pulse is applied to the system per mercury drop, late in the drop life. Approximately 20 to 40 milliseconds after the application of the pulse, it is assumed that the charging has decayed to almost zero. Measurement of the current remaining after this time (faradaic) is then made. The polarogram is a plot of the faradaic current produced by the pulse versus the applied potential.

Normal Pulse Polarography

In Normal-pulse polarography (NPP), each potential step begins at the same value (a potential at which no faradaic electrochemistry occurs), and the amplitude of each subsequent step increases in small increments. When the Hg drop is dislodged from the capillary (by a *drop knocker* at accurately timed intervals), the potential is returned to the initial value in preparation for a new step.

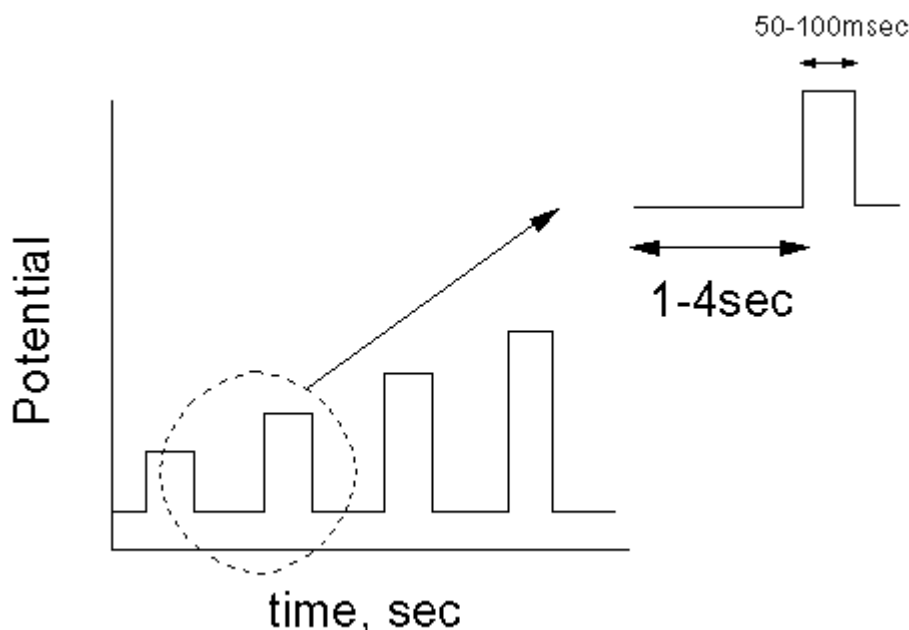


Fig. 2.5 Normal Pulse Polarogram

For this experiment, the polarogram is obtained by plotting the measured current vs. the potential to which the step occurs. As a result, the current is not followed during Hg drop growth, and normal pulse polarogram has the typical shape of a sigmoid. By using discrete potential steps at the end of the drop lifetime (usually during the last 50-100 ms of the drop life which is typically 2-4 s), the experiment has a constant potential applied to an electrode with nearly constant surface area. After the initial potential step, the capacitive current decays exponentially while the faradaic current decays as the square root of time. The diffusion current is measured just before the drop is dislodged, allowing excellent discrimination against the background capacitive current. The normal pulse polarography method increases the analytical sensitivity by 1 - 3 orders of magnitude (limits of detection 10^{-7} to 10^{-8} M, relative to normal [dc polarography](#)). The later form of instrumentation is better form of normal pulse polarography because it subtracts DC effects from the readout¹⁰⁰.

Differential Pulse Polarography(DPP)

From analytical point of view, the sensitivity of DPP is even better than that of NPP. The pulse is sequenced with the dropping mercury electrode so that it occurs once for each drop at exactly the same time after drop dislodgement. The drop lifetime is controlled by a drop-knocker that can be adjusted to give lifetimes that correspond to the pulse repetition period. The pulse is applied immediately before a drop is dislodged when the surface area is at its maximum value. The pulse repetition period and drop time is typically set at 0.5 to 5 s.

The pulse magnitude we typically set between 5 and 100 mV. The current is sampled twice during a drop lifetime: (i) at just before the pulse, and (ii) at just before the drop falls (Fig. 2.6). The polarogram represents the current difference as function of the base potential. The curve is peaked shaped. (Fig. 2.7).

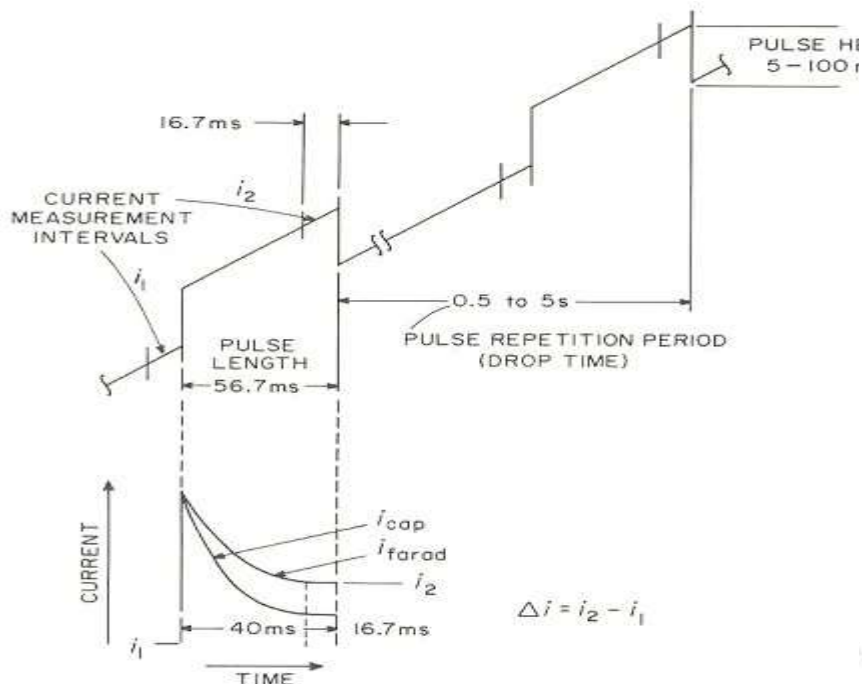


Figure 2.6 Differential pulse excitation waveform and resulting current time behavior

A current measurement is made immediately before each pulse i_1 and at the end of each pulse i_2 as indicated in Fig. 2.6. The difference between these two currents ($\Delta i = i_2 - i_1$) is displayed on the recorder for each pulse. When the pulse is applied, a surge of current occurs immediately to charge the electrode to the new potential. This capacitance current (i_{cap}) decays rapidly. Another component of current is the faradaic current (i_{farad}) due to electrolysis of the electroactive species being determined in the sample. This current decays more slowly as shown in Fig. 2.4, since new material diffuses to the electrode surface. By measuring the current i_2 at the end of the pulse after i_{cap} has decayed, the interference due to i_{cap} is minimized. This results in a lower detection limit for differential pulse polarography than for normal pulse polarography.

The differential pulse polarogram has a peak shape with the peak potential E_p corresponding to $E_{1/2}$ of the normal dc polarogram.

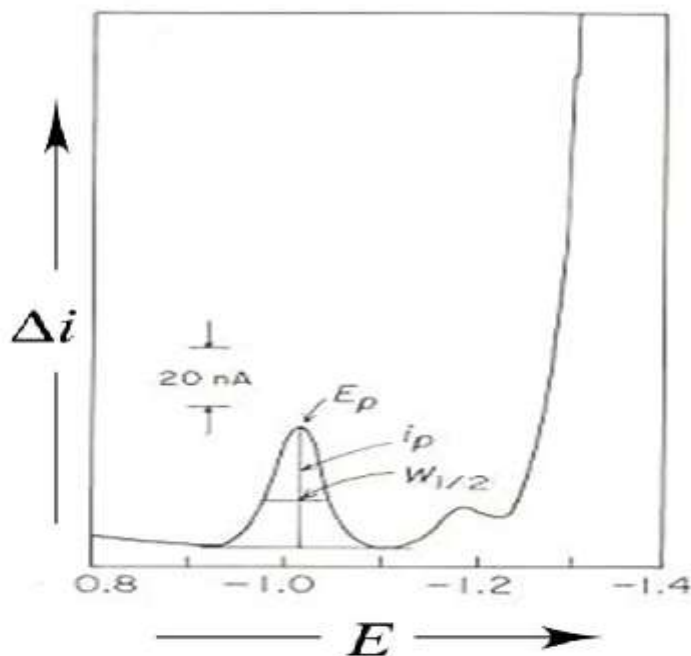


Figure 2.7 Differential-pulse polarogram

The value of E_p is also dependent on the pulse amplitude ΔE as shown in the following equation.

$$E_{\text{peak}} = E_{1/2} - \frac{\Delta E}{2}$$

The width of the wave is related to the electron stoichiometry, n . The peak half-width ($W_{1/2}$) is 90 mV for $n = 1$ and 45 mV for $n = 2$ for a small pulse amplitude.

The peak height i_p is proportional to concentration. Thus, quantitative determinations are made by measuring i_p .

REFERENCES:

1. M. Heyrovský, *Introduction and development of polarography in Prague*.
www.ilg.at/texte/symposium/2009/Heyrovsky_Polarography.pdf
2. P. Zuman, *Crit. Rev. Anal. Chem.*, **31**, 281, 2001.
3. G. Kucera, *Ann. Physik*, **11**, 529, 1903.
4. J. Heyrovsky, *Chem. Listy.*, **16**, 256, 1922.
5. W. Kemula. *Advances in Polarography*, Pergamon Press, Oxford, **1**, 105, 1960.
6. G. Henze *Introduction to Polarography and Voltammetry*, Monograph, Metrohm, **1**, 2003.
7. P. Zuman, *Acta Chim. Slov.*, **56**, 18, 2009.
8. J. Heyrovsky, D. Ilkovic, *Coll. Czech. Chem. Comm.*, **7**, 198, 1935.
9. J. Wang, *Analytical Electrochemistry*, VCH Publishers, New York, **2**, 2000.
10. P. Zuman, *Analytical Letters*, **33(2)**, 163, 2000.
11. J. Heyrovsky, M. Shikata, *Rec. Trav. Chim. Pays-Bas*, **44**, 496, 1925.
12. J. Heyrovsky, *Phil. Mag.*, **45**, 303, 1923.
13. Y. Hann, E. Son, *Arch. Pharm. Res.*, **23(3)**, 197, 2000.
14. J. Heyrovsky, *Chem. Listy*, **40**, 222, 1946.
15. W. Kemula, Z. Kublik, *Anal. Chim. Acta*, **18**, 104, 1958.
16. W. M. Peterson, *Am. Lab.*, **11**, 69, 1979.
17. T. M. Florence, *J. Electroanal. Chem.*, **27**, 273, 1970.
18. B. Yosypchuk, L. Novotny, *Crit. Rev. Anal. Chem.*, **32**, 141, 2002.
19. R. W. Murray, *Electroanalytical Chemistry Marcel Dekker, New York*, **13**, 1984.
20. J. Migdalski, Z. Kowalski, *Chem. Anal.*, **44**, 635, 1999.
21. J. Heyrovsky, J. Kuta, *Principles of Polarography*, Academic Press, New York, **1**, 1966.
22. R. Kalvoda, *Techniques of Oscillographic Polarography*, Elsevier, Amsterdam, **2**, 1965.
23. B. Breyer, H. H. Bauer, *Alternating Current Polarography and Tensammetry*, Interscience, New York, 1963.
24. G. C. Barker, A.W. Gardner, *Z. Anal. Chem.*, **173**, 79, 1960.
25. E. P. Parry, R. A. Osteryoung, *Anal. Chem.*, **37**, 1634, 1965.
26. G. C. Barker, I. L. Jenkins, *Analyst*, **77**, 685, 1952.
27. D. K. Gosser, *Cyclic Voltammetry Simulation and Analysis of Reaction Mechanisms*, VCH, New York, 1993.
28. B. Sanghavi, A. Srivastava, *Electrochimica Acta*, **55**, 8638, 2010.
29. J. Wang, *Stripping Analysis*, VCH, Deerfield Beach, 1985.
30. K. B. Oldham, J. Spanier, *J. Electroanal. Chem.*, **26**, 331, 1970.
31. L. Trnkova, O. Dracka, *J. Electroanal. Chem.*, **348**, 265, 1993.
32. L. Meites, P. Zuman and others, *Handbook Series in Organic Electrochemistry*, CRC Press, Boca Raton, Florida, **1-4**, 1977–1983.
33. L. Meites, P. Zuman and other, *Handbook Series in Inorganic Electrochemistry*, CRC Press, Boca Raton, Florida, **1-8**, 1980.
34. P. Zuman, *Acta Chim. Slov.*, **56**, 18, 2009.
35. U. Tas, K. Yilmaz, G. Somer, *Turk J Chem*, **35**, 201, 2011.
36. G. Feroci, A. Fini, P. Zuman, *J. Electroanal. Chem.*, **29**, 91, 1992.
37. G. Feroci, A. Fini, G. Fazio, P. Zuman, *J. Colloid Interface Sci.*, **166**, 180, 1994.
38. G. Feroci, G. Fazio, A. Fini, P. Zuman, **94**, 119, 1995.
39. G. Feroci, A. Fini, G. Fazio, P. Zuman, *Anal. Chem.*, **67**, 4077, 1995.
40. A. Fini, G. Feroci, P. Zuman, *Chem.* **1**, 69, 1994.
41. G. Feroci, A. Fini, G. Fazio, P. Zuman, *Microchem. J.*, **55**, 382, 1997.
42. A. Fini, G. Feroci, G. Fazio, P. Zuman, *J. Inorg. Biochem.*, **68**, 251, 1997.
43. P. Zuman, A. Fini, G. Feroci, *Encyclopedia of Surf. Colloid Sci.*, 2006.

44. C. A. Paden, A. S. Frank, B. A. Pethica, P. Zuman, L. Jurasek, *ACS Symposium Series*, **214**, 241, 1983.
45. F. Kulik, J. Wieber, B. Pethica, P. Zuman, *J. Electroanal. Chem.*, **214**, 331, 1986.
46. J. Wieber, F. Kulik, B. A. Pethica, P. Zuman, *Colloids Surf.*, **35**, 141, 1988.
47. E. Pehlivan, A. Richardson, P. Zuman, *Electroanal.*, **16**, 1292, 2004.
48. S. Ainso, C. Paden, B. A. Pethica, P. Zuman, *Colloids Surf.*, **33**, 133, 1988.
49. P. Zuman, S. Ainso, C. Paden, B. A. Pethica, *Colloids Surf.*, **33**, 121, 1988.
50. P. Zuman, E. Rupp, *Electrochem. Soc. Proc.*, **95(12)**, 267, 1995.
51. J. Ludvík, P. Zuman, *Microchem. J.*, **64**, 15, 2000.
52. P. Zuman, E. Rupp, *Int. J. Environment Conscious Design Manuf.*, **10**, 23, 2001.
53. P. Zuman, E. Rupp, *Chem. Anal.*, **40**, 549, 1995.
54. P. Zuman, E. Rupp, *Collect. Czech. Chem. Commun.*, **66**, 1125, 2001.
55. P. Zuman, E. Rupp, *Croat. Chem. Acta*, **79**, 57, 2006.
56. P. Zuman, *Substituent Effects in Organic Polarography*, Plenum Press, New York, 1962.
57. M. S. Baymak, H. Celik, J. Ludvík, H. Lund, P. Zuman, *Tetrahedron Lett.*, **45**, 5113, 2004.
58. M. S. Baymak, H. Celik, H. Lund, P. Zuman, *J. Electroanal. Chem.*, **589**, 7, 2006.
59. H. Celik, G. Ekmekci, J. Ludvík, J. Pícha, P. Zuman, *J. Phys. Chem. B*, **106**, 6785, 2006.
60. H. Celik, J. Ludvík, P. Zuman, *Electrochim. Acta*, **52**, 1990, 2007.
61. N. Kucharczyk, M. Adamovský, H. Horák, P. Zuman, *J. Electroanal. Chem.*, **10**, 503, 1965.
62. G. Nisli, D. Barnes, P. Zuman, *J. Chem. Soc. B*, 764, 1970.
63. S. Singer, P. Zuman, *J. Org. Chem.*, **39**, 836, 1974.
64. A. Streitwieser, R. W. Taft, *Prog. Phy. Org. Chem., Science*, **5**, 150, 2009.
65. G. Nisli, D. Barnes, P. Zuman, *J. Chem. Soc. B*, 778, 1970.
66. V. Hanu, R. Brdika, *Chem. Listy*, **44**, 291, 1959.
67. P. Zuman, M. Fedoročko, *Z. Physikal. Chem.*, **209**, 376, 1958.
68. R. Zahradník, P. Zuman, *Collect. Czech. Chem. Commun.*, **24**, 1132, 1959.
69. P. Zuman, R. Zahradník, *Z. Physikal. Chem.*, **280**, 135, 1957.
70. O. Manou, P. Zuman, *Biochem. Biophys. Acta*, **44**, 393, 1960.
71. P. Zuman, O. Manou, *Collect. Czech. Chem. Commun.*, **26**, 2134, 1961.
72. M. Privman, P. Zuman, *Heterocycles*, **37**, 1637, 1994.
73. P. Zuman, Z. Fijalek, *Anal. Letters*, **23**, 1201, 1990.
74. M. Privman, P. Zuman, *J. Electroanal. Chem.*, **455**, 235, 1998.
75. J. Ludvík, J. Jirkovský, J. Urban, P. Zuman, *J. Agric. Food Chem.*, **47**, 3879, 1999.
76. P. Ārsky, P. Zuman, V. Horák, *Collect. Czech. Chem. Commun.*, **30**, 4316, 1965.
77. P. Zuman, V. Horák, *Collect. Czech. Chem. Commun.*, **31**, 827, 1966.
78. V. Horák, P. Zuman, *Collect. Czech. Chem. Commun.*, **31**, 3889, 1966.
79. N. Sleszynski, P. Zuman, *J. Org. Chem.*, **52**, 2622, 1987.
80. F. Rusling, P. Zuman, *Heterocycles*, **26**, 3071, 1987.
81. P. Zuman, Z. Fijalek, *J. Org. Chem.*, **56**, 5486, 1991.
82. P. Zuman, B. Shah, *Chem. Rev.*, **94**, 1621, 1994.
83. N. Verma, K.S. Pitre, *Indian J. Chem.*, **A-31**, 210, 1992.
84. Ukida, S. Usami, T. Kominame, *Talanta*, **12**, 1163, 1966.
85. A.F. Williams, *Advances in Polarography*, Pergamon Press, **2**, 1960.
86. B. Breyer, *Polarography*, McMillan, **49**, 1966.
87. J.H. Karchmer, *Anal. Chem.*, **30**, 80, 1958.
88. K. Gangawat, O. Khatri, S. Kumbhat, *Trans. SAEST*, **39**, 36, 2004.
89. F. Khan, A. K. Kesharwani, *J. Indian Chem. Soc.*, **80**, 47, 2003.
90. J.E.B. Randles, *Trans. Faraday. Soc.*, **44**, 322, 1948.
91. M. Heyrovsky, K. Micka, *Electroanal. Chem.*, Marcel Dekker, **2**, 1972.

92. G.C. Barker, *Progress in Polarography*, Wiley, New York, **2**, 411, 1962.
93. B. Breyer, H.H. Baur, A.C. *Polarography and Tensammetry*, Interscience, New York, 1963.
94. A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, **2**, 2001.
95. Nicholson, R. S.; Irving. Shain. *Anal. Chem.* **36 (4)**, 706, 1964.
96. Heinze, Jurgen *Angewandte Chemie*, **23 (11)**, 831, 1984.
97. P. Delahay, *J. Am. Chem. Soc.*, **75(5)**, 1187, 1953.
98. H. Mastuda, Y. Ayabe, *Z. Electrochem.*, **63**, 1164, 1959.
99. G. C. Barker, A. W. Gardner, *Z. Anal. Chem.*, **173(1)**, 79, 1960.
100. J.H. Christie, R.A. Osteryoung, *J. Electroanal. Chem.*, **49**, 301, 1974.

