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Recent advances in polarographic analysis

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Polarography, originated by Heyrovský in 1922 is again gaining more and more attention among analytical chemists. This is because of the availability of cheap instruments – mainly for differential pulse polarography (d.p.p.) – with higher sensitivity by several orders than the classical d.c. polarograph. New sensitive polarographic methods are applied mainly for trace metal analysis in environmental chemistry and for the determination of organic compounds like drugs, remedies, toxic and carcinogenic compounds, and pesticides. D.p.p., in combination with the stripping method, represents one of the most sensitive analytical methods for trace metal analysis.

New types of sensor are described (static mercury drop electrode, Pt electrode with thermal regeneration, microelectrodes) and their special advantages in application explained. New trends in stripping analysis, such as the analysis of solid substances adsorptive accumulation permitting the analysis of organic compounds, and electrolysis at the interface between two immiscible electrolytes, are discussed. The advantages of semi-integration and semidifferentiation are outlined. Polarography is finding many applications in measurements in flowing liquid systems and in construction of single-purpose gas analysers. The combination of polarography with h.p.l.c. should be one of the most important analytical methods of the near future.

IMPROVEMENTS IN POLAROGRAPHY AND THEIR IMPORTANCE FOR ANALYTICAL CHEMISTRY

After a period of decrease of interest in polarography mainly in the years 1950–70, the importance of polarography quickly regained wide acceptance in all branches of analytical chemistry. The reason lies in the fact that the original method introduced by Heyrovský in 1922 was improved in sensitivity by several orders of magnitude.

The handicap of the original method is in the charging current, which charges the polarographic electrode to the applied potential: at a depolarizer concentration of 10^{-5} M this current is comparable with the faradaic current. An increase in sensitivity of the classical d.c. polarographic method thus requires a discrimination against this unwanted but necessary charging current. Two methods have practically solved the problem. In both of them a sinusoidal voltage or voltage pulse or train of pulses with an amplitude of several millivolts are superimposed on the ramp voltage polarizing the electrode. In the first case the a.c. current is measured after phase-sensitive detection: by measuring the component in phase with the superimposed a.c. voltage, the charging current, which is 90° out of phase, is eliminated. The second method, and up to now the most effective, is based on the fact that by polarizing the electrode by a voltage pulse, the charging current decays with time more rapidly than the electrolytic current. Thus when measuring the current at the end of the voltage pulse, only the faradaic component of the signal is recorded. On this principle square wave polarography (Barker & Jenkins 1952) and pulse polarography (Barker & Gardner 1960) work. At present the most frequently used method is differential pulse polarography (d.p.p.), which raised substantially the worldwide interest in polarography. In this method the electrode is polarized with one voltage pulse (duration approx. 100 ms) at the end of the drop time of the dropping mercury electrode. The current is measured just before the application of the pulse (for 20 ms) and at the end of the duration of the polarization pulse. The difference of both values is then recorded in dependence on the applied voltage. D.p.p. can be used for the determination of all types of ions and compounds as in classical d.c. polarography, but with the advantage of higher sensitivity up to depolarizer concentrations of 10^{-8} M (in some cases to 10^{-9} M). D.p.p. is therefore used not only for the determination of inorganic ions (such as trace metal ions in environmental chemistry) but also for the analysis of organic compounds. The high sensitivity frequently allows the solution of problems that could not be solved with d.c. polarography (and sometimes also not with other methods), e.g. in the field of purity determination of remedies, drugs, determination of their toxic degradation products, and following of metabolites in biochemical and medical applications.

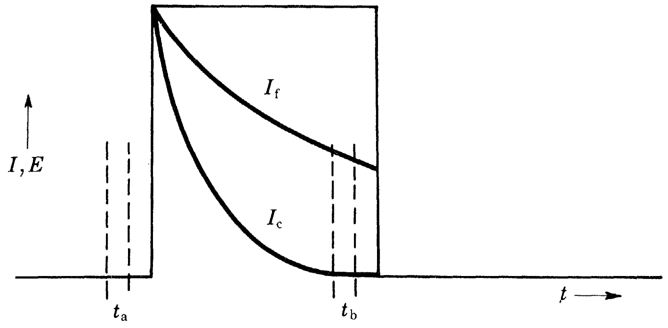

FIGURE 1. A schematic course of the faradaic (I_f) and charging (I_c) currents after the application of a voltage pulse; t_a, t_b, sampling period.

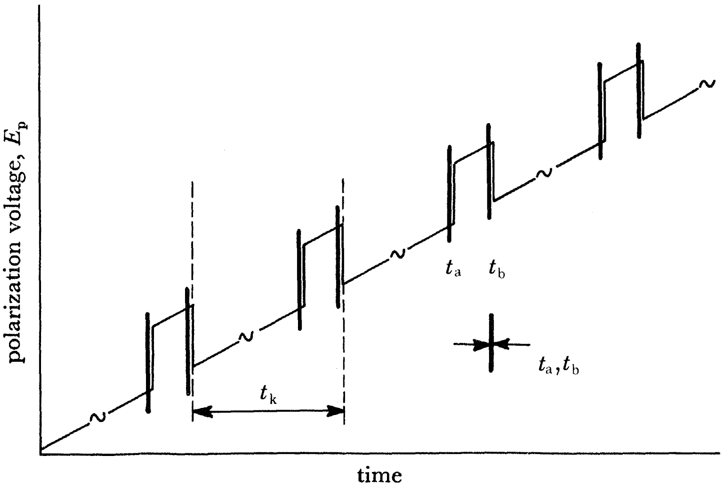

FIGURE 2. A schematic polarization voltage waveform in d.p.p.: t_k, drop time of the d.m.e.; t_a, t_b, current sampling period.

On the market today excellent instruments are available for pulse polarography. Nevertheless, possibilities of further improvements in sensitivity (mainly by improvement of the signal: noise ratio and elimination of the last traces of charging current), automation and data acquisition are being studied and the results rapidly applied in new models of polarographs. For routine analysis the fast-scan d.p.p. was developed, which enables one to record the polarogram within the lifetime of one drop of the d.m.e. with scan rates up to 100 mV s^{-1} (Blutstein & Bond 1976). This method, decreasing the time for the record of the polarogram from minutes to seconds contributes also to some increase in sensitivity due to the higher scan rate. To guarantee the theoretical shape of the polarographic peak in this method the signal processing circuitry must have a very low time constant (round 1 ms) while preserving a good signal: noise ratio (Podolák & Gajda 1982).

NEW TYPES OF SENSORS AND THEIR APPLICATIONS

In close connection with the polarographic equipment the importance of suitable sensors should be mentioned. Instead of the classical dropping Hg electrode a new type of Hg electrode, the static mercury drop electrode (s.m.d.e.), was developed and is now in commercial production (Princeton Applied Research Corporation, U.S.A., Tesla Laboratorní přístroje, Czechoslovakia).

This type of electrode can serve either as a hanging Hg electrode or as a dropping Hg electrode. The electrode can be used also as a dropping electrode 'with constant surface area' after the drop is formed. The polarization of such a dropping electrode in the moment when the surface area is just constant, contributes to the decrease of charging current and enables one to achieve higher sensitivity. The use of the sampled d.c. method (also known as the Tast method) improved by using integration (Kalvoda 1977) of the polarographic current brings practically the same sensitivity as d.p.p. but with a better signal:noise ratio owing to simpler circuitry. In this static mercury drop electrode a needle (Gokhstein & Gokhstein 1962; Novotný 1980*a*) or other kind of valve opens and closes the mercury flow through the capillary. Thus the drop is stopped at a determined instant of its growth. The current measurement is made when the drop area is no longer changing. The movement of the needle or other capillary closing device up and down is controlled electronically from the polarograph. When the s.m.d.e. is used as a dropping electrode, a tapper dislodges the old mercury drop periodically from the capillary. The end of the glass capillary has a spindle-shaped inner space (similar drawn-out capillaries were used by Heyrovský in his first polarographic experiments). The spindle-shaped capillary yields a drop time of high reproducibility and enables adsorption measurements of high precision and sensitivity to be carried out (Novotný 1980*b*).

Many types of solid electrodes were developed from various materials, mainly for following oxidation processes, and are the object of further steady improvement. The disadvantage of these electrodes in comparison with the mercury electrode is in general the poor long-term stability and reproducibility. The regeneration of such an electrode is therefore important. An interesting and effective method for regenerating a platinum wire electrode is based on periodically heating the Pt wire (typically to 600 °C) by passing current from an external current source through it (Tenygl 1980). At this temperature all organic substances are removed from the electrode surface. After this regeneration period the electrode is dipped again into the solution for analysis. This regeneration and measuring step is made periodically and automatically in defined steps lasting several seconds. The thermally regenerated electrode is suitable for the determination of phenols and other compounds that frequently passivate the electrode. Among the frequently used electrodes the graphite-paste electrode is important for the determination of some toxic and carcinogenic compounds (in the microgram to nanogram per gram range) like amines, phenols and polycyclic compounds (Smyth & Osteryoung 1980). For the electrooxidation of organic compounds, rotating disc electrodes with glassy carbon or Pt as electrode material are also frequently used. The fact that an immense number of organic compounds can be reduced or oxidized on this convenient type of electrode is now exploited for electrochemical detection in h.p.l.c. (see later).

For measurements of neurotransmitters (dopamine, adrenalin, serotonin) *in vivo*, special microelectrodes were developed of a diameter of several micrometres, prepared mostly from carbon fibres (Weightman 1981). An interesting property of these electrodes is the steady-state current obtained at their polarization with a voltage scan: thus a plateau of diffusion-controlled current is obtained on the current-voltage curve. A further advantage is the relative insensitivity of these electrodes to the movement of the solution in contrast to larger electrodes. Because of small currents, measurements can be performed in solutions of high resistance.

New trends in stripping analysis

A very powerful tool for microanalysis in the nanogram per gram range and below is the combination of d.p.p. with stripping analysis, where the analysed metal ions or compounds are first accumulated on the electrode and then polarographically analysed by applying the voltage scan. The development of the instrumentation for this method is most oriented towards the automation of the whole working procedure where the sequence of all operations as well as their duration are programmed. Such automation not only simplifies the performance of the analysis but contributes to a higher precision and accuracy, because all parameters are held strictly constant. Fully automatic devices can also be used for field investigation of trace metal ions in natural waters. The stripping current signal is stored in the memory or transferred to a cassette tape for subsequent manipulation by computer (Turner *et al.* 1980).

Anodic stripping analysis is mostly used for heavy metal trace analysis in environmental chemistry. The method for trace analysis of Cu, Pb, and Cd in sea water is the most sensitive method that can be used at the site of sample collection (Nürnberg 1979). The anodic stripping method, in contrast to other methods (like a.a.s.), allows the discrimination of free metal ions from metals bound into a complex. The speciation of metal ions in sea water is gaining more and more interest among environmentalists (Nürnberg *et al.* 1976). The advantage and reliability of stripping water analysis can be demonstrated by the fact that the method was established as a norm for the simultaneous determination of Cu, Cd, Pb, and Zn as well as Pb and Tl in drinking water (Deutsche Einingkeitsvorschritten zur Wasseruntersuchung, B.R.D.) (Klahre *et al.* 1978). According to Eisner & Mark (1970), stripping voltammetry is more sensitive than neutron activation analysis for the determination of silver at the 10^{-11} M level in connection with weather modification by cloud seeding by silver iodide. Also, aerosols of heavy metals can be determined by the stripping method (Grebenovský *et al.* 1977; Sturrock & Mendez-Merced 1977). With cathodic stripping polarography, compounds yielding mercury salts on the Hg electrode can be determined, as well as compounds after their oxidative accumulation (Smyth & Davidson 1980). An interesting field is the stripping analysis of solid substances (Brainina & Vydrevich 1981). Information is provided mostly by the electrochemical transformation of solid substances and of products of their dissolution. A carbon paste containing the electroactive substance is used for these investigations.

In stripping analysis the adsorptive preconcentration of surface-active compounds at the electrode surface can also be used. The desorption peak is then recorded during the stripping process. The height of this tensammetric peak is partly dependent on similar parameters to those in the electrolytic stripping mode as well as on the surface-activity properties of the respective compound. Thus many electro-inactive organic compounds such as alkaloids, remedies and detergents can be determined in the microgram to nanogram per gram range. The adsorptive accumulation effect can also be exploited for the adsorptive stripping analysis of electro-active surface-active organic compounds or some metal ions (by using a base solution containing complex-forming compounds) like GeO_2, Cu^{2+}, Ni^{2+} and Co^{2+}; the method is suitable mainly for metals where amalgam formation is complicated, or for metals with a low solubility in mercury. In this case the reduction peak of the adsorbed compound is recorded. For details see Kalvoda (1982).

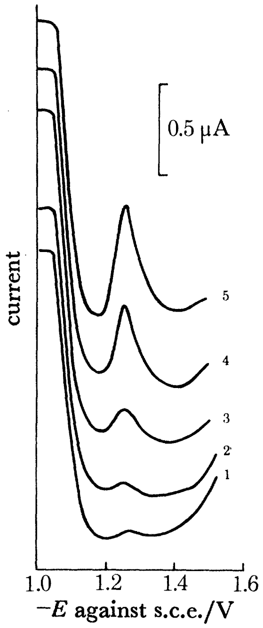

FIGURE 3. Stripping analysis with adsorptive preconcentration: 8×10^{-8} M codeine in 5 M NaOH. Curve 1, normal DPP record without preconcentration; curve 2, unstirred during preconcentration step, accumulation time 60 s; curve 3, as curve 2, but accumulation time 180 s; curves 4 and 5, stirred during preconcentration step, accumulation times 20 and 40 s respectively. Accumulation potential −1.0 V against s.c.e.

For stripping analysis various types of electrodes, electrode systems and techniques have been developed (Vydra *et al.* 1976; Kalvoda 1980). As an example one may take thin-layer cells with a volume capacity of some microlitres, where the entire volume of solution undergoes electrolysis. Sophisticated constructions of electrodes permit the elimination of interfering ions. Stripping analysis can be combined with some other separation techniques (extraction, preconcentration on columns, continuous exchange of the analysed solution for another electrolyte, etc.). The adsorptive stripping method can be combined with liquid chromatography.

A new area in analytical chemistry is electrolysis at the interface between two immiscible electrolyte solutions, which can be exploited in stripping analysis (Mareček & Samec 1982*b*): some alkali and alkaline earth metal cations can be transported across the interface between the immiscible electrolyte solutions when a suitable ionophore is present in the organic phase. A hanging electrolyte drop electrode is used for these measurements. Figure 4 shows the d.p.p.

stripping curve of Ba^+. By this type of stripping analysis acetylcholine was also determined (Mareček & Samec 1982*a*). Electrolysis at the interface of two immiscible electrolyte solutions has also been used for the analysis of macrocyclic antibiotics (Koryta 1980*a*).

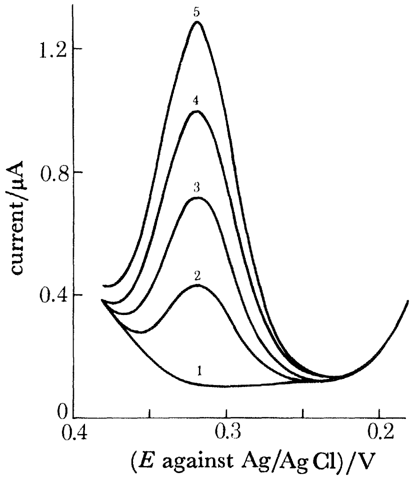

Figure 4. Stripping d.p.p. curves of barium ions in 5×10^{-3} M tetrabutylamonium-tetraphenylborate in nitrobenzene and 2.5×10^{-3} M $MgCl_2$ in H_2O, with the use of a hanging electrolyte drop electrode. Concentration of Ba^{II}: curve 1, 0×10^{-6} M; curve 2, 1; curve 3, 2; curve 4, 3; curve 5, 4. Accumulation time 60 s at 0.380 V. Mareček & Samec (1982*b*).

AUTOMATION AND MATHEMATICAL OPERATIONS WITH POLAROGRAPHIC DATA

From the historical point of view the Heyrovský-Shikata polarograph is the first automatic instrument introduced to analytical chemistry yielding a permanent record of the performed analysis. The full automation of polarographs, as of other physicochemical or physical instruments used in analytical chemistry, is permitted by means of minicomputers and microcomputers. The computer controls the function of the whole equipment and also enables data acquisition. With the polarographic curve stored in the memory many mathematical operations can be performed, like averaging at repeated accumulation, baseline subtraction and resolution of overlapping peaks, as well as some transformations of the raw data obtained. The instrument frequently prints the peak potential and sample concentration onto the record of the polarographic curve. The analogue presentation of the polarographic curve still remains very important, because the digital readout (which occurs with many measuring instruments yielding only digital data) sometimes masks deficiencies that are readily apparent on the polarographic curve. It should also be kept in mind that the microprocessor cannot improve improperly collected data.

A perspective mathematical operation with the polarographic current is semi-integration (Goto & Oldham 1973) and semi-differentiation. Semi-integration brings an advantage for work with solid electrodes because the signal obtained is constant in time and proportional to the concentration of the depolarizer. The shape of the semi-integral current–voltage curve is similar to the d.c. polarographic curve. The method will perhaps find practical applications mainly in the analysis of slowly flowing solutions in various types of analyser. Another application is to sweep methods on constant electrode area for the analysis of multicomponent systems, mainly with overlapping peaks. Semi-differentiation permits a better peak separation than with the normal voltammetric curve and hence a better chance is given of peak height measurement (Goto & Ishi 1975).

Polarography in flow-through systems and h.p.l.c.

Polarography and voltammetry are not only used for analysis of discrete samples but are finding many applications for measurements in flowing liquid systems, of course mostly in the amperometric mode: this means that the current is measured at a fixed electrode potential. In the flow-through systems the electrodes in the vessel are the most important parts of the whole device, because the measuring electrode is here often working under stringent conditions. This is so mostly with solid electrodes, which can, and frequently do, lose their sensitivity and long-term stability due to passivation or adsorption. It is therefore often necessary to provide for reactivation or regeneration of the electrode mainly in measurements continuing for long periods, as is usual in industrial applications, environmental analysis, etc. Sometimes a device is included in the system for a periodically calibration and zeroing, with a feedback to the signal processing circuit. Care must be devoted also to temperature control, sample flow rate, oxygen elimination and the stability of the reference electrode.

The main application field of flow-through systems is in the electrochemical detection of electroactive compounds in h.p.l.c., where the sensitivity of polarography is combined with the excellent separation capabilities of h.p.l.c. An amperometric mode is mostly used for these measurements. On the market there are different types of detectors with either a Hg electrode (for electroreduction) or a graphite paste, glassy carbon or platinum as electrode materials. These last electrodes are used mostly for electrooxidation processes (drugs, alkaloids, pharmaceutical preparations, vitamins, pesticides, carcinogenic compounds, phenolic compounds, polycondensed hydrocarbons, etc.) (Smyth 1980). The cells are constructed mostly as thin-layer cells or as wall jet arrangements. The detection limit is in the nanogram, sometimes in the picogram, region. Similar detectors are finding application in the flow-injection method (Iwaska & Ryan 1980). It can be expected that h.p.l.c. with electrochemical detection will in the near future be one of the most important analytical methods. More details on flowing liquid systems are given by Rucki (1980).

Single purpose analysers

Single-purpose gas detectors, analysers and monitors for SO_2, CO, O_2, NO_x, CN^-, Cl_2 etc., which are also available on the market, are based mainly on polarographic or voltammetric principles. They work mostly with electrocatalytic porous or membrane electrodes. Amperometric enzyme electrodes are also used for these purposes. The trace analysis of aqueous solutions in which the solute of interest forms a volatile electroactive product that is flushed from solution by using an electroactive gas is performed with s.c. pneumatoamperometry (Gifford & Bruckenstein 1980). A gas-porous electrode is used. The detection limit for Hg^{II}, As^{III}, I^- and IO_3^- is in the nanogram per gram range or lower.

Conclusion

Recent developments in polarography are currently finding more and more practical use in all branches of science, technology and everyday life where chemical analysis is used. As this article cannot cover all recent advances and future trends in polarography, the following monographs are recommended for further information: Bond (1980), Fatt (1976), Koryta (1980*b*), Smyth (1980) and Vydra *et al.* (1976).

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Discussion

J. D. R. Thomas (*Chemistry Department, U.W.I.S.T., Cardiff, U.K.*). What are the factors involved in establishing suitable conditions for the tensammetric–adsorptive application of polarography, and how can the accumulation time be selected for routine use?

R. Kalvoda. The necessary conditions for the adsorptive accumulation of the compound under investigation are first studied with the dropping Hg electrode (and differential pulse polarography) for a record of the tensammetric curve in the whole accessible potential range. The optimal supporting electrolyte, the optimal adsorption potential and all usual parameters are worked out in these studies. Adsorptive accumulation can be used only in cases where the compound yields a well developed tensammetric peak in the concentration level from 10^{-5} to 10^{-6} M. (Such strongly adsorbable compounds have usually an adsorption coefficient of about 10^{-3} M^{-1} l or higher in the respective supporting electrolyte.) The accumulation effect is then proved in that way – now with the hanging Hg-drop electrode – that after the record of the curve with the tensammetric peak the same curve but after previous adsorptive accumulation at the most suitable potential (lasting 1–2 min in unstirred or 30 s in stirred solutions) is repeated: an increase in the peak height is the proof of accumulation. From this experiment the accumulation time for routine use can also be selected.