

J. Heyrovský and the Developments Leading to Square Wave and Pulse Polarography

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As with many other discoveries, that of polarography happened because the right man was in the right place at the right time. The man was right, because he had a sufficient background in chemistry to be able to develop a new scientific idea, because he had the inquisitive nature and drive that gave him the incentive to work hard on the development of his ideas and to sacrifice other enjoyments to achieve his goal, and because he also had the ability to observe and distinguish important new phenomena from those that were peripheral.

The discoverer of polarography, Jaroslav Heyrovský (Fig. 1), was born in 1890 into the family of a university professor in Prague, which proved to be a fertile ground for the development of his intellect.

His growth was further stimulated by attending a demanding high (grammar) school, where he showed an early predisposition for the natural sciences. He learned about the development of a new area on the borderline between chemistry and physics, physical chemistry. As this branch of chemistry was not taught in 1910 at the Charles University in Prague, where he matriculated, he received permission and the necessary financial support from his strict father to continue his studies at University College in London (Fig. 2). His initial tutor, Sir William Ramsay, retired in 1913 and was succeeded by F. G. Donnan (Fig. 3), an eminent physical chemist, whose interest lay mainly in electrochemistry. This circumstance proved to be one of the most decisive factors in the scientific career of Heyrovský. His experimental research was aimed at the determination of the electrode potential of aluminium.

To avoid complications due to passivation of solid aluminium electrodes, Professor Donnan advised Heyrovský to use a dilute aluminium amalgam, which would be allowed to flow slowly out of a glass capillary. Even when the experiments with the aluminium amalgam electrode were only slightly better than those obtained with solid aluminium electrodes, due to the evolution of hydrogen, Heyrovský was made aware of the advantages of liquid metallic electrodes, based on their renewable surface, and learned how to use capillary electrodes.

His stay in London was interrupted by World War I, when Heyrovský visiting his parents in Bohemia in the summer of

1914 was unable to return to London. In 1915 he was called up for service in the Austro-Hungarian Army (Fig. 4) and was posted as dispensing chemist and röntgenologist to hospitals in Southern Bohemia and Austria. This, however, gave him the opportunity to prepare his thesis and in September 1918 passed his final examinations and was granted a Ph.D. degree by the Charles University in Prague.

The final examination consisted of oral tests in chemistry and physics. The physics examination was given by Professor Kučera (Fig. 5), and became another milestone in the career of young Heyrovský. Professor Kučera had developed a new experimental technique for recording electrocapillary curves,¹ based on weighing drops of mercury detached from a glass capillary, which was connected to a reservoir of mercury. In the course of the examination, Professor Kučera gave Heyrovský a question dealing with electrocapillarity of mercury. Heyrovský demonstrated that he was well-acquainted with Kučera's research² and the latter then described for the candidate his unpublished results, which dealt with anomalous electrocapillary curves obtained in solutions exposed to atmospheric oxygen. Professor Kučera invited



Fig. 2 Heyrovský as a student in London, about 1913



Fig. 3 Professor Donnan, University College, London, about 1913

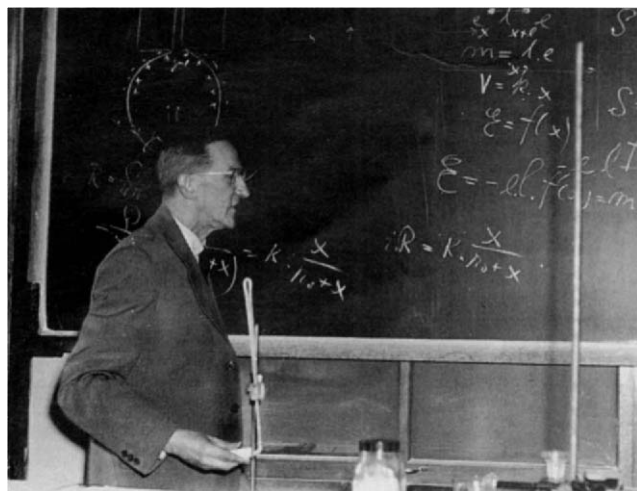


Fig. 1 Professor Heyrovský at the meeting at Smolenice Castle, Czechoslovakia, 1954



Fig. 4 Heyrovský (right) in the Austro-Hungarian army, about 1916



Fig. 5 Professor Kučera, Charles University, Prague, about 1919

Heyrovský to visit him the following day and showed him how to construct a dropping mercury electrode (DME) (Fig. 6). Over the next two years, Heyrovský, together with a young physicist named Šimůnek, spent hours collecting a known number of drops of mercury, which had fallen off the capillary electrode, and plotting the weight of mercury as a function of the applied voltage to obtain electrocapillary curves.

As the counting and weighing of mercury drops was tedious, Heyrovský developed a modification of the above procedure, based on the measurement of the drop-time. On electrocapillary curves obtained in this way he observed changes when certain metal ions (*e.g.*, Zn^{2+} , Cd^{2+} , Mn^{2+} and Ba^{2+}) were present in the solution under study. He also investigated the possibility of using electrocapillary curves for the determination of the 'decomposition voltages' for these ions.

In 1921 Heyrovský developed the idea of measuring the current flowing through the electrolytic cell in order to investigate the processes at the DME rather than determining the drop-time. The first experimental attempt to measure such a current was carried out on January 1, 1922, but was unsuccessful. The amperometer used was unfortunately insufficiently sensitive. Heyrovský did not give up. He borrowed a sensitive galvanometer and applied it to measurements of the current flowing through an electrolytic cell (Fig. 7), using a potentiometer as the voltage source. The first curve was

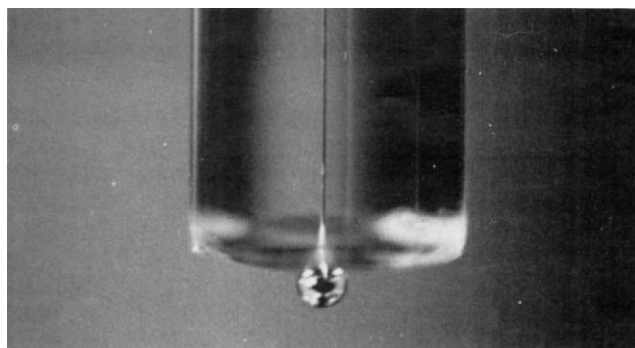


Fig. 6 Dropping mercury electrode, orifice of the glass capillary

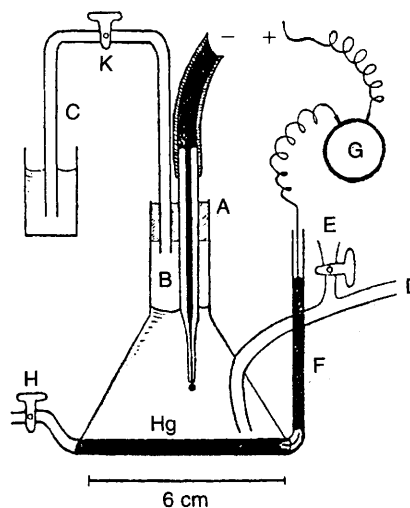


Fig. 7 Polarographic cell used for the first recordings of current-voltage curves. Reproduced with permission from ref. 5

recorded with such a circuit in a solution containing $1 \text{ mol dm}^{-3} \text{ NaOH}$ on February 10, 1922. For polarography we, therefore, not only know the circumstances that led to its discovery, but also the exact day on which the first polarographic current-voltage curve was recorded. On the recorded curve, Heyrovský correctly attributed the increase in current in the region between -1.9 and -2.0 V to the deposition of Na^+ ions, forming an amalgam. Soon the complication with the current-voltage curves as a result of the reduction of dissolved oxygen was recognized. Starting in April 1922 Heyrovský removed such oxygen by the introduction of a stream of hydrogen, which had been generated in a Kipp apparatus, into the studied solution (placed in electrolytic cell). Over the next two years a number of reduction reactions at the DME of both inorganic (Fig. 8) and organic species were investigated in Heyrovský's laboratory.³⁻⁵ In these studies the measured current was plotted manually as a function of the applied potential.

Some possibilities for the use of electricity in carrying out transformations of various species were understood some hundred years ago. Nevertheless, in the period around the turn of this century, the applications of electric current for carrying out transformations of certain compounds were almost exclusively restricted to processes where the current was controlled. In some instances the potential of the working electrode was measured. Heyrovský's innovation was to measure the current while the potential was controlled. It turned out that some important information could be obtained about the composition and properties of the solution studied under conditions where the current was measured and the potential was controlled, which were not accessible when constant current was imposed on the two electrodes in a cell.

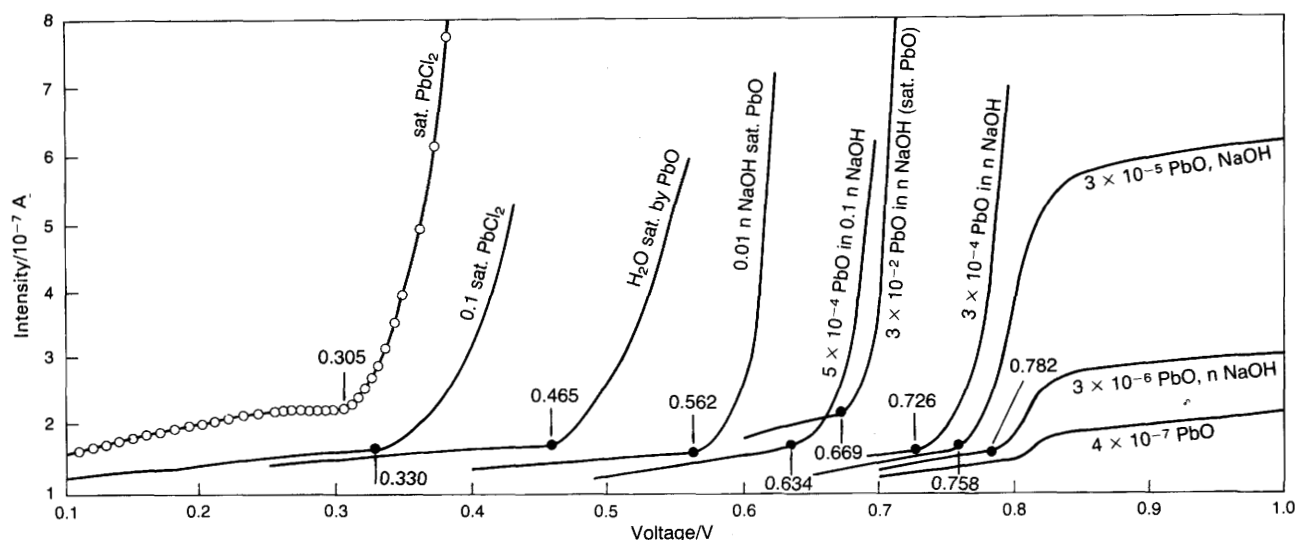


Fig. 8 Set of manually recorded current–voltage curves for various solutions. Reproduced with permission from ref. 5

Since 1926, manual plotting of current–voltage curves has been replaced by an automated instrument called a polarograph (Fig. 9). In this apparatus recording was carried out photographically, using a reflection of the light beam off the mirror of a galvanometer. This instrument was developed⁶ in cooperation with a Japanese chemist, Shikata (Fig. 10), who spent some time in Heyrovský's laboratories in Prague in 1924.

In the initial polarographic investigations in the 1920s the main thrust was to find the potential ranges, in which a given species was reduced at the DME. Later, systems were studied that could undergo electro-oxidation and those which yielded polarographic current resulting from the formation of slightly soluble salts or stable complexes at the surface of the mercury electrode.

Soon the importance of the information offered by limiting currents became obvious. This current was observed for reductions, when the potential became sufficiently negative, the rate of the electro-reduction became so large that the transport of the reducible species to the electrode became the process governing the size of the current. Similarly for oxidations, the limiting current was observed at sufficiently positive potentials, where the rate of transport of the oxidizable species to the electrode became governing. The limiting current was easily recognized on most current–voltage curves, because this current remained unchanged over a range of potentials (Fig. 11).

The nature of the transport process was varied. The first recognized^{7,8} type of transport was migration, which resulted from the transport of ions in the electrical field between two electrodes in the electrolytic cell. As this current represented an unwanted complication of the study of processes in which electro-reduction or electro-oxidation occurs (called faradaic processes), attempts were made to suppress it. It can be minimized by the addition of an electrolyte in high concentration to the solution to be investigated by electrolysis. This electrolyte, containing components that are neither reduced nor oxidized over the potential range investigated, is called the 'supporting electrolyte' or 'base electrolyte'.

In a potential range where the rate of electrolysis is sufficiently high to ensure that the concentration of the electroactive species at the electrode surface is depleted (provided that the effect of convection is minimized), the principal mode of transport of an electroactive species from the bulk of the solution to the surface of the electrode is by diffusion. Kemula⁹ was first to observe that capillaries with equal flow-rates of mercury yield approximately equal limiting

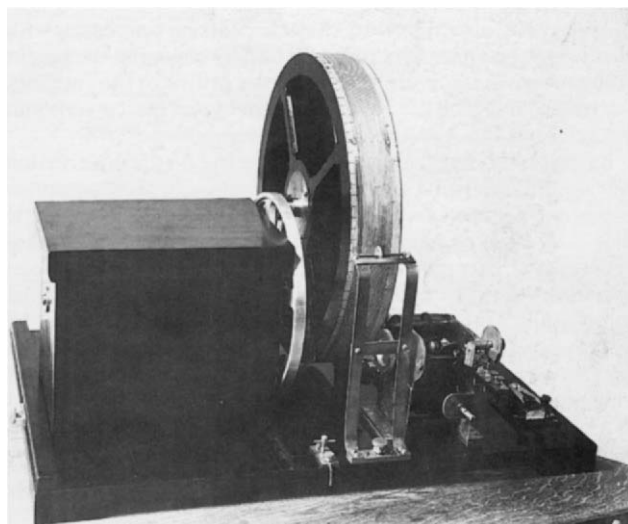


Fig. 9 One of the first five photographically recording polarographs, Prague, 1925 (galvanometer and lamp not shown)



Fig. 10 Professor Heyrovský (right) and M. Shikata, 1923

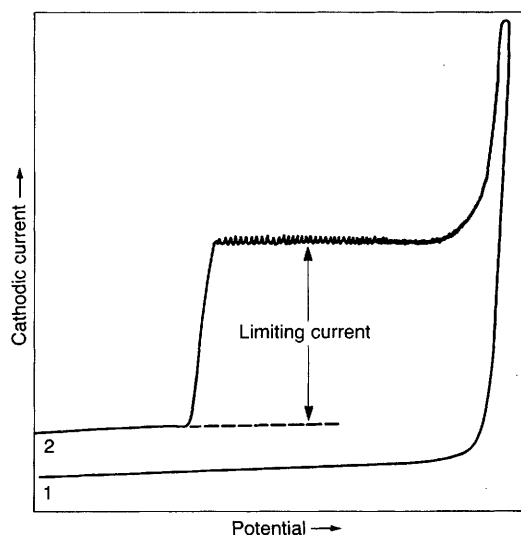


Fig. 11 Polarographic limiting current. 1, Current–voltage curve in supporting electrolyte ($0.1 \text{ mol dm}^{-3} \text{ NH}_3$, $0.1 \text{ mol dm}^{-3} \text{ NH}_4\text{Cl}$); and 2, current–voltage curve in the presence of $5 \times 10^{-4} \text{ mol dm}^{-3} \text{ Cd}^{2+}$ in the same supporting electrolyte

currents. He also reported that the current increases with increasing pressure of mercury, varied by changing the height of the mercury reservoir relative to the orifice of the capillary electrode, and that the relationship between the current and the height of the mercury column is parabolic.

Based on this experimental evidence and on the observation that the limiting current is a linear function of the concentration of the electroactive species, a theoretical physicist Ilkovič (Fig. 12), derived an expression, indicating the relationship between the current and properties of the electrode on one side [drop-time (t_1) and rate of flow of mercury (m)] and the composition of the solution on the other [concentration of the electroactive species (c) its diffusion coefficient (D) and the number of electrons transferred (n)]. For a description of the transport to a growing mercury drop he considered diffusion to a planar electrode, which had a surface area that increased with time. For the mean limiting diffusion current Ilkovič^{10,11} derived the following equation bearing his name:

$$\bar{i}_u = 607ncD^{1/2} m^{2/3} t_1^{1/6}$$

(where the numerical factor has a given value of 607 when the concentration c is expressed in mmol dm^{-3} , the diffusion coefficient D in $\text{cm}^2 \text{ s}^{-1}$, the rate of flow of mercury in mg s^{-1} and the drop-time t_1 in s). In conventional use this equation proved to be sufficiently accurate, within the generally accepted accuracy of current measurements of $\pm 3\%$.

Transport to the electrode surface can also be affected by chemical reactions. If the compound to be investigated can exist in two forms in equilibrium, one electroactive and one electroinactive, and in the bulk of the solution the electroinactive one predominates, it is this form that is transported from the bulk, by diffusion, to the surface of the electrode. In the vicinity of the electrode surface, where the concentration of the electroactive species is decreased by electrolysis, the consumed electroactive species can be replaced by a chemical reaction that converts the electroinactive form into the electroactive one. When the composition of the solution is such that the rate of conversion of the electroinactive form into the electroactive species is slow, when compared with the rate of diffusion, the current is governed by the rate of the chemical reaction. Such currents are denoted kinetic currents.^{12–14}

Another type of electrode process occurs when the product of an electrode process is rapidly converted into the starting material by a chemical reaction. An example of this type of process is the oxidation of a reduction product by an oxidizing



Fig. 12 Professor Ilkovič

agent that is present (usually in excess) in the studied solution. The increase in current due to re-oxidation is called the catalytic current.^{15–18}

Measurements of polarographic currents can be used in both fundamental and theoretical studies of electrode processes and accompanying chemical reactions or, more frequently, in practical analytical applications. Even when Professor Heyrovský, due to his erudition as a physical chemist, was interested primarily in the course of the electrolysis, he showed a keen interest in analytical applications and this is reflected in his publications. His first monograph,¹⁹ published in Czech in 1933, dealt with applications of polarography in practical chemistry. Similarly his large German monograph²⁰ of 1941 contained a large section dealing with analytical applications. In addition, his later monographs on Practice of Polarography²¹ and Introduction to Practical Polarography²² were aimed at an analytical audience. His first review, which caught the attention of a world-wide audience,²³ also dealt with the analytical applications of polarography. Moreover, Professor Heyrovský cultivated the interest of his collaborators in analytical applications, both by discussing possible analytical aspects of their findings and also by requesting them to solve simple analytical problems, posted to himself by the chemical, metallurgical and food industries (including manufacturers of alcoholic beverages) or by manufacturers of glass containers of drugs to name a few. His collaborators also had to deal with problems brought to his attention by the medical profession. Professor Heyrovský strongly supported the introduction of polarographic methods into the field of industrial hygiene, pioneered in the late 1940s and 1950s by his friends, Professors Teisinger and Škramovský. Readers involved in environmental analysis might be interested to learn that Heyrovský, in the late 1930s and 1940s, supported projects dealing with, for example, the determination of oxygen in waters, the presence of surfactants in waters²⁴ or lead in blood.²⁵ He also acted as a catalyst for the publication of the first monograph on the applications of polarography in medicine, biochemistry and pharmacy written by his young collaborators.²⁶

The broader success of polarography as an analytical tool was dependent on the availability of commercial instruments. The first commercial photographically recording polarographs were manufactured by Nejedlý (Fig. 13) (one of Heyrovský's collaborators) in Prague, followed by instruments manufac-

tured by Leybold in Cologne and Sargent in Skookie, IL, who was the holder of the patent in the US (but without compensation to Heyrovský). Probably the last photographically recording commercial instruments were the 'micropolarographs' manufactured in collaboration with Heyrovský simultaneously by Cambridge Instruments and Zbrojovka (Prague) and the LP55 produced in Prague by Laboratorní Přístroje (Fig. 14).

It seems that the first pen recording polarographs were produced in the early part of 1938 by Radiometer (Copenhagen) under the trade name Polariter. The first instrument in this series, the PO1, used a galvanometer with the movement transmitted to a pen, to record the current-voltage curve on paper. A similar principle was used in the pen-recording instrument (voltammograph) produced in the 1940s and 1950s by the Cambridge Instrument Company. Unfortunately, this instrument never became popular outside the UK, probably due to non-aggressive sales practices. (Unfortunately, the same fate involved the multipurpose polarograph 82P, also developed by the Cambridge Instrument Company in the late 1960s; this excellent instrument built on a modular principle, was on a par with the best available in the world at that time. To our knowledge, fewer than 30 instruments were ever built.) The polarograph produced by Tinsley Industrial Instruments (Fig. 15) also contained a galvanometer, a reflected light beam was followed by a phototube and the photocurrent was amplified electronically. In other instruments, such as those produced by the E. H. Sargent Company, in the US, the measured current passed through a resistor and the resulting potential difference was recorded by a potentiometric recorder with an automatic electronic balance. Pen-recording instruments were also produced by Yanagimoto and Shimadzu in Japan.

The sensitivity of d.c. polarography allowed the majority of electroactive species to be determined with an accuracy of about $\pm 3\%$ over the range from 10^{-3} to 10^{-5} mol dm $^{-3}$, with estimates in favorable cases of up to 10^{-6} mol dm $^{-3}$. This concentration range was sufficient for the demands of chemical analysis in most fields during the 1940s and 1950s, with the exception of the determination of lead in blood, where the available sensitivity was on the borderline of being able to distinguish between the toxic and non-toxic level. By the middle of the 1950s and certainly in the 1960s the demands on the sensitivity limits for analytical methods had increased. It was probably the generation of atomic energy with its high demands on the purity of materials used that was the first area which required the sensitivity of analytical methods to be higher than that offered by d.c. polarography. Increasingly lower limits for permitted levels of toxic components led to demands of increased sensitivity in environmental analysis. The improved efficiency of prescription drugs resulted in decreases in the administered dosages and, hence, increased demands on the sensitivity of analytical techniques used in

pharmacological and clinical studies of the fate of drugs in organisms and of products of their metabolism.

It would seem that an increase in the sensitivity of electroanalytical methods would simply demand a development of accurate measurements of smaller currents. Progress made in electronics in the late 1940s and early 1950s would alone allow that, but the lower limit of the sensitivity of d.c. polarography is affected by another factor, the capacity current. As opposed to the above mentioned currents, which result in a chemical change due to an electron transfer (such currents are often denoted as faradaic), there are two other main types of currents accompanying electrolysis that do not involve electron transfers to or from an electroactive species, and are observed even in solutions which do not contain any species oxidized or reduced in the studied potential range. One type of such non-faradaic currents accompanies adsorption and desorption of surface-active materials, the other corresponds to the electrical charge that must be transferred on an electrode to bring it to a given potential. This current, called charging or capacity current, is observed even in the blank supporting electrolyte.

This capacity current is usually independent of the concentration of the electroactive species. Using the common types of capillary electrodes and the measurement of the mean current using suitably damped circuits, faradaic currents for solutions containing from 10^{-3} to 10^{-4} mol dm $^{-3}$ of electroactive component are sufficiently larger than the capacity

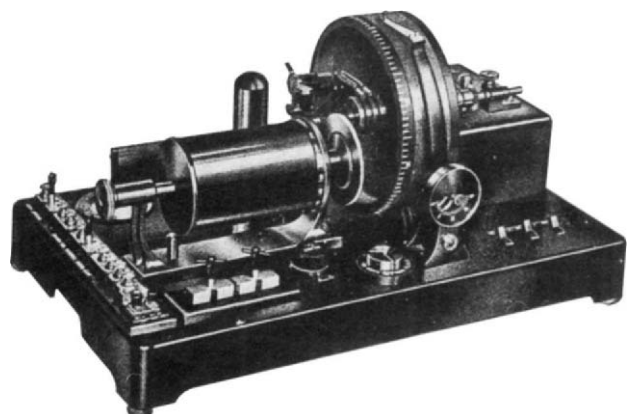


Fig. 13 Polarograph with photographic registration, V. Nejedlý Company, Prague, about 1938

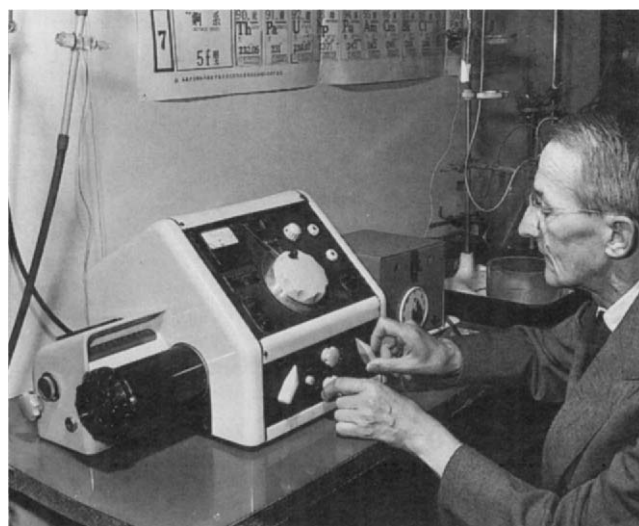


Fig. 14 Professor Heyrovský with a photographic recording polarograph LP55, Prague, about 1955



Fig. 15 Mrs Lamb demonstrates the new model Tinsley polarograph to Professor Heyrovský during his visit in England, mid-1950s



Fig. 16 Professor Semerano, Fermo, Italy, 1987

current and corrections for it offer no problems. For solutions where the concentration of the electroactive species is of the order of 10^{-5} mol dm $^{-3}$, faradaic and charging currents are comparable and corrections for the latter must be made. For those solutions where the concentration of the component to be determined is of the order of 10^{-6} mol dm $^{-3}$, capacity current may be larger than faradaic and subtraction of the signal due to the blank becomes more difficult.

The first attempts to minimize the effect of the capacity current on polarographic curves were already made in 1932 by Ilkovič and Semerano²⁷ (Fig. 16). These investigators used the fact that the capacity current rises almost linearly with increasing voltage and subtracted from the measured current a counter-current, decreasing linearly with increasing voltage. But this approach yielded measurable polarographic waves only for solutions containing more than about 5×10^{-6} mol dm $^{-3}$ of electroactive species.

To solve this problem, Professor Heyrovský experimented in the late 1940s with two other approaches that were based on classical instrumentation. The first was recording the derivative curves $di/dE = f(E)$, using either two electrodes to which potentials differing by 5–10 mV were applied²⁸ (Fig. 17) or an electrical circuit, with a resistance parallel and a capacitor in series with the current measuring device.^{28,29} This device enabled the separation of two closely located waves (Fig. 17) and the determination of a low concentration of a species reduced more negatively than the reducible component present in excess, but did not decrease the detection limit below 5×10^{-6} mol dm $^{-3}$. The second approach was based on measurement of the difference between the currents flowing through two parallel electrolytic cells, one containing the solution to be analysed and the other a blank.²⁸ In principle this approach was promising, but not only did the two capillaries have to have exactly the same drop-time (which can be achieved by synchronization), but also identical flow-rates of mercury, which was more difficult to achieve. For practical work the system was too sensitive to malfunctions.

The question may be posed as to why Heyrovský did not make use of the developments in electronics in the post-war period to lead the way in the development of more sensitive polarographic instrumentation. The answer could be that he had no 'hands-on' knowledge of electronics and that the electronics expert who collaborated with him (J. Forejt) was sold on instrumentation that allowed the application of a constant cell current rather than a controlled potential. One should not forget that it was long before the age of operational amplifiers. Heyrovský was aware of the importance for fundamental studies of cyclic variations for the detection of primary products of electron transfer reactions and in following their fate. But, his choice in following the $di/dE = f(E)$ curves in so-called oscillographic polarography^{30,31} over that of $i = f(E)$ in cyclic voltammetry^{32,33} in his laboratory

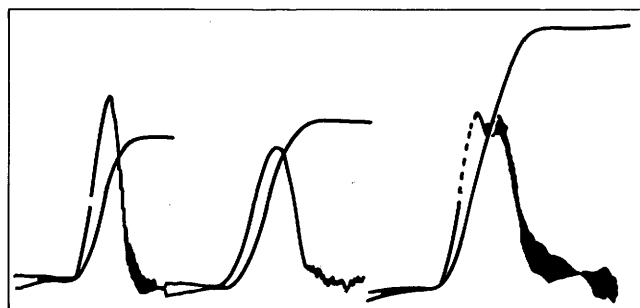


Fig. 17 Primitive and derivative curves recorded by Heyrovský, 1949. From left to right the curves were obtained in 1×10^{-3} mol dm $^{-3}$ Pb $^{2+}$, 2×10^{-3} mol dm $^{-3}$ Tl $^{+}$ and in a mixture of 1×10^{-3} mol dm $^{-3}$ Pb $^{2+}$ and 2×10^{-3} mol dm $^{-3}$ Tl $^{+}$. Derivative curve of the mixture shows the separation of two waves



Fig. 18 Professor Heyrovský and his collaborators at a seminar at the Polarographic Institute of the Czechoslovak Academy of Science, Prague, early 1960s

experiments in the 1950s and 1960s was not one that contributed significantly to the progress of electrochemistry.

The developments at Harwell that under the guidance of G. C. Barker, revolutionized the practical use of electroanalytical methods in the second half of this century, had a modest predecessor in Prague. To identify and follow electrolysis products Kalousek³⁴ used rectangular voltage polarization with a relative low frequency, in which the voltage was periodically changed from a constant value, at which the electrolysis product was formed, to a gradually increasing value. During the second period the current corresponding to the oxidation or reduction of the electrolysis product was recorded as a function of the applied potential. In the original instrument, built in an era when only unreliable relays were available, a Singer sewing machine was used, with a needle periodically immersed into a pool of mercury to achieve the periodic on-off switching. The instrument was developed to obtain information about electrolysis products rather than for analytical applications. Only recently have similar principles found some analytical use.

To increase the sensitivity of polarographic methods, Barker modified classical d.c. polarography in two aspects: first, he replaced the linear increase of applied voltage with time by either a square-wave voltage or voltage pulses; and second, he replaced the measurement of the mean current (over the life of a drop of mercury), by a measurement of current over a short period of time, usually during the last third of the life of a drop. The latter type of measurement minimizes the effect of capacity current for the following reasons: (i) when a potential is suddenly (in a step or pulse) applied to an electrode, the capacity current decreases with



Fig. 19 Professor Heyrovský as a guest of the British Council, London, mid-1950s

time much faster than the faradaic current; and (ii) when the measurement of the current is postponed until the capacity current has decayed, the measured faradaic current is affected considerably less by the capacity current than is the mean current. This approach enables square-wave and pulse-polarographic methods to extend their sensitivity limits to concentrations of 1×10^{-7} mol dm⁻³ and in some cases even 1×10^{-8} mol dm⁻³ in the electroactive species. The sensitivity limit depends on the number of transferred electrons and the rate (reversibility) of the electrode process involved. More information about the origin of these techniques and the fate of the developed instruments will be found in the contribution by Barker in this issue.

It remains to comment on the attitude of Heyrovský to the development of square-wave and pulse polarography. His information about the progress in this area originated from two sources. First, in the Polarographic Institute of the Czechoslovak Academy of Sciences (of which Heyrovský was director in the 1950s and 1960s) Thursday mornings were devoted to seminars usually from 9 to 12 a.m. (Fig. 18). To be kept abreast of progress in fundamentals and applications of polarography, his collaborators in the Institute had to report about the progress of their own work and about publications dealing with polarography. The progress in square-wave and pulse polarography was most often reported at these meetings by Kalvoda. The audience at these seminars was rather critical and ready to dissect information in the literature, but the contributions of the Harwell group were unanimously considered as extremely important.

Second, during his visits to the UK in the 1950s (Fig. 19) Heyrovský had the opportunity to see several laboratories equipped with square-wave polarographs. Barker met Heyrovský only once, when he visited AERE Harwell. During his visit Heyrovský inspected and approved the square-wave polarograph and, according to his host, expressed the impres-

sion 'that the instrument did not look like a polarograph' (in the form he was used to).

Professor Heyrovský's foresight about the role of square-wave and pulse polarography was correct, we can conclude that the development of these techniques was the single most important event in electroanalytical chemistry in the second half of this century. The general acceptance of pulse and square-wave polarography in practical, analytical applications is sufficient proof. We all have to be thankful to Geoffrey Barker for his important contribution to the progress of analytical chemistry.

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