# The Current Role of Polarography in the Light of the Coming 90<sup>th</sup> Anniversary of Its Discovery (A Reflection)

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• Dedicated to the memory of Professor Jaroslav Heyrovský, on the occasion of 90<sup>th</sup> anniversary of the invention of polarography and to the memory of Professor Robert Kalvoda, his student and a great propagator of his legacy •

**Abstract:** Since 1922, when Professor Jaroslav Heyrovský had carried out his pioneering experiment with a dropping mercury electrode, polarography showed remarkable ability to adjust to ever increasing demands on the sensitivity and selectivity and, up to now, mercury electrodes are among the best sensors for electroanalytical measurements. The aim of this contribution is to remind some facts — maybe, not well-known to everyone — about the discovery of polarography, discuss the position of polarography in scientific research today, and outline also some future prospects of this concededly fascinating electrochemical technique.

**Keywords:** Polarography; Dropping mercury electrode; History; Review.

#### Introduction

Almost ninety years ago, on February 10, 1922, Professor Jaroslav Heyrovský had carried out his pioneering experiment with a dropping mercury electrode (DME) from which polarography gradually evolved. Since then, polarography became a mature analytical method capable to absorb increasing demands on the sensitivity and selectivity and we believe that, up to now, mercury electrodes are among the best sensors for electroanalytical measurements [1].

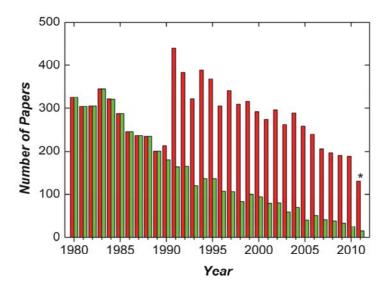
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Limits of determination gradually decreased from  $10^{-5}$  mol L<sup>-1</sup> in the case of classical DC polarography (DCP), through  $10^{-6}$  mol L<sup>-1</sup> for DC tast polarography (DCTP) and  $10^{-7}$  mol L<sup>-1</sup> for AC polarography (ACP), normal pulse polarography (NPP), and differential pulse polarography (DPP) to  $10^{-8}$  mol L<sup>-1</sup> for square-wave polarography (SWP) [2]. History of the development of the polarographic method, from the birth of Professor Jaroslav Heyrovský in 1890, up until the Nobel Prize award in 1959 was recently described in detail [3]. Nevertheless, we think it is useful to remind yet the most important milestones in the development of polarography and related measurements and especially nowadays, when the polarography and, mainly, the DME struggle for the naked existence although it may, in some respect, successfully compete with modern separation and spectrometric techniques.

The most common polarographic working electrode is the classical DME. The need of use of mercury for polarography raises a fear and this has an increasing tendency (see also this issue and other two articles devoted to mercury and mercury electrodes). There is a general opinion that polarography is dead because of the fear of mercury poisoning [4]. On TV, one is occasionally witnessing careful transportation of bottles of mercury, if found somewhere, by chemistry rescue brigades. At the same time, one can learn from toxicology books that mercury in the liquid state is not poisonous; the events are mentioned that even after the intake, mercury quickly leaves the gastrointestinal tract due to its physical properties. The situation is obviously different in case of mercury vapors, organometallic and some other mercury compounds, and penetration of mercury through skin [5].

In the years 1950–1970, another reason responsible for the decreased use of polarography in analytical chemistry emerged – its insufficient sensitivity. Applications of polarography are limited to the systems in which high sensitivity is not required, namely to the determinations at the micromolar level. This sensitivity is too low in many determinations. In the fundamental research, DME is still used in kinetic studies or to establish the reaction mechanism. Quick renewal of the electrode surface is here the main advantage. A qualitative improvement in polarography, in fact its renaissance, followed the discovery of the methods effectively eliminating the charging current, which limits the sensitivity of classical polarography. As soon as highly sensitive polarographic instruments became commercially available, the interest in polarography reappeared, especially among trace analysts. Differential pulse polarography and square-wave polarography in particular opened new possibilities in this discipline [4].

At present, we are living in the era when the worldwide use of polarography in fundamental research is still lesser. This can be seen well from the number of papers on the subject "polarography" published, according to the *Web of Knowledge* [6], between the years 1980 and 2011 (Fig. 1). A decreasing trend is more than obvious; enhanced number of papers beginning in 1991 is only due to the fact that all papers in the *Web of Knowledge* database have been accompanied with the abstract since 1990/1991. We have found 190 papers published within the years 2006–2010, containing the keyword "polarography" in their title. According to the origin country of the corresponding authors of these papers, polarographic research has been done in 35 countries. On the basis of this search, we can find three countries with the highest publication impact in the field of polarography in the last five years: India (18.9%), Turkey (13.2%), and Czech Republic (10.0%).



**Fig. 1**: The number of papers on the subject "polarography" (keyword: polarograph\*) identified by Web of Knowledge [6]. Legend: **red columns** – keyword searched in the filed "Topic", **green columns** – keyword searched in the field "Title", \* – till November 1, 2011.

In this article, we would like to remind some facts, maybe not well-known to everyone, about the discovery of polarography, discuss the position of this technique in today's scientific research, and look to the near future of this concededly fascinating electrochemical technique. And all above, this article is an expression of our tribute to *Professor Jaroslav Heyrovský* and to all his students and followers – the pioneers of polarography.

# The Origin of Polarography

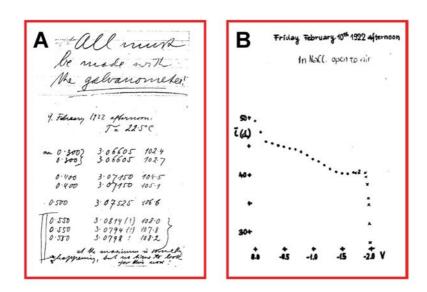
The discovery of polarography belongs to those events in the history of science where the exact date of the disclosure of the crucial point can be traced [7]. Jaroslav Heyrovský, who had been interested in chemistry and physics in his grammar school years, was immatriculated at the Charles University in Prague in 1909. He spent only two terms there.

As he was interested in physical chemistry and no important school of this subject existed in Austro-Hungarian Empire, he went to London to study at the University College in the autumn of 1910. After obtaining his Bachelor's degree in 1913, he entered the laboratory of Professor Frederick George Donnan to work on his Ph.D. His task was to determine the standard (normal) potential of aluminium. Heyrovský's work was supervised by Dr. Roland Edgar Slade who had been interested in the electrochemistry of aluminium previously.

In the summer of 1914, Heyrovský had returned to Bohemia for a holiday. The outbreak of World War I prevented him from coming back to London to complete his thesis. He was soon recruited to the Austro-Hungarian army where he had served in the Medical Corps. During his service, he used most of his free time for simple experimentation in the hospital laboratory and for attempts (unfortunately futile) to work out a theory for the complicated phenomena occurring at aluminium electrodes. Finally, in 1918, he had collected all his results and wrote out his thesis, of which he presented to the Faculty of Philosophy of Charles University in Prague. The oral examination took place on June 27, 1918. One of the examiners was the Professor of Experimental Physics, Bohumil Kučera, the originator of the DME, of which he had been using for electrocapillary measurements. Prof. Kučera, who at that time was mainly interested in radioactivity, obviously found in Heyrovský's work with a dropping amalgam a suitable opportunity to come back to his former field of interest. In the discussion on the electrocapillarity of mercury, he pointed out the discrepancy between his own results and those obtained in the classical work of Gabriel Jonas Lippmann and Louis Georges Gouy. Heyrovský was quite attracted by Kučera's problem presented to him during the examination. Kučera invited him to work in his laboratory and Heyrovský, who had just become a university lecturer and, already in 1920, a Docent (i.e., Associate Professor) at the Chemical Institute of the Charles University in Prague, divided his research interest between investigations of the equilibria of aluminium complexes (still a residual research line from his London studies) and rather tedious measurements of the weight of mercury drops according to Kučera's wishes (at a later stage, Heyrovský preferred to measure the drop lifetime instead).

In 1921, it became clear that the anomalies, previously observed by Kučera, were due to the electrode processes. Heyrovský hoped initially that he would develop a new method for the determination of decomposition potentials. Finally, he decided to connect a galvanometer in the potentiometric circuit he used for electrocapillary measurements. Unfortunately, on January 1, 1922 when he had made the first experiment of this kind, his galvanometer was not sensitive enough so that only erratic current—voltage curves were obtained; apparently, due to polarization of the electrode to extremely negative potentials.

At the end of January, 1922, he had returned to the determination of the decomposition potential of electrolytes containing aluminium ions; but, finally decided to investigate solutions of NaCl. On February 2, 1922, he measured electrocapillary curves in 1 M NaCl (open to air). He obviously had some new research in mind, which is shown by his own penned remark about some irregularities on the electrocapillary curve: "At the maximum is something happening, but no time to look for this now!" (Fig. 2A).



**Fig. 2**: Facsimile of two selected pages from Heyrovský's laboratory notebook [10]. Legend: **A**) protocol from February 9, 1922, **B**) plot recorded on February 10, 1922.

On February 10, 1922, he connected a mirror galvanometer, an instrument with sufficiently high sensitivity, to the circuit. By a point-to-point measurement, he had succeeded in obtaining the first polarogram (Fig. 2B).

At the beginning, he was not interested in the reduction process of oxygen but looked mainly for the data in the potential range from -1.9 to -2.0 V vs. ref., where the decomposition potential of Na<sup>+</sup> was situated.

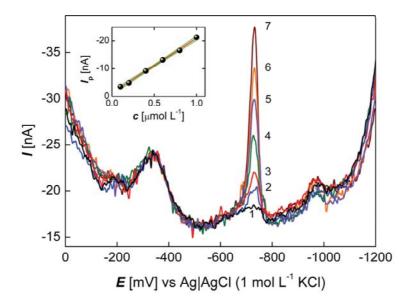
Heyrovský recognized at once that he had made a first-class discovery. In the following days, he studied the current–voltage curves in various electrolytes and at various drop lifetimes. He collected the falling drops into a small cup in order to prove that their potential corresponding to that of a dilute amalgam. Finally, he wrote up his results, sent in his manuscript to the Czech chemical journal, *Chemické Listy*, having left, almost exhausted, for vacation on July 27, 1922. His classical paper appeared in the October issue of that journal [8] (for English version see ref. [9]).

## The Current Role of Polarography

It is necessary to admit that routine applications of polarographic methods are not too frequent at present. This is caused by fast developments of modern spectrometric and separation techniques, by concerns about mercury toxicity, by the lack of properly validated methods, and by a lower activity of producers of electroanalytical instrumentation as compared with producers of spectrometric and separation instruments. The dwindling number of university teachers involved in electroanalytical research plays a negative role, as well as shrinking position of electroanalytical methods in the curriculum of most universities. Nevertheless, we strongly believe that polarography should be seriously considered in the process of choice of suitable method for the determination of a given compound in a given matrix for the following reasons:

- Broad linear dynamic range and low limits of determination from 10<sup>-7</sup> mol L<sup>-1</sup> for DPP (see Fig. 3 as an illustrative example) down to even 10<sup>-9</sup> mol L<sup>-1</sup> for SWP [2];
- Diversity of determinable analytes (inorganic, organic, organometallic);
- Low running and investment costs;
- Reasonable selectivity especially in combination with preliminary separation and sample clean-up using, e.g., liquid-liquid extraction, solid phase extraction, thin-layer or column chromatography.
- Electroanalytical methods present an independent alternative to prevailing spectrometric or separation methods which is important in those cases where the analytical results should be "beyond reasonable doubts" (speaking in law terms)

- which, according to many regulations, requires the application of several independent analytical methods.
- Thousands of reliable polarographic methods are available in scientific journals, monographs, tables, and databases and plenty of new polarographic methods are published every year during last ten years confirming that polarography can be a viable alternative to other instrumental methods.



**Fig. 3**: Differential pulse polarograms of 2-aminofluoren-9-one recorded at DME in the lowest attainable concentration range in the spiked river water $-0.2 \text{ mol L}^{-1}$  acetate buffer pH 4.0 (9:1) sample [11]. Legend: concentrations of 2-aminofluoren-9-one in river water [µmol L<sup>-1</sup>]: 0 (1), 0.1 (2), 0.2 (3), 0.4 (4), 0.6 (5), 0.8 (6), and 1.0 (7). Experimental conditions: electronically controlled mercury drop lifetime 1.0 s, height of the mercury reservoir 81 cm, mercury drop lifetime 3.4 s, flow rate of mercury through the capillary 2.22 mg s<sup>-1</sup>, polarization rate 4 mV s<sup>-1</sup>, pulse amplitude -50 mV, pulse width 100 ms. The corresponding calibration straight line is in the inset; the confidence bands are constructed for  $\alpha = 0.05 (n = 3)$ .

Mercury is, according to our opinion, the best electrode material not only for polarographic measurements. Easily renewable and atomically smooth surface of mercury eliminates or minimizes problems with electrode passivation and fouling. Broad potential window enables reaching negative potentials up to -2.5 or even -3 V, which makes mercury the best available material for the determination of electrochemically reducible analytes.

Existing objections to the use of mercury in analytical laboratories, based on its toxicity, are not rational because mercury is practically innocuous at room temperature (toxic organomercury compounds are not formed during polarographic measurements). Moreover, the amount of mercury consumed in analytical laboratories can be profoundly decreased by applying static mercury drop semi-micro- and microelectrodes.

Alternatively, completely non-toxic solid amalgam electrodes can be used [12-14]. Solid electrodes (noble metals, various types of carbon, *etc.*) are not in general suitable for cathodic reduction and, thus, they cannot compete with mercury in this region. Carbon paste electrodes [15,16] offer the advantage of easy surface renewal, however, their application in cathodic region is also limited. Thus, only bismuth film electrodes [17] seem to be a promising alternative to mercury ones and other solid electrodes for direct cathodic electrochemical detection especially of organic compounds.

Unfortunately, electroanalytical methods are not too frequently considered as methods of choice nowadays and spectrometric and separation methods are quite frequently applied notwithstanding whether they are really the best methods for a particular case. For certain, admittedly not too frequent cases, modern polarographic techniques are really the best method and, quite frequently, they are among the "fit for the purpose" methods. The polarographic methods developed in our UNESCO Laboratory of Environmental Electrochemistry for the determination of micromolar (as an illustrative example, see Fig. 4 overleaf) or submicromolar concentrations of selected chemical carcinogens [18], nitrated pesticides, or growth stimulators [19] and dyes [20] can serve as examples.

# Possibilities and Limitations of Polarography in the Future

According to our opinion, mercury electrodes will be successfully applied in the following fields:

 Mechanistic studies (especially of organic compounds) which are important for basic research, structure–activity relationship investigation, study of supramolecular interactions, etc. Thus, the information obtained can give us a useful clue for the study of biological redox processes and the transformation of investigated substances in ecosystem, when providing an outline for optimal conditions of both electroanalysis and electrosynthesis [22].

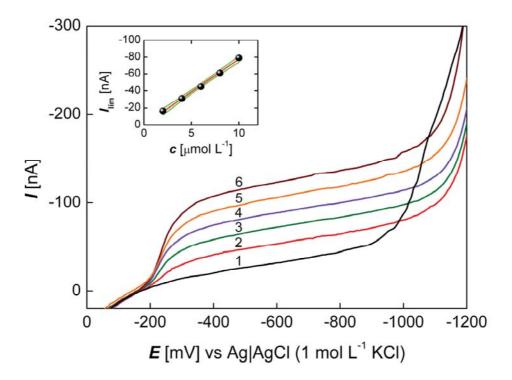


Fig. 4: DC tast polarograms of 4-nitroindane recorded at DME in the lowest attainable concentration range in the  $0.01 \text{ mol } L^{-1} \text{ HCl-methanol}$  (1:1) medium [21]. Legend: concentrations of 4-nitroindane [µmol  $L^{-1}$ ]: 0 (1), 2 (2), 4 (3), 6 (4), 8 (5), and 10 (6). Experimental conditions: electronically controlled mercury drop lifetime 1.0 s, height of the mercury reservoir 64 cm, mercury drop lifetime 3.3 s, flow rate of mercury through the capillary 2.63 mg s<sup>-1</sup>, polarization rate 4 mV s<sup>-1</sup>. The corresponding calibration straight line is in the inset; the confidence bands are constructed for  $\alpha = 0.05$  (n = 3).

- Trace metal determination and speciation where polarography can play a very important role in bioavailability studies and in soil and water analysis.
- Trace determination of organic substances where modern polarographic techniques can successfully compete with other instrumental methods in the field of pharmaceutical analysis (both the determination of selected drugs in pharmaceutical preparations and their traces or metabolites in body fluids, such as whole blood, plasma, urine), food analysis (determination of residues of selected pesticides or growth stimulators), forensic analysis (determination of traces of gun powder or explosives), toxicology (determination of selected toxic substances in the general or working environment and their metabolites in body fluid, biological monitoring of the exposition to toxic substances, etc.), and environmental analysis (determination of

selected anthropogenic pollutants, pesticides, genotoxic substances, chemical carcinogens, ecotoxic dyes, *etc.* in rain, surface, river, sea and drinking water and in other constituents of the environment).

- Metal speciation where polarography can be useful tool providing information about the oxidation state of the metal and the possibility to determine the free metal and metal ion in different individual complexes.
- Screening methods that can represent a cost effective alternative. The absence of a polarographic wave and its appearance after a standard addition can be a sufficient proof of the absence of the analyte in the test sample at the corresponding concentration level. However, in the presence of the signal, the presence of the analyte should be confirmed by some other, more sophisticated but obviously more expensive technique (ICP-MS, HPLC-MS, GC-MS, *etc.*). Taking into consideration the fact that substantial proportion of samples does not contain the sought analyte, this approach can substantially decrease the cost of monitoring projects.

Modern polarographic methods are undeservedly perceived as less selective, but they offer certain degree of selectivity because not all constituents of most samples are polarographically active. This can be demonstrated by simple determination of nitrated polycyclic aromatic hydrocarbons in the presence of parent polycyclic aromatic hydrocarbons, which do not interfere, by the determination of drugs in tablets, injection liquids, or body fluids, by metal speciation, *etc.* Polarographic determinations can be carried out in certain cases in the presence of colloid particles, solids, and surface-active substances.

Moreover, the selectivity of modern polarographic methods can be further increased by their combination with a preliminary separation using liquid—liquid extraction, solid phase extraction, and thin-layer or column chromatography. The improvements in electronics, computers and instrumentation, the availability of increasingly sophisticated and user friendly software, together with the increasing reliability of commercially available mercury electrodes of various types and with advancement in theory and the development of new programming of potential ramps and improved treatments of the current responses, could result in a renaissance of polarographic methods in coming years because of increasing importance of economic consideration. However, the most important impetus for further development and more frequent practical applications would be the enthusiasm of innovative electrochemists.

## **Conclusions**

Polarography, represented by DC polarography with DME, shall perhaps find its permanent position in the investigations of kinetics [23], equilibria [24], and mechanisms of organic reactions [25,26] as it is represented by Zuman's school [27]. Here, we can commemorate a part of the Nobel talk (for the Nobel Prize medal see Fig. 5) given by Professor Jaroslav Heyrovský (on December 11, 1959): "The reason why I keep some 38 years to the electrochemical researches with the dropping mercury electrode is its exquisite property as electrode material. Its physical conditions of dropping as well as the chemical changes during the passage of the electric current are well defined, and the phenomena displayed at the dropping mercury electrode proceed with strict reproducibility. Owing to the latter property the processes at the electrode can be exactly expressed mathematically."



Fig. 5: The Nobel Prize medal awarded to Professor Jaroslav Heyrovský [30].

The classical polarography of Heyrovský has and shall always have an impact on the further progress of electroanalysis and upon the development of related instrumentation and methodology. In this context, one new technique should be mentioned – the elimination polarography (EP). It enables elimination of selected currents (namely: charging current, diffusion current, and kinetic current) contributing to the measured total current. As stated by Trnková [28,29], the EP improves sensitivity and selectivity of determination of electroactive compounds, helping to solve some problems associated with complex electrode processes.

In spite of the wide range of fully automated spectroscopic, chromatographic, and other modern instrumentation available in the laboratories, new developments in polarography (voltammetry) have strongly revived this method making it one of the easiest and most economical measuring technique. Many citations available in scientific databases like, *e.g.*, *Web of Knowledge* [6] demonstrate versatility of the discussed methods in the wide field of analytical chemistry and shall arouse the interest to find new fields for their application.

## Acknowledgements

Financial support of this work, provided by The Ministry of Education, Youth and Sports of the Czech Republic (Projects MSM 0021620857, LC 06035, and RP 14/63), is gratefully acknowledged.

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