CROATICA CHEMICA ACTA CCACAA **70** (1) 151–165 (1997)

ISSN–0011-1643
*CCA–2412*

*Author's Review*

# Renewed Mercury Electrodes – Versatile Research Tools in General Chemistry*

*Ladislav Novotny and Michael Heyrovsky*

*Institute of Physical Chemistry Academy of Sciences of the Czech Republic*
*Dolejškova 3, 182 23 Prague 8, Czech Republic*

Received February 2, 1996; accepted June 6, 1996

The latest forms of the renewed mercury electrodes are reviewed and examples of their various recent applications are given.

## INTRODUCTION

In 1996 it will be 125 years since the primary form of renewed mercury electrodes (RMEs), the dropping mercury electrode (DME), was for the first time mentioned in literature.[1] From then on this simple instrument of research, acting as an ideal transmitter of electric charge to and from solutions as well as a sensitive indicator of changes of interfacial tension, has been undergoing an important development which was driven, above all at the later stage, by the practical aspects of utilization in chemical analysis. The main aim of the present paper is to provide a survey of the actual situation in the field of RMEs. The special features of the exactly renewable metal/solution interface, particularly in its forms available at present, open wide possibilities beyond the limits of purely analytical applications. Our review brings some examples of recent results of research undertaken also in this direction.

---

* Dedicated to Marko Branica on the occasion of his 65th birthday.

## THE ADVANTAGES OF RENEWED MERCURY ELECTRODES

Before opening the subject of RMEs we consider it appropriate to summarize the reasons why this type of electrodes deserves special attention of chemists and of scientists in general.

For electrochemistry mercury has the advantages both of a metal and of a liquid which it maintains in the temperature range from liquid ammonia to molten salts. It can be easily prepared – by repeated distillation – in a high degree of purity. It has a good metallic conductivity; as a noble metal it is chemically stable towards many reagents which attack other metals. As a liquid it has homogeneous and isotropic surface all atoms of which have identical properties. Its surface tension can be easily measured with high precision. The geometrical surface area of a mercury drop is identical with its real surface – in electrochemical terms its roughness factor equals one. On repeated renewal the mercury electrode confronts the surrounding medium (gas, liquid or solution) each time with an exactly defined simple surface consisting of pure metal atoms – this represents an ideal model of a versatile two-phase system which can serve for precise studies of many interfacial phenomena.

As electrode, mercury has of all metals the highest overpotential for the reaction of electrolytic evolution of hydrogen – in aqueous alkaline solutions the alkali and the alkaline earth metal cations are electrodeposited on mercury at less negative potentials than hydrogen ions. The existence of the high hydrogen overpotential opens a wide potential »window« for various catalytic reactions which lower this overpotential to various extent and thus provide ways for analytical determination of many compounds. On the positive side of the potential scale the use of mercury as electrode is limited by the anodic dissolution of the metal in form of ions which occurs at +0.4 V *versus* saturated calomel electrode. Electrooxidations of many compounds cannot be hence followed on mercury; on the other hand, many anions and organic compounds which react with mercury ions can be followed and determined indirectly because their reactions shift the mercury dissolution characteristically to more negative potentials. Moreover, with a stationary mercury drop covered by a layer of the product of such a reaction (*e.g.* of calomel in a chloride-containing solution) it is possible to reach potentials more positive than with a platinum electrode and to study various oxidation processes.[2,3]

The renewal of the mercury electrodes can occur either spontaneously or in a controlled manner, usually automatically (see below); in either way it can proceed with high precision and reproducibility over a wide range of frequencies – from the hanging mercury drop to the mercury jet. The spontaneously renewed mercury electrode – by dropping – serves for surface tension measurements, as the changes of drop-time are strictly proportional to the changes of surface tension. For other purposes the automatic ways of electrode renewal are used nowadays. The size of the RME can be varied according to need : in a continuous or a discontinuous manner, also during measurement, and within wide limits, from the macro- to the microscale, and can be very precisely measured – by weighing, by optical or by electrochemical methods; it has been ascertained that the shape of the mercury drops, of the size commonly used for electrodes, is strictly spherical.[4] The dependence of an electrochemical process on the electrode size or on its surface area cannot be measured more precisely with any other electrode than with a RME. The preferred small size of a RME with a small surface area brings about only a negligible electrolytic conversion in the solution and, besides, it allows measurements to be designed on a miniature scale.

The fear of mercury as a poisonous substance is not substantiated – in a well aerated laboratory at normal room temperatures the metal does not represent any health risk whatsoever, as has been confirmed in course of several decades of experience in the authors' and many other laboratories. Mercury becomes dangerous only when it appears in highly poisonous organometallic compounds (methylmercury and derivatives thereof) which can be generated by microbial action – either upon mercury compounds, *e.g.* those used in the past in agriculture as fungicides, or upon metallic mercury in dumps of unassorted waste.

## THE PRESENT FORMS OF RENEWED MERCURY ELECTRODES

### *The Dropping Mercury Electrode (DME)*

The drawn-out tapered glass tubes, used for the DME by the early researchers[5] including Kučera and the first polarographers, were replaced for convenience sake in the late thirties by thick-walled cylindrical capillaries. Those could be either simply cut from thermometer tubes to the required length without any glass-blowing operation, or later directly ordered from the companies supplying electroanalytical equipment; this type has survived in many laboratories till these days.

With higher requirements on the sensitivity and reproducibility of measurements with the DME it became important to suppress the so-called »capillary response«,[6] *i.e.* the distinct response of the polarographic circuit to penetration of the solution to the capillary interior in the first instants after the drop detachment, or after discontinuous application of a potential pulse to the electrode, with the result of electrolysis taking place partly also along the mercury thread inside the capillary. This process changes the effective surface area of the electrode (and hence the total current) in an irregular manner, and generates products which accumulate at the inner walls of the capillary. That affects the rate of flow of mercury (thereby affecting the size of the drop), or even interrupts the electric contact, *e.g.*, as a result of aggregation of microscopic bubbles of hydrogen inside the capillary. In the at present most frequently used polarographic methods, in which the drop time is automatically controlled, the mercury drop is polarized only for a fraction of the drop-time and the current is measured only for a short period of that fraction, the problem of capillary response is not as serious as in classical polarography or in electrocapillary measurements. For electrocapillary measurements in the gas phase where the capillary response does not occur, the cylindrical capillaries give reproducible drop-times[7]. For measurements in solutions, however, better precision than with the cylindrical capillaries was obtained with the original conical ones[8] but best of all suited proved to be the spindle type capillary.[9–11] That one is made from the cylindrical thick-walled tube in which the bore is blown up into an asymmetrical spindle-shaped cavity, ended with a wide cone at the orifice. By this modification the penetration of the solution into the capillary is minimized : after the drop detachment a reproducible mercury meniscus remains sitting at the capillary end from which the next drop gradually grows. A reproducibility of drop-time within 20 ms can be achieved with this type of capillary for drop-times as long as several hundred seconds; this precision was the primary condition for the development of the »controlled convection« method of electrocapillary measurements.[12]

The dependence of drop-time on electrode potential follows the electrocapillary curve which is the basis of the Kučera's method; however, for measurements of current the change of drop-time with potential is not particularly desirable. For that reason the DMEs used in polarography are nowadays as a rule provided with an electromagnetic timing device which keeps the drop-time constant – the drops are detached in regular intervals by possibly gentle mechanical impulses imparted to the capillary. For d.c. polarography this device enriches the diagnostic criteria in electrode kinetic studies as compared with voltammetry on stationary electrodes: while the surface area of the DME depends on the product of the rate of flow of mercury and the drop-time, the timing device allows to follow the effect of each of these two parameters on polarographic waves separately.

The d.c. polarographic measurements carried out with an ordinary vertically fixed cylindrical capillary suffer notoriously from depletion of the electroactive substance and from accumulation of the electrolytic products in the solution immediately surrounding the mercury drop under the capillary end; the polarographic curve in that case does not represent the true response of the bulk solution. This drawback can be practically eliminated in a simple way:[13] by bending the capillary tube in a flame in a right angle and by cutting it then in the middle of the bend under the angle of 45° we obtain two capillaries with inclined fronts; when the drop falls from this capillary it takes along a slight stream of solution which rinses the capillary tip and brings fresh bulk solution to the electrode. The polarographic diffusion current recorded with this capillary corresponds to the Ilkovič equation corrected for spherical diffusion – a result which could not be achieved even with pointed thin- walled capillaries.[14] There is another way how to avoid the accumulation of electrolytic products around the capillary tip, which has been used in some of the commercial polarographs : the polarizing voltage is applied only to every alternative or every third drop and in the meantime the products are carried away with the intermediate drops. In the advanced polarographic/voltammetric methods when the electrode is polarized only for a fraction of a second this problem plays practically no role.

### *The Hanging Mercury Drop Electrode (HMDE)*

When the hanging mercury drop is used as working electrode, according to officially accepted terminology polarographic measurements change into voltammetric. The reproducible d.c.polarographic curve obtained with tens of renewed droplets of mercury is replaced by the voltammetric curve, equally well reproducible, but obtained with only a single exactly renewable mercury drop. In distinction to the DME the HMDE carries with itself its own »history« from the beginning of its polarization. The informations that can be gained from the two types of RMEs are complementary for understanding processes occurring at mercury electrodes. The manifold possibilities of applications of the HMDE became obvious soon after it had been introduced into laboratories.[3]

A definite number of drops collected from the DME and suspended in form of a little sphere on a short piece of wire can serve as a HMDE.[15] However, it was demonstrated experimentally that the metal of the wire affects the electrochemical properties of such a mercury electrode.[16] It is hence preferable to produce the HMDE without bringing mercury into contact with other metals.

If the flow of mercury through the polarographic capillary is suddenly stopped, a mercury drop remains hanging at the capillary tip. At the beginning the stoppage of the mercury flow was realized manually – first by a stopcock,[17] then by a micrometric screw.[18–20] In the present HMDEs the mercury flow is stopped automatically by different closure mechanisms operating a piston,[21] a needle valve[5,22–25] or a thin wire valve;[22–25] a precise control of gas pressure above the mercury level in the sealed mercury reservoir has been also used[10,22–26,31] for stopping and, in general, monitoring the growth of the drop. The reproducibility and the stability of HMDE depends on the type of capillary used and on the quality of the closures. The spindle type capillary provides a stable drop support by the mercury meniscus forming at the orifice, and hence it is particularly well suited for the HMDE. The period of time for which the piston or the valve is lifted determines the size of the drop. Opening the flow of mercury into a relatively narrow capillary for 30 ms without additional gadgets can result in producing a mercury microelectrode of no less than about 30 m diameter;[22,23] reaching smaller sizes requires overcoming the back pressure which increases inversely with the drop size. Some methods have been already designed how to overcome it and to generate the highly desirable automatically renewable, reproducible mercury micro- or ultramicro electrodes.[10,22–25,27,28]

### *The Static Mercury Drop Electrode (SMDE)*

The periodic growth of the DME is often considered as a drawback which complicates the system electrode/solution in polarography by the time dependence of the electrode surface area. This inconvenience was solved by the introduction of the SMDE, based on a combination of the DME and HMDE principles.[10,21–25,29,30] In the SMDE the drop is formed by a fast mercury flow through a wide bore capillary in the first moments of the drop life; then the flow is automatically stopped and the potential is applied to the electrode only after it has become static. When the given drop-life is over, the old drop is dispatched and a new one is produced by an automatically repeated sequence of steps. In this way the SMDE makes it possible to carry out measurements with constant surface area of a periodically renewed mercury surface. However, as the course of the instantaneous current on a stationary electrode differs from that on a growing DME, the classical equations for polarographic currents do not apply for the SMDE.

### *The Contractile (Compressible) Mercury Drop Electrode*

In the studies of interfacial phenomena with renewed mercury electrodes it is convenient to have the possibility at a certain stage of a heterogeneous process to contract the electrode surface. This has been achieved by connecting the atmosphere in the mercury reservoir for the DME with a vacuum system.[10,22–26] The mercury drop once formed can thus be contracted to 1/100 of its original size.[10,22–25] Such a contraction can prove useful in voltammetric determination of surfactants.[31]

Figure 1. represents an example of the block scheme of a contractile (contractible, compressible) RME. The electrode 1 with the spindle capillary 2 in the circuit of the measuring system 3 dips with the other electrodes 4 into the solution 5. The measuring system is connected to the source of overpressure or vacuum 6 which controls the electrode 1. According to the pressure program a mercury drop 7 of usual size is first formed at the end of the capillary, which then gets contracted to the required extent during the »suction« phase. After the measurement the drop is renewed and the sequence of operations can be periodically repeated.

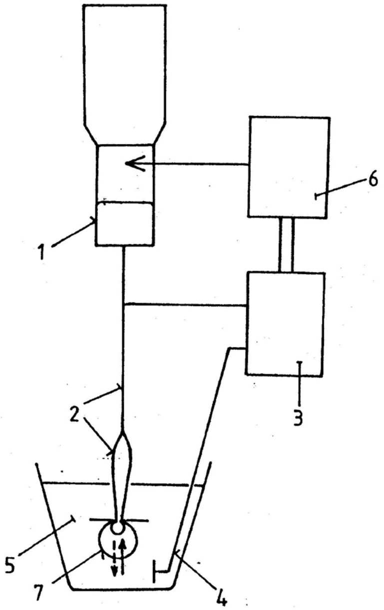

Figure 1. A block scheme of a contractile RME (description in the text).

### ThE Multi-Purpose Mercury Drop Electrodes

The commercially available renewed mercury electrodes nowadays enable the user to work in either of the DME, HMDE or SMDE modes by simply adjusting the controls on one instrument. These multi-purpose mercury drop electrodes are often fixed on one solid stand the design of which sometimes allows the mercury electrode to be replaced by another type of polarizable working electrodes. However, some more advanced versatile general mercury drop electrodes can operate independently of the stand and in various positions. An example of these is the pen-type universal mercury mini- and micro-electrode, patented first in 1978 and since then further improved.[10,22–25]

The *pen-type mercury drop electrode*[29–32] consists of a body and a capillary. In the cylindrical body 9 cm long and 2 cm thick are encased a small plastic reservoir for 3 ml of mercury and a relay which operates the valve controlling the flow of mercury into the capillary. The capillary is easily exchangeable: according to need cylindrical, conical or spindle capillaries of different inner dimensions are used; in this way mercury drops of different sizes can be produced. The spindle capillary serves for precise drop-time measurements and for generating stable mercury drop and meniscus electrodes. If desired the mercury reservoir can be connected to a combined source of vacuum and gas pressure and thus the contractile mercury drop can be realized. The pen-type electrode has three leads – one joins the electrode to the electrolytic circuit and two connect the valve-controlling relay with an electronic source of voltage impulses. Another relay activates the drop detaching device. By varying the signs, the amplitudes and the frequency of impulses imparted to the two relays the renewed mercury electrode of practically any desired property is available. The sequence of impulses is provided most conveniently from the computer-controlled polarograph by an appropriate computer program. The so-called »stepwisely growing drop electrode«[33] is one of the possibilities contained already in the pen-type.[32]

In Figure 2 is introduced the above described multi-purpose RME for measurements in all the mentioned modes, Figure 3 shows an advanced version of it in an operating position in the polarographic stand, connected to a PC unit through a special interface. The whole system is flexible, allowing changes of working configuration as well as of the computer, and in connection with a lap-top or note-book type of PCs it is portable, independent of the mains.

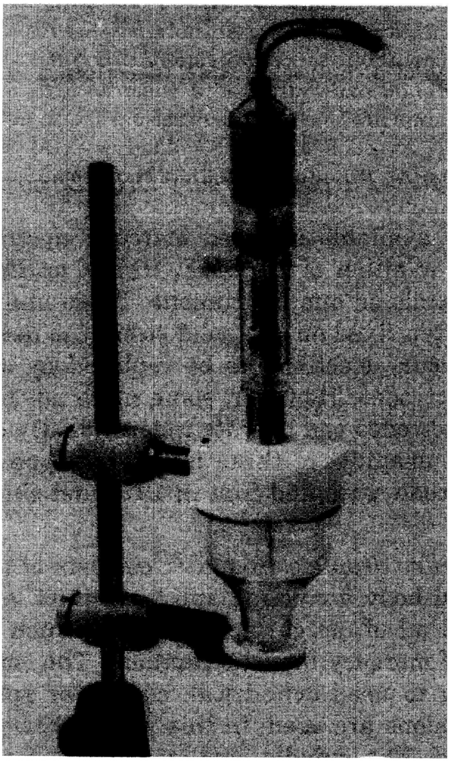

Figure 2. A multi-purpose RME for measurements in various regimes and modes (description in the text).

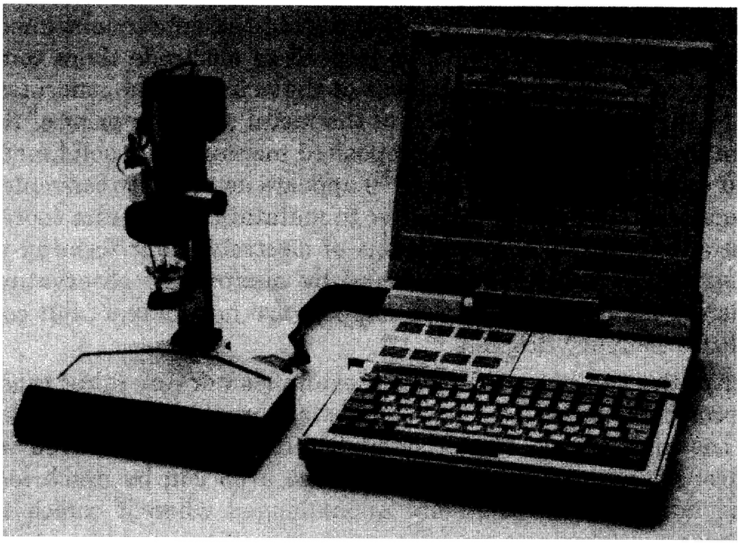

Figure 3. The multi-purpose pen-type RME in the polarographic stand, connected to a lap-top PC unit.

### *Other Renewed Mercury Electrodes*

The surface of the *mercury jet electrode* is constantly fast renewed and has at the same time constant surface area; it is realized by a definite length of a coherent jet of mercury streaming into the solution from a tapered glass tube. The definite length is achieved either by sending the mercury stream in an inclined direction upwards out of the solution through the surface[34] or by fixing at a certain distance from the nozzle a glass target, on which the mercury jet breaks into small droplets.[35] Due to the fast flow of mercury through the solution only fast processes can be followed with the mercury jet electrode. For purposes of fundamental research this electrode offers useful possibilities; for practical applications, however, there are the drawbacks of high charging currents and a high consumption of mercury. The quantitative reproducibility of results is limited by the difficulty of maintaining constant electrode surface area, *i.e.*, constant length of the coherent mercury jet, especially when polarized over a wider potential range.

*The mercury film electrode (MFE).* In the anodic stripping technique when amalgam-forming metals are electrolytically accumulated in the mercury electrode the volume of the latter determines the rate and the sensitivity of the analytical operation: i) a given concentration of amalgam is attained faster by electrolysis into a smaller volume of mercury, and ii) if the given amount of electrolytically deposited metal dissolves in a smaller volume of mercury, the relative concentration of the ensuing amalgam becomes higher and so will be the peak recorded during the subsequent anodic scan of the amalgam. When mercury drop is used as electrode there comes also the undesired factor of an effective loss of the active metal concentration at the mercury surface due to diffusion of the metal to the interior of the drop. Thus a thin layer of electrolytically deposited mercury on a solid metal (iridium proved empirically as best suited[36]) appears as a highly convenient electrode for analytical purposes.[37] In order to maintain the results reproducible it is essential to keep all the conditions of electrolysis for forming the film electrode strictly constant. It was found by microscopic observations that thin mercury films on glassy carbon support are not compact but consist of arrays of little mercury droplets.[38]

Neither of the two above mentioned examples nor any other types of renewed mercury electrodes (*mercury cup,*[39] *mercury pool,*[40] *flowing mercury,*[41] *etc.*) have the high degree of reproducibility that can be achieved with the mercury drops (error in reproducing surface area can be much less than 0.1 %). The latter remain therefore unchallenged when it comes to exact measurements.

## RECENT APPLICATIONS OF RENEWED MERCURY ELECTRODES

The introduction of personal computers into polarographic/ voltammetric techniques in the nineteen-eighties spurred a rapid technical development and refinement of the appropriate hardware, above all of the electrodes. The versatility of the latest types of RMEs, the wide available choice of their parameters and the verified possibility of their use in long-time fully automatic measurements[42] brought a variety of their new applications, examples of some of which are presented below.

### *Analytical Chemistry*

*Environmental analysis* or *ecoanalysis* represents the widest field of practical applications of the RMEs. The control of pollution of waters has been worked out to a particularly high degree of perfection. A special immersible device equipped with an automatically renewable HMDE has been constructed for in situ determination of traces of heavy metal ions in lakes or seas at the nM level by the method of anodic stripping.[43] Voltammetric control of the level of nitrates[44] and nitrites[45] by means of HMDE in sources of drinking water has become widely used. Numerous are the applications of HMDE for following the pollution of waters by surfactants – a task for which this electrode is especially well suited – by measuring either the electrode capacitance,[46–49] the differential voltammetric capacitive signal in deaerated sample solution,[50,51] or the effect of the water sample on the current signal due to reduction of oxygen on HMDE,[52] in all cases after adsorptive accumulation at the electrode surface. The method of adsorptive stripping voltammetry in which HMDE is the electrode of the first choice, finds ever wider applications.[53]

*Triboanalysis*, an analytical method for diagnosing the degree of wear of parts of engines and motors without dismounting them, by following the levels of abrasion metals in oil and other lubricants, was originally the domain of atomic absorption spectrophotometry. Later it was ascertained that the concentration of metals in oil samples can be determined with equal precision and at a much lower cost by voltammetry with HMDE, after extraction into aqueous HCl.[54]

For polarography as well as for voltammetry it was demonstrated that with the small mercury droplets the same quantitative results are obtained whether the electrode drops/dips into the solution bulk or into a fraction of a solution drop held by surface tension in a small loop of silver wire of diameter only slightly exceeding the size of the electrode.[55]

### *Physical Chemistry*

The RMEs are useful in studies of the problems of electrode kinetics, particularly if these concern various kinds of interactions of the studied substance with the electrode. Recently it was shown by a combination of electrocapillary, polarographic and voltammetric measurements how the type of adsorption of cystine changes with the potential of mercury electrode from pure chemisorption to a complex reversible surface interaction.[56] – On the case of the anodic reaction of mercury ions with cysteine it could be demonstrated[57,58] that the electrolytic dissolution of mercury begins with dimeric mercurous ions, $Hg_2^{2+}$, which at more positive potentials undergo currentless reversible disproportionation into mercuric ions, $Hg_2^{2+}$, and metallic mercury, provided there is free mercury accessible at the electrode surface; in the negative case the $Hg_2^{2+}$ ions are electrooxidized to two $Hg^{2+}$ ions. – The ideally pure surface of DME has enabled a study of electrolysis of pure water on mercury electrodes in absence of any electrolyte, and of the gradual build-up of the ionic double layer on addition of electrolytes, by means of photocurrents due to photoemission of electrons from the DME and the ensuing scavenging reaction of the photogenerated hydrated electrons with water molecules in the diffuse part of the double layer.[59]

The technique of studying the processes of electrochemical nucleation and growth of surface films on HMDE has become a highly advanced field of exact research.[60] It has been found[61] that an originally two-dimensional surface layer on mercury can under certain conditions undergo a slow three-dimensional reconstruction characterized by an effective fractal dimension of 2.16. – Spectacular potential-dependent effects of crystal growth can be observed on the mercury drop electrodes when metals are electrodeposited from concentrated solutions of their compounds.[62,63] – Measuring instantaneous currents passing through a DME, which starts growing above the solution and just touches the surface in the last fraction of drop-life before it falls (the »current spike polarography«),[64] brings new possibilities for measuring surface potentials and for gaining deeper insight into surface phenomena. – DME can also serve for determining characteristic properties of hydrophobic aggregates in aquatic environment.[65] – The properties of the DME appeared very convenient also for continuous measurement of viscosity of liquids.[66]

Ultrasmall metal oxide colloids of semiconductor nature were found to be reduced on RMEs in a diffusion-controlled process which differs from that known with true solutions; it could be established that the mechanism of the electrolytic reductions of colloids consists primarily either in reactions occurring at the surface of the particles or in electron transfer from the electrode to their conduction band.[67–70]

## *Biochemistry*

In the studies of nucleic acids and their components the RMEs continue providing excellent service. The strong adsorptivity of DNA and RNA on mercury was the main condition for working out the method of *adsorptive transfer stripping voltammetry (AdTSV)*[71] which has opened wide possibilities for studies of interactions of nucleic acids with biologically important compounds[72] and at the same time reduced to minimum the amount of the rare biological material necessary for such experiments. The HMDE is dipped into a droplet of solution of the nucleic acid which gets strongly adsorbed at the mercury surface. The electrode is then rinsed and transferred into a normal volume of solution in the electrolytic cell where the nucleic acid sticking to the electrode is subjected to voltammetric analysis in presence of biological agents. Among the most important recent results achieved with this method is the determination of small amounts of RNA in presence of DNA and *vice versa,* a procedure which has not been achieved so far in any other way.[73] The distinction between the two nucleic acids and their determination in presence of each other is possible thanks to the high sensitivity of the mercury surface to the complex specific interaction which it undergoes with each of the two important macromolecules.

The high electrochemical reactivity of mercury with compounds bearing the -SH group makes the RMEs ideal instruments for determination of many biologically important compounds. A simple method was described for continuous monitoring of activities of many enzymes and related substrates, based on the anodic wave obtained with the DME in presence of thiols.[74] DME and HMDE are being used for the study of structure and properties of the *metallothioneins,*[75–77] the specific metalloproteins essential in the reactions of animal organisms towards metals, and of their plant counterparts, the *phytochelatins*. Electrochemistry with RMEs thus contributes to the knowledge of the presently intensively studied compounds.

## REFERENCES

1. C. F. Varley, *Phil. Trans.* **101** (1871) 129–136.
2. T. Kuwana and R. Adams, *Anal. Chim. Acta* **20** (1959) 60–67.
3. W. Kemula, *Voltammetry with the hanging mercury drop electrode*, in I. S. Longmuir (Ed.), *Advances in Polarography*, Pergamon Press, Oxford, 1960, Vol. I., pp. 105–143.
4. G. S.Smith, *Trans. Faraday Soc.* **47** (1951) 63–70.
5. M. Heyrovsky, L. Novotny, and I. Smoler, *The past and future of the dropping electrode,* in: J. T. Stock, and M. V. Orna (Eds), *Electrochemistry, Past and Present*, ACS Symposium Series 390, Am. Chem. Soc., Washington D. C., 1989, pp. 370–379.
6. G. C. Barker, *Anal. Chim. Acta* **18** (1958) 118–131.
7. R. Labin and I. Oref, *J. Appl. Phys.* **48** (1977) 406–408.
8. I. Smoler, *J. Electroanal. Chem.* **51** (1974) 452–455.
9. L. Novotny, in *Proc. J. Heyrovsky Mem. Congress on Polarography,* Prague 1980, Vol. II, p.129.
10. L. Novotny, PhD Thesis, J. Heyrovsky Institute, Prague, 1981.
11. L. Novotny and M. Heyrovsky, *Trends Anal. Chem.* **6** (1987) 176–181.
12. L. Novotny and I. Smoler, *J. Electroanal. Chem.* **146** (1983) 183–8.
13. I. Smoler, *J. Electroanal. Chem.* **6** (1963) 465–479.
14. J. Flemming and H. Berg, *J. Electroanal. Chem.* **12** (1966) 391–396.
15. H. Gerischer, *Z. physik. Chem. (Leipzig)* **202** (1953) 302–310; *Anal. Chem.* **31** (1959) 33–39.
16. W. Kemula, Z. Kublik, and Z. Galus, *Nature (London)* **183** (1959) 1795.
17. V. Ćermák, *Collect. Czech. Chem. Commun.* **24** (1959) 831–838.
18. J. E. B. Randles and W. White, *Z. Elektrochem.* **59** (1955) 669–671.
19. W. Kemula and Z. Kublik, *Anal.Chim.Acta* **18** (1958) 104–111.
20. J. J. Vogel, *J. Electroanal. Chem.* **8** (1964) 82–84.
21. W. M. Peterson, *International Lab.* **112** (1980) 51–62.
22. L. Novotny, *Czech patents* AO 202316, 202772, Praha 1978; AO 220439, 224754, 219475, 207871, Praha 1979/80, etc; V-22864/89, Praha 1989; *US Pat.* 5173101, 5294324 (1990); *Europat. Appl.* No 91101283 (1990).
23. L. Novotny, *Proceedings of the Conference »Analytik-treffen« Neubrandenburg,* Univ. Leipzig, 1985, p. 59.
24. L. Novotny, *Electroanalysis* **2** (1990) 287.
25. L. Novotny, *Fresenius J. Anal. Chem.* in press.
26. R. Dias, C. Buess-Herman, and L. Gierst, *J. Electroanal. Chem.* **130** (1981) 345–349.
27. A. Baars, M. Sluyters-Rehbach, and J. H. Sluyters, *J. Electroanal. Chem.* **283** (1990) 99–113.
28. R. M. Town, M.-L.Tercier, N. Parthasarathy, F. Bujard, S. Rodak, C. Bernard, and J. Buffle, *Anal. Chim. Acta* **302** (1995) 1–8.

29. L. Novotny, *Principles of Interfacial Measurements and Adsorption Voltammetry with Mercury Electrodes*, in: K. Štulík and R. Kalvoda (Eds), *Electrochemistry for Environmental Protection*, UNESCO Lab., Charles Univ. and Acad. Sci. C. R., Prague, 1995, pp. 43–67.
30. L. Novotny, *Vod. hospodáøství*, in press.
31. L. Novotny, *Electroanalysis* **7** (1996) 1–4.
32. L. Novotny, *Fresenius J. Anal. Chem.*, in press.
33. Z. Kowalski, *Analyst* **113** (1988) 15–19.
34. J. Heyrovsky and J. Forejt, *Z. physik.Chem.* **193** (1943) 77–96.
35. J. Koryta, *Coll. Czech. Chem. Commun* **19** (1954) 433–443.
36. S. P. Kounaves and J. Buffle, *J. Electroanal. Chem.* **216** (1987) 53–69.
37. E. Barendrecht, *Stripping Voltammetry*, in A. J. Bard (Ed.) *Electroanalytical Chemistry*, New York, Marcel Dekker, 1967, Vol. 2, p. 87.
38. M. Štulíková, *J. Electroanal. Chem.* **48** (1973) 33–45.
39. R. Kalvoda, *Techniques of Oscillographic Polarography*, Amsterdam, Elsevier, 1965, p. 171.
40. C. A. Streuli and W. D. Cooke, *J. Phys. Chem.* **57** (1953) 824–826.
41. V. S. Griffiths and W. J. Parker, *Anal. Chim. Acta* **14** (1956) 194–200.
42. P. Valenta, L. Sipos, L. Kramer, P. Krampen, and H. Rützel, *Fresenius Z. Anal. Chem.* **312** (1982) 101–108.
43. M.-L.Tercier and J. Buffle, *Electroanalysis* **5** (1993) 187–200.
44. K. Markušová, *Anal. Chim. Acta* **221** (1989) 131–138.
45. J. Polák, L. Janáček, and J. Volke, *Chem. Listy* **83** (1989) 760–764.
46. H.-J. Ulrich, W. Stumm, and B. Ćosović, *Environ. Sci. & Technol.* **22** (1988) 37–41.
47. Z. Kozarac, R. Klarić, D. Dragević, and B. Ćosović, *Coll. & Surf.* **56** (1991) 279–291.
48. B. Ćosović and V. Vojvodić, *Marine Chem.* **28** (1989) 183–198.
49. Z. Kozarac, B. Ćosović, B. Gašparović, A. Dhathathreyan, and D. Möbius, *Langmuir* **7** (1991) 1076–1081.
50. R. Kalvoda and L. Novotny, *Coll. Czech. Chem. Commun.* **51** (1986) 1587–1594.
51. N. K. Lam and M. Kopanica, *Anal. Chim. Acta* **161** (1984) 315–324.
52. L. Novotny and T. Navrátil, *Analyst*, in press.
53. R. Kalvoda, *Fresenius J. Anal. Chem.* **349** (1994) 565–570.
54. M. Kovac, R. Kalvoda, L. Novotny, and A. Berka, *Electroanalysis* **5** (1993) 171–176.
55. R. Heyrovská, *J. Electrochem. Soc.* **139** (1992) L 50–L 53.
56. M. Heyrovsky, P. Mader, V. Veselá, and M. Fedurco, *J. Electroanal. Chem.* **369** (1994) 53–70.
57. V. Vavøička and M. Heyrovsky, *J. Electroanal. Chem.* **375** (1994) 371–373.
58. M. Heyrovsky and V. Vavøička, *J. Electroanal. Chem.* (1996) submitted.
59. M. Heyrovsky and F. Pucciarelli, *Internat. Rev. Phys. Chem.* (1996) in press.
60. R. DeLevie, *Chem. Rev.* **88** (1988) 99–109.
61. L. Pospíšil, *J. Phys. Chem.* **92** (1988) 2501–2506.
62. A. Calusaru and J. Kùta, *J. Electroanal. Chem.* **20** (1969) 383–392.
63. A. Calusaru, *Electrodeposition of Metal Powders*, Chapter VIII, Materials Science Monographs 3, Amsterdam, Elsevier, 1979, pp. 266–293.
64. R. Heyrovská, *Langmuir* **9** (1993) 1962–1964.
65. N. Ivošević, J. Tomaić, and V. Žutić, *Langmuir* **10** (1994) 2415–2418.
66. J. Matysik and A. Persona, *J. Polym. Sci. Polym. Chem. Ed.* **20** (1982) 3451–3452.

67. M. Heyrovsky and J. Jirkovsky, *Langmuir* **11** (1995) 4280–4292.
68. M. Heyrovsky, J. Jirkovsky, and B. R. Müller, *Langmuir* **11** (1995) 4293–4299.
69. M. Heyrovsky, J. Jirkovsky, and M. Štruplová-Bartáčková, *Langmuir* **11** (1995) 4300–4308.
70. M. Heyrovsky, J. Jirkovsky, and M. Štruplová-Bartáčková, *Langmuir* **11** (1995) 4309–4312.
71. E. Paleček and I. Postbieglová, *J. Electroanal. Chem.* **214** (1986) 359–371.
72. E. Paleček, *Bioelectrochem. Bioenerg.* **20** (1988) 179–194.
73. E. Paleček and M. Fojta, *Anal. Chem.* **66** (1994) 1566–1571.
74. J. Homolka, *J. Clin. Chem. Clin. Biochem.* **25** (1987) 805–809.
75. B. Raspor, J. Pavčić and M. Branica, *Marine Chem.* **28** (1989) 199–214.
76. I. Šestáková, D. Miholová, H. Vodičková, and P. Mader, *Electroanal.* **7** (1995) 237–246.
77. S. Duquesne, M. A. Jouquin, and C. Hogstrand, *Fresenius J. Anal. Chem.* **352** (1995) 589–595.

## SAŽETAK

### Obnovljene živine elektrode - svestrana sredstva za istraživanje u općoj kemiji

*Ladislav Novotny i Michael Heyrovsky*

Pregledni prikaz najnovijih oblika obnovljenih živinih elektroda s primjerima njihovih raznih primjena.