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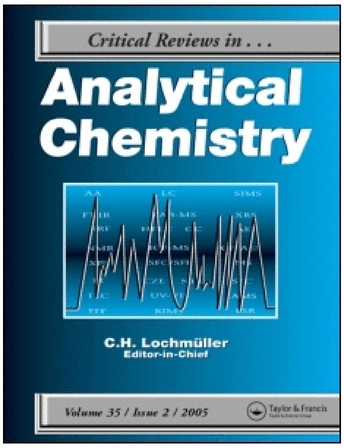

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Polarography and Voltammetry at Mercury Electrodes

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ABSTRACT: Scope and limitations of modern polarographic and voltammetric techniques on mercury electrodes are discussed and many practical examples of their applications in practical analysis are given to demonstrate that even in the third millennium polarography and voltammetry at mercury electrodes can be very useful analytical tools, which in certain cases can successfully compete with modern spectroscopic and separation techniques.

KEY WORDS: review, polarography, voltammetry, mercury electrodes.

TABLE of CONTENTS

ABBREVIATIONS: **AC**, alternating current; **ACS**, American Chemical Society; **ACV**, alternating current voltammetry; **ASV**, anodic stripping voltammetry; **AdSCP**, adsorptive stripping chronopotentiometry; **AdST**, adsorptive stripping tensammetry; **AdSV**, adsorptive stripping voltammetry; **APD**, ammonium pyrrolidine dithiocarbamate; **BES**, *N*,*N′*-*bis*(2-hydroxyethyl)-2-aminoethane sulphonic acid; **CME**, chemically modified electrode; **CSV**, cathodic stripping voltammetry; **CV**, cyclic voltammetry; **DME**, dropping mercury electrode; **DPP**, differential pulse polarography; **DPV**, differential pulse voltammetry; **FS DPV**, fast scan differential pulse voltammetry; **HEPES**, *N*-2-hydroxyethylpiperazine-*N′*-2-ethane sulfonic acid; **HMDE**, hanging mercury drop electrode; **HPLC-ED**, high-performance liquid chromatography with electrochemical detection; **ISE**, ion-selective electrodes; **IUPAC**, International Union for Pure and Applied Chemistry; **LOD**, limit of detection; **LSV**, linear scan voltammetry; **M**, molar concentration (mol.dm^{-3}); **MFE**, mercury film electrode; **NPP**, normal pulse polarography; **NPV**, normal pulse voltammetry; **PSA**, potentiometric stripping analysis; **s**, seconds; **SCV**, staircase voltammetry; **SMDE**, static mercury drop electrode; **SPE**, solid phase extraction; **SWP**, square wave polarography; **SWV**, square wave voltammetry; τ, time of the drop; **UV**, ultraviolet radiation

1040-8347/01/$.50

I. INTRODUCTION

In 1922, the Czech chemical journal Chemické Listy published a paper[1] in which Jaroslav Heyrovský described for the first time certain phenomena from which polarography was gradually developed. More than 40 years ago, on October 26, 1959, Jaroslav Heyrovský was awarded the Nobel Prize "for his discovery of the polarographic methods of analysis". On December 20, 2000 we commemorated 110 anniversary of the birth of professor Heyrovský. In order to commemorate the 40th anniversary of the award of the Nobel Prize to Jaroslav Heyrovský, an international conference "Modern Electroanalytical Methods"[2] was organized and held at Sec in the Czech Republic. To commemorate 110 anniversary of the birth of professor Heyrovský, the memorial symposium was organized.[3] Both meetings showed clearly that over almost 8 decades the technique is still maturing and remains an important part of the armoury of electrochemical and analytical experimental procedures. Personal contribution of Professor Jaroslav Heyrovský to this field cannot be overestimated (see papers[4,5]). His main contribution was the recognition of the importance of potential and its control, the analytical opportunities offered by measuring the limiting currents and the introduction of dropping mercury electrode as an invaluable tool of modern electroanalytical chemistry.[6]

The capabilities of the technique and its application range are well known and widely utilized. Its unique principles enable a wide range of applications that continue to illustrate the usefulness and elegance of polarographic and voltammetric analysis.[7] Nevertheless, it is perhaps useful from time to time to reiterate the continuing importance of these techniques in modern analytical chemistry, and that is one of the purposes of this article. It should be stressed that polarography was the first major electroanalytical technique and was used for decades before other techniques working with non-mercury electrodes were introduced.

To commemorate Jaroslav Heyrovský's contribution, this article concentrates mainly on polarography and voltammetry on mercury electrodes, despite the enormous and ever-increasing importance of solid electrodes, carbon paste electrodes, screen printed electrodes, and chemically modified electrodes. It concentrates on the development during recent years and its aim is to show that even in the third millennium polarography and voltammetry at mercury electrodes can continue to be very useful analytical tools, which in certain cases can successfully compete with modern spectroscopic and separation techniques. We believe that because of the competitive features of advanced electroanalytical methods they should continue to be considered for industrial and environmental analyses. Many examples of the use of polarography and voltammetry, as well as discussions of their advantages and limitations for these determinations, have been published.[8,9] The comparison of polarographic and other analytical techniques is depicted in Figure 1.

II. TECHNIQUES

The theory of polarographic and voltammetric techniques is well described in monographs.[10,11,12] Voltammetric methods used today in analytical laboratories comprise a suite of techniques, the creation of which was made possible by rapid advances in instrumentation, by the computerized processing of analytical data, and particularly by innovative electrochemists. Advances in microelectronics and in particular the early introduction of operational amplifiers and feedback loops have led to major changes in electroanalytical instrumentation. Indeed, many functions can be performed now by small and reliable integrated circuits. Voltammetric analyzers consist of two such circuits: a polarising circuit that applies the potential to the cell and a measuring circuit that monitors the cell current. The working electrode is potentiostatically controlled, and this minimises errors from cell resistance. Electroanalytical procedures can be fully programmed and can be driven automatically by means of a personal computer with a user-friendly software.[10]

All this results in the possibility of fast "time-resolved" sampling of the current from dropping mercury electrode. The mercury drop emerging from the capillary monitors current that consists of that due to charging of the double layer and the faradaic current produced by reduction or (less

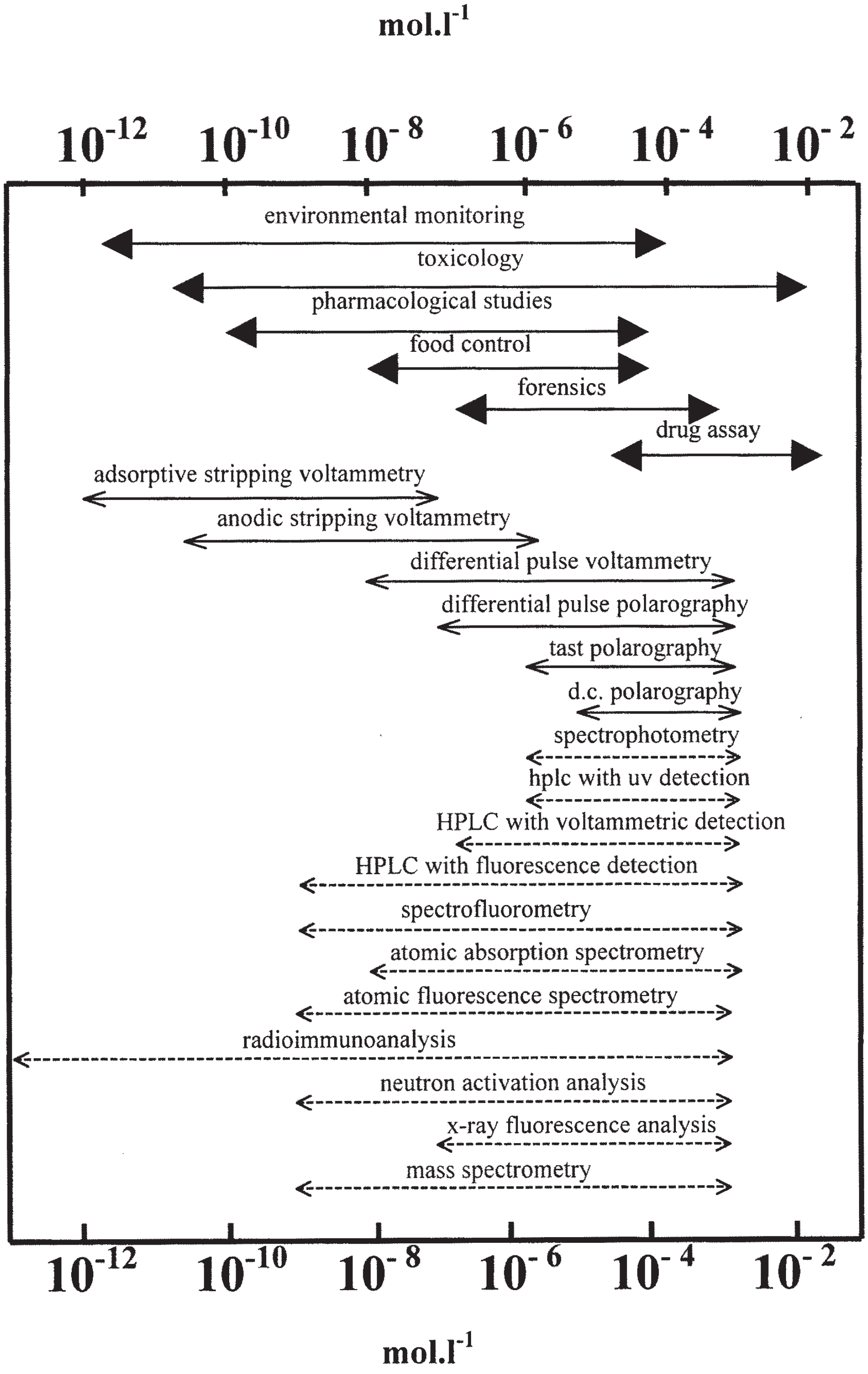


FIGURE 1. The application range of various analytical techniques and their concentration limits when compared with the requirements in different fields of chemical analysis.

frequently) oxidation of the analyte in solution. The contribution of the capacitance current becomes less as the drop increases in size and the rate of increase in area becomes much smaller. Thus, if the current is sampled at a long enough time after the drop has started to emerge from the capillary, the capacitance current is discriminated against to the faradaic current: this is utilized in its simplest form in TAST polarography, but it is utilized also when more advanced pulse waveforms are used. Pulse waveforms improve further signal-to-noise ratio for other reasons as well.[13,14] LOD can be further decreased by a new method to obtain the signal associated with a blank in DPV and stripping voltammetry.[15] In this method, the signal assigned to the blank is obtained by direct integration of the background noise extrapolated values of the base-peak width at different concentrations. All pulse techniques (NPP, DPP, SWP, and SCV) are chronoamperometric and are based on a sampled current potential-step experiment.[16] After the potential is stepped, the charging current decreases rapidly (exponentially), while the faradaic current decays more slowly. Another technique that allows the separation of the contributions of the faradaic and charging current is ACV, which involves the superimposition of a small amplitude AC voltage on a linearly increasing potential, where the charging current is rejected using a phase sensitive lock-in amplifier.

Stripping analysis is one of the most sensitive voltammetric methods. A detailed description of stripping voltammetry has been given in a monograph by Wang.[17] Its high sensitivity is due to the combination of an effective preconcentration step (electrolytic or adsorptive) with advanced measurement procedure. Because analytes are preconcentrated onto the electrode by factors of 100 to 1000, detection limits are lowered by 2 to 3 orders of magnitude to those of voltammetric measurements that do not utilize prior accumulation. A survey of the theory and practical applications of the preconcentration methods can be found in monographs[18,19] and reviews.[20,21] The preconcentration in ASV is based on electrolytic deposition (reduction of metal ion to the amalgam) and its subsequent dissolution (reoxidation) from the electrode surface by means of an anodic potential scan. It has been the most widely used form of stripping analysis for determination of metals. Classic CSV involves the anodic deposition of the analyte, followed by a negative going stripping scan. It is used to measure a range of organic and inorganic anionic substances capable of forming insoluble salts with the electrode material (mercury, much less commonly silver or copper). PSA differs from ASV in the method for stripping of the amalgamated analyte. Its great advantage over ASV is that deoxygenation is not necessary. After preconcentration the potentiostatic control is disconnected and the reoxidizing is done by using a chemical oxidizing agent [oxygen, Hg(II)] present in solution, or by applying a constant anodic current on the electrode. Representative applications of stripping techniques using either electrolytic (ASV, CSV, PSA) or nonelectrolytic preconcentration steps for determination of trace metals has been summarised.[22] AdSV[17] uses nonelectrolytic adsorptive preconcentration where the analyte accumulation is a result of its adsorption on the electrode surface or that of a surface active complex of the analyte. It exploits the reduction of a metal or of a ligand in the adsorbed complex.[23] The adsorption can be coupled in some cases with catalytic reactions. The theoretical aspects of electrocatalysis on HMDE are described in Ref. 24 AdSV proved to be suitable for measuring trace amounts of metals in complexes with chelating agents and of many surface active organic compounds (drugs, vitamins, pollutants, and many others). It has been applied in many environmental and clinical studies[25] as well as in drug analysis.[26] Possibilities of stripping voltammetry with an emphasis on adsorptive stripping voltammetry and on the use of modified or ultramicro electrodes[27] and chemically modified electrodes, including mercury ones,[173] have been reviewed. The pros and cons of the reactant adsorption in pulse techniques together with the survey of phenomena due to reactant adsorption and with practical guidelines of treating it have also been discussed.[28] Important features of AdSV and AdSCP (often not correctly called adsorptive stripping potentiometry) together with their historical backgrounds are discussed in recent review.[29] It is stressed in this review that AdSV development started from some observation made with oscillographic polarography, another brainchild of professor Heyrovský. The important basis of electrochemical knowledge obtained polarographically and resulting from Heyrovský's original ideas on the development of later electroanalytical techniques, such as CSV and CME, is recognized in an extensive review devoted to the different aspects of CSV at HMDE and non-mercury disposable sensors.[30] For a comprehensive survey of methods mentioned above with their basic parameters see Table 1.

III. WORKING ELECTRODES

The performance of voltammetry is strongly influenced by the working electrode material. Ideally, the electrode should provide a high signal-to-noise ratio as well as a reproducible response. Hence, the majority of electrochemical stripping methods use HMDE or MFE[31] for use in the cathodic potential area, whereas solid electrodes (Au, Pt, glassy carbon, carbon paste) are used for examining anodic processes.

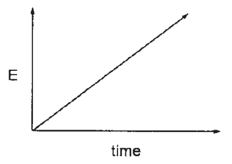
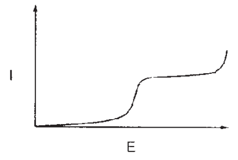
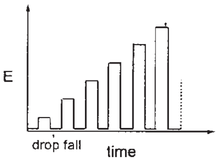
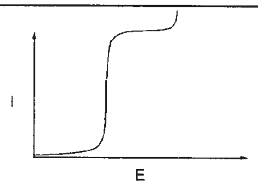
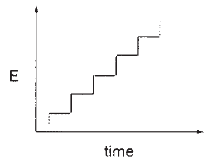
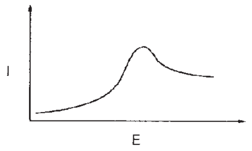
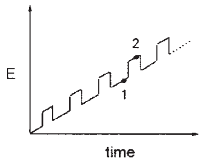
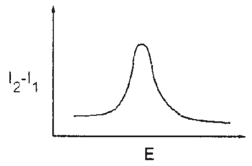
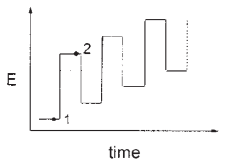
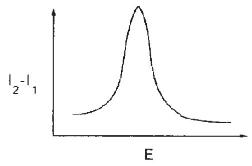
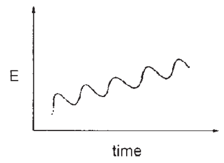
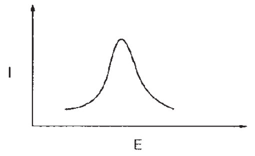
The greatest advantage of mercury electrodes is the fact that new drops or new thin mercury films can be readily formed, and this "cleaning" process removes problems that could be caused by contamination as a result of the previous analysis. This is not generally the case for electrodes made from other materials, with the possible exception of carbon paste electrodes, where the electrode cleaning is made by cutting off a thin layer of the previous electrode surface. Another advantage is the possibility to achieve a state of pseudostationarity for LSV using higher scan rates.[32] The extensive cathodic potential range of mercury electrodes (from +0.4 to –2.5 V according to supporting electrolyte) is also significant. Very interesting possibilities are offered by stepwise growing mercury drop or shrinking mercury drop,[33] as demonstrated by distinction between native and denaturated DNA by means of a compression mercury drop electrode.[34] Micro MFE was applied to the determination of picograms of Pb, Cd, Zn, and Cu in single rain drops and microvolumes of rain water.[35] The precision of electrochemical measurements can be further increased by various modifications of commercial static or hanging mercury electrodes.[36] Controlled potential electrolysis with the dropping mercury electrode, in which a small volume (typically 0.5 to 1.0 mL) of the electrolyzed solution, is stirred by the falling off drops, enables coulometric and mechanistic studies unaffected by products formed at the electrode surface.[37] Miniaturized and contractible (compressible) mercury electrodes offer new possibilities in voltammetry of biologically active species and surfactants.[38] Important features of mercury electrodes in polarography and voltammetry are summarized in Table 2.

IV. PRACTICAL ARRANGEMENT

Three electrode cells are commonly used in potentiostatic experiments. Saturated calomel, silver chloride, or mercury sulfate electrodes are used as reference electrodes, often insulated from the sample solution by means of an intermediate bridge or a fritt in order to prevent the contamination of the solution to be analyzed. Inert conducting materials (platinum wire or graphite rod) are used as the auxiliary electrode. They allow the current flow: the reference electrode is not connected into the polarizing circuit. The cell design is selected according to the experiment and is made mainly of glass. The plastic-tip capillaries and cells are recommended for use in fluoric acid or other glass corroding media.[39] The cell volume usually varies between 1 to 10 mL. However, measurement in a single drop of solution is feasible.[35] This is important especially if limited amount of a sample is available (blood of a newborn child) or a preconcentration is involved. (The dissolution of a residue after evaporation of organic solvent after liquid or solid phase extraction in a smaller volume of the base electrolyte solution increases the preconcentration factor.)

The most widely used solvent is water. Other solvents that are sometimes used are mixed solvents such as mixtures of water with methanol or dioxane, or nonaqueous solvents such as acetonitrile, dimethylsulfoxide, propylene carbonate, and others.[40] Supporting electrolytes lower the resistance of the solu-

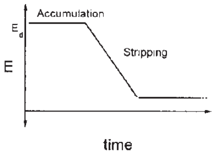
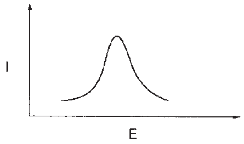
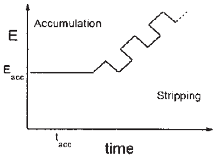
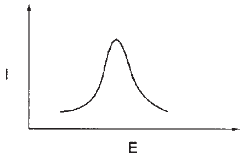
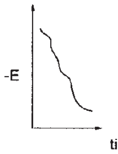
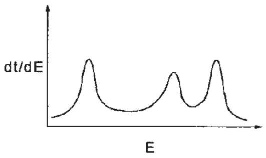
TABLE 1
Basic Parameters of Modern Polarographic and Voltammetric Techniques

Technique	*Applied potential program*	*Current response*	*Working electrode*	*LOD*
TAST			DME	~ 10^{-6} M
NPP (NPV)			DME (HMDE)	~ 10^{-7} M (~10^{-7} M)
SCV			HMDE	~ 10^{-7} M
DPP (DPV)			DME (HMDE)	~ 10^{-7} M ~ 10^{-8} M
SWP (SWV)			DME (HMDE)	~ 10^{-8} M ~ 10^{-8} M
ACP (ACV)			DME (HMDE)	~ 10^{-7} M (~10^{-8} M)

tion, eliminate electromigration effects, and assure a constant ionic strength. Inorganic salts (ammonium chloride, sodium hydroxide, lithium hydroxide, potassium chloride) or mineral acids (hydrochloric and sulfuric) are used most frequently in aqueous solutions. Tetraalkylammonium salts (tetraethylammonium hydroxide, tetrabutylammonium phosphate) are used in organic solvents. Phosphate, acetate, citrate, and Britton-Robinson buffers are used when maintaining a constant pH is necessary. This is usually the case with organic analytes.

Polarographic and voltammetric analyzers are nowadays mostly provided in potentiostat/galvanostat designs with internal or external electrode stands. This electrochemical instrumentation is available from different manufacturers.

TABLE 1 (continued)

Technique	*Applied potential program*	*Current response*	*Working electrode*	*LOD*
ASV ^{a,c,d} (CSV) ^{a,b,c,d}			HMDE, MFE	~10^{-10} M (~10^{-9} M)
AdSV ^{b,d}			HMDE, MFE	~10^{-11} M ~10^{-12} M
PSA			MFE	~ 10^{-12} M

a - electrolytic preconcentration, b - adsorptive preconcentration, c - DC stripping step, d - DP stripping step, 1 – current sampling before the pulse, 2 – current sampling at the end of pulse

The cost of voltammetric instruments is considerably less than that for alternative methods such as chromatography. Characteristics of modern polarographs (voltammographs) currently available from well-known and recently founded manufacturers of instrumentation for electrochemical research can be found in review.[41] A partial list of suppliers is given in Table 3.

V. CONTEMPORARY TRENDS

Advances in the methodology and applications of electrochemistry involving mercury electrodes and characterization of inorganic, organic, and organometallic couples were reviewed.[42,43,44,45] A renewed mercury multipurpose microelectrodes for PC-controlled measuring systems were described recently.[46] The two most quickly growing areas of development in voltammetry are represented now by the combinations of recently developed techniques with separation techniques[47] and by research on new electrodes and electronic equipment.[48] Nucleic acid-modified electrodes can be cited as particularly exciting representatives of modified electrodes.[49] They can be easily prepared by simple immersion of a mercury electrode into a DNA or RNA solution: the resulting electrodes give the high sensitivity demanded in biological and biomedical research.[50,51]

Electrochemical detectors with HMDE and MFE have been applied recently for selective and sensitive determinations in flowing streams.[52,53] The detection limits attainable in voltammetry at mercury electrodes are being pushed even lower and lower, for example, by the use of adsorptive accumulation coupled with catalytic process (mainly catalytic hydrogen wave reactions). This can allow subpicomolar detection limits to be attained.[54] Catalytic AdSV combining adsorptive stripping preconcentration with the catalytic reaction provides a significant enhancement of the voltammetric response resulting in a considerable decrease of LOD.[54,55] Improvement of the sensitivity in trace

TABLE 2
Summary of Working Mercury Electrodes

Working Electrode	*Characteristics*	*Advantages*	*Disadvantages*
DME	-mercury freely dropping from a capillary, $\tau = 1-5$ s	-simplicity -reliability -renewable surface	-LOD~10^{-5} M, -high consumption of mercury -higher charging current
SMDE	-valve mechanics and a hammer -stopped growth of drop surface for each new drop at a given time -drop periodically detached by a hammer	-LOD~10^{-7} M -lower charging current, -lower consumption of mercury	-lower reliability -high demands on valve mechanics
HMDE	-valve mechanics and a hammer -electrode surface not renewed during one analysis -whole analysis on one drop	-LOD~10^{-7} - 10^{-10} M -high reproducibility -low consumption of mercury -adsorptive or electrolytic accumulation -possibility of chemical modifications	-demands on stand mechanics -increased danger of passivation -more complex mechanics and electronics
MFE	-a thin mercury layer electrolytically plated on a solid electrode	-LOD~10^{-11} M -possibility of chemical modifications -stable in flow applications -no mercury reservoir -no complex mechanics and electronics	-passivation -time consuming preparation -irregularities of Hg plating

TABLE 3
Some Commercial Voltammetric Analyzer Suppliers and Their Websites

Supplier	*Location*	*Contact*
Amel	http://amelsrl.com	amel@amelsrl.com
Bioanalytical Systems	http://www.bioanalytical.com	bas@bioanalytical.com
CH Instruments	http://www.chinstruments.com	info@chinstruments.com
Cypress Systems	http://www.cypresshome.com	mwebercysy@earthlink.net
ECO Chemie	http://www.ecochemie.nl	autolab@ecochemie.nl
ESA	http://www.esainc.com	info@esainc.com
Gamry Instruments	http://www.gamry.com	sales@gamry.com
Metrohm	http://www.metrohm.ch	info@metrohm.ch
PAR (now Perkin-Elmer)	http://instruments.perkinelmer.com	info@perkin-elmer.com
Polarosensors	http://www.polarsen.cz	henako@login.cz
Radiometer	http://www.radiometer-analytical.com	radiometer@nalytical.com

analysis of several hundreds percent without any increase in the noise level can be achieved by enhanced mass transport by use of low-frequency sound.[56] Adsorptive stripping tensammetry (AdST) is another promising technique working with mercury electrodes suitable for the determination of surface-active substances, which are important from the environmental point of view. Its importance for the analytical practice is best proven by the marked increase of publications on AdST in the last few years.[57] Further enhancement of the analytical signal in differential pulse AdST can be achieved through the application of external resistance.[58] The possibilities of DP polarography in the elucidation of organic electrode reactions was reviewed.[59]

Finally, a statistical overview of standard (IUPAC and ACS) and new procedures for determining the limits of detection and quantification of voltammetric methods can provide a useful aid for many analytical chemists.[60] A new overview discussing IUPAC terminology of modern electrochemical methods was published recently.[61]

It is worth mentioning that the Internet-boom enhances communication between electroanalytical chemists, as well as others. The world-wide-web provides a fast way of receiving or providing the required information. Many interesting links for electrochemistry including lists of literature publishers and on-line electrochemical journals or databases, commercial links, government agencies, resources, organizations, etc. can be found on educational or commercial servers.[62,63] WWW sites, societies, newsgroups, and frequently asked questions with important chemistry sites, academic centers, etc. are available.[64]

VI. EXAMPLES OF DETERMINATION OF ORGANIC SUBSTANCES

The ever-increasing group of newly synthesized organic compounds can be determined successfully by appropriate polarographic and voltammetric techniques at mercury electrodes. Many organic species that have predicted or proven dangerous properties are wide spread pollutants, after being used to serve mankind as pharmaceuticals, dyes, or herbicides. Extended overviews of organic analytes and of electrochemical methods for these analytes are given by Bersier and Bersier.[65,66,67,76] A survey of many essential theoretical and practical applications of organic polarography can be found in Zuman's articles [6,68,69] and in his review on application of polarography in investigations of kinetics of chemical reactions of organic substances in homogeneous and nonhomogeneous systems.[70]

Organic compounds with reducible or oxidizable moieties (see Table 4) are electrochemically active. These substances yield faradaic current as a result of redox process and they can be determined by direct polarographic or voltammetric methods. Classic techniques such as conventional d.c. polarography or liner scan voltammetry are generally not sensitive enough to provide detection limits at submicromolar levels. However, their sensitivity can be increased by electrochemical or adsorptive accumulation at the surface of the working electrode by stripping methods using analyte preconcentration.[17,71,72] Electroinactive organic compounds can be determined in the same way after derivatization[73,74] and also by adsorptive tensammetry if they provide a tensammetric peak on the polarization curve in the area of desorption of the analyte.[75,76] Concise reviews have been published listing the most frequently determined compounds, their reducible functional groupings, and bonds and electrochemical techniques used, sometimes in combination with preliminary separation techniques.[77,78] Some selected examples of polarographic and voltammetric determination of important group of organic substances are given below. These examples were chosen to illustrate the applicability of mercury electrodes. The complete survey of thousands of methods published is out of the scope of this review.

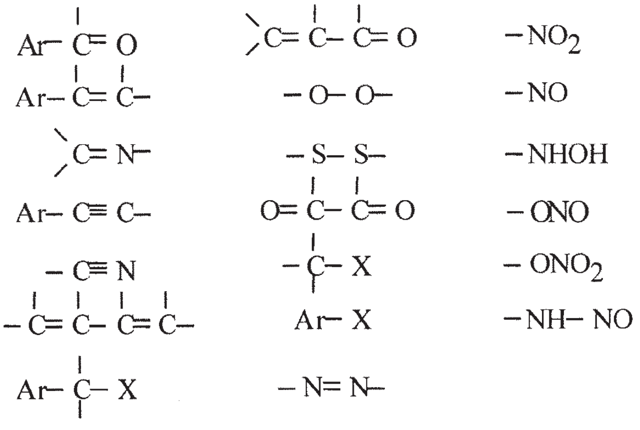
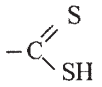
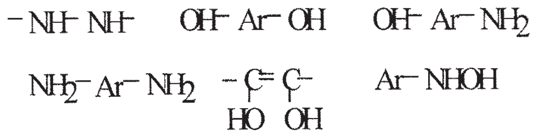
A. Chemical Carcinogens

The approximately 20% cancer mortality together with the fact that environmental causes contribute to the significant number of cancers, emphasize the potential benefits of environmental detection of chemical carcinogens, and raises the monitoring of carcinogenic substances in general and working environment to the highest priority. It is challenging for electrochemistry that in many cases a link can be drawn between polarographic or voltammetric behaviour and the genotoxic properties of organic species.[79,80,81,82] The knowledge of an electrode process of studied compounds (carcinogens, mutagens, and anticancer drugs) provides a useful aid for understanding enzymatic processes, dangerous radical reactions, and its inactivation pathways in living cells.[83] Nitrated polycyclic aromatic hydrocarbons belong among the substances whose occurrence in the environment can be related to an increased cancer rate. Because of their easy polarographic reduction, they can be determined using modern polarographic and voltammetric techniques at nanomolar and subnanomolar levels.[84,85,86] Trace amounts of bromophenyl-[87,88] (see Table 5), and (phenylazo)phenyl-[89] dimethyltriazenes were determined by DPP and AdSV on HMDE. Low concentrations of substituted *N*-nitroso-*N*-methylanilines[90] and 4-nitrobiphenyl [91] were determined by FSDPV and by LSV with adsorptive accumulation on HMDE. The relationship between carcinogenic activity and polarographic behavior of triphenylmethane dyes was studied.[81] Polarography and voltammetry were successfully applied for monitoring the efficiency of the destruction of chemical carcinogens, which had been carried out by chemical oxidants, reduction agents, or UV irradiation.[84,92] Direct electroreductive determination of polychlorinated biphenyls in aqueous media is not possible in the available potential range, but a tensammetric determination using their adsorptive properties in buffered neutral water-methanol solutions was described.[93]

B. Pesticides and Herbicides

The determination of trace amounts of various agrochemicals (pesticides, growth stimulators, etc.) in foodstuffs, soils, natural waters, and body fluids continues to be important in analytical chemistry. However, despite the fact that most herbicides are

TABLE 4
Organic Functional Groups Reducible or Oxidizable on Mercury Electrodes

cathodic waves	aldehydes, ketones,  $Ar-C=O$ $>C=C-C=O$ $-NO_2$ $Ar-C=C-$ $-O-O-$ $-NO$ $>C=N-$ $-S-S-$ $-NHOH$ $Ar-C\equiv C-$ $O=C-C=O$ $-ONO$ $-C\equiv N$ $-C-X$ $-ONO_2$ $-C=C-C=C-$ $Ar-X$ $-NH-NO$ $Ar-C-X$ $-N=N-$ heterocycles (O,S,N) with double bonds, alkaloids, vitamines, hormones, steroids, saccharides
anodic waves	groups reacting with Hg : $-Cl$ $-Br$ $-I$ $-SH$  $-C(=S)SH$ oxidizable substances :  $-NH-NH-$ $OH-Ar-OH$ $OH-Ar-NH_2$ $NH_2-Ar-NH_2$ $-C(OH)=C(OH)-$ $Ar-NHOH$ -NH-NH$_2$ -CS-NH-R -NH(R)$_2$ -NH-CO-NH- -NH-CS-NH-

directly reducible at the DME, relatively few determinations appeared in the recent literature.[66,67,94] Polarography and voltammetry are usually used after appropriate sample preparation (preliminary separation, clean-up, and preconcentration).[95,96] Nitrated dipropylaniline, ethylaniline, pentylaniline, phenyloxime, and glycolate pesticides were determined in model samples and in artificially contaminated soils by DPV and AdSV,[97] and some substituted s-triazine herbicides[98,99] were determined at nanomolar concentrations by these methods at the HMDE. Many other examples can be found in reviews.[94,95,96] The DPP method was applied to the determination of dinobuton in agricultural formulations and in spiked water samples[100] and for monitoring of the photochemical degradation of metamitron and imidacloprid.[101] The DPP determination of imidacloprid based on the first reduction

TABLE 5
Selected Voltammetric Determinations of Organic Substances at Mercury Electrodes

Analyte	*Description*	*Technique*	*Supp. Electrolyte*	*Application*	*LOD*	*Ref*
1-(4-bromo-phenyl)-3,3-dimethyl triazene	mutagenic substance	AdSV at HMDE	Britton-Robinson buffer-MeOH (99.5-0.5v/v) pH 5.1	standard solution	2.10^{-10} M	87
[2-propylamino)-o-propiono-toluidine] N-nitrosamine	prilocaine, local anaestethics	DPP at DME	Phosphate buffer, pH 3.5	pharmaceuticals	6.10^{-7} M	116
Riboflavin	vitamine B2	SW AdSV at MFE	NaOH, pH 12	vitamins	5.10^{-10} M	125
9,10-anthracene -dione,1-[(2-hydroxyethyl) amino]-4-(methyl amino)	Ostacetate Blue P3R, dye	AdSV at HMDE	Britton-Robinson buffer-EtOH (10-90 v/v), pH 4.7	river water, dye added artificially	2.10^{-8} M	126
3,4-dimethyl-2,6-dinitro- -N-(3-pentyl)-aniline	Pendimethalin, nitropesticide	AdSV at HMDE	Britton-Robinson buffers - MeOH (51-49v/v), pH 7.7	after SPE in artificially contaminated soils	$1,3.10^{-8}$ M	97
Nifuroxazide	drug	AdSV at HMDE	-	in human serum	5.10^{-9} M	127

peak of this compound in Britton-Robinson buffer pH 8.0 is applicable in the concentration range from 10 to 200 ng/ml.[102] Oil-in-water emulsions were used as suitable working media for the direct polarographic determination of aziprotryne and desmetryne from its organic extracts in water samples.[103] The simultaneous polarographic determination of atrazine-simazine and terbutryn-prometryn binary mixtures is reported. The polarographic signals of these compounds show high overlap, and for this reason different multicomponent approaches such as partial least squares (PLS) and artificial neural networks (ANNs) were utilized to determine each compound in their respective mixtures.[104]

C. Dyes

A great percentage of world wide dye production enters the environment after dyeing processes in the form of wastewater and sediments. Many dyes exhibit mutagenic or ecotoxic properties, which necessitates their monitoring in the environment. All dyes and fluorescence agents include reducible moieties. The polarographic reduction of a number of azo, anthraquinone, oxazine, phenazine, thiazine, triphenylmethane, and xanthene dyes were reviewed.[94,105] CSV with nanomolar detection limits of reactive and hydrolyzed reactive dyes (substituted triazines, quinoxalines, phthalazines) is described in a review.[106] Selected triazine-based azo dyes with different reactive groups were determined by polarography and voltammetry at nanomolar levels.[107] The possibilities of these techniques in direct simultaneous determinations of the different 2-oxy-naphtholsulfonic acids in sulfonation reaction mixtures, in simultaneous assay of anthraquinone and anthrone and in determinations of several another dyes and dye intermediates were discussed recently.[94,108,109] The determination of the vinylsulfone azo dye, remazol brilliant orange 3R, by cathodic stripping voltammetry gives LOD in ng/ml range.[110] Supramolecular inclusion complex formation of β-cyclodextrin with heteroanthracene ring cationic dyes can be monitored by differential pulse polarography and use to immobilize dyes on an electrode.[111]

D. Pharmaceuticals

Pharmaceutical analysis represents perhaps the largest group of applications of polarographic methods. Most analytes are well defined or their composition is approximately known in a drug assay. A review by Bersier and Bersier[65] provides a detailed information about applied polarographic and voltammetric techniques in this field with an extended survey of pharmaceuticals, classified according to their therapeutic use. Another reviews[112,113] deal with numerous modifications of advanced electroanalytical techniques and with a broad area of theoretical applications of voltammetry for correlations between redox behavior and metabolism, for drug interactions, etc. Other publications[114,115] describe typical applications to pharmacologically active compounds. Electrochemical reduction of prilocaine as its *N*-nitrosamine can be cited as an example of drug assay. Prilocaine [2-(propylamino)-*o*-propionotoluidide] is a frequently used local anaesthetic. Although it cannot be directly reduced on the mercury electrode, after nitrozation it can be determined by DPP on DME at submicromolar level.[116] HPLC and DPP methods are in good agreement, but polarography enables a rapid analysis with simple apparatus, does not require a tedious clean-up step, and it provides better reproducibility and accuracy. Differential-pulse polarographic determination of some *N*-substituted phenothiazine derivatives in dosage forms and urine through treatment with nitrous acid gives results in agreement with those given with the official methods.[117]

An AdSV determination of phenazopyridine hydrochloride in biological fluids and pharmaceutical preparations with a subnanomolar detection limit has been published.[118] Anodic polarographic determination of aztreonam in dosage forms and biological fluids in DC or DPP mode gives LOD around $10^{-5} M$.[119] Experimental design and multivariate calibration in the development, set-up, and validation of a differential pulse polarographic and UV spectrophotometric method for the simultaneous plasmatic determination of the therapeutic metronidazole-pefloxacin combination was published.[120] A method was proposed for the simultaneous determination of amiloride and hydrochlorothiazide in pharmaceutical preparations using differential pulse polarography.[121] Recent developments in electroanalytical chemistry of cephalosporins and cefamycins (antibiotics with a broad spectrum of antimicrobial and antibacterial properties) were reviewed with special attention to mercury electrodes.[122] Progress in the area of electroanalysis of drugs focuses on new selective electrodes, modified electrodes, and microelectrodes for analysis of body fluids, electrochemical immunoassay, and on combination of chromatographic and polarographic methods.[123] An article by Bersier and Bersier with many references reviews polarography, voltammetry, and HPLC-ED of pharmaceuticals.[124]

Selected examples of voltammetric determinations of organic substances are summarized in Table 5.

E. Other Species

Space is not available to mention many other types of organic compounds. However, it is possible to give a few further examples. The assay of tensides, humic compounds, oily substances, and other surface active adsorbable molecules was made with the use of electrocapillary measurements, measurement of charging currents, AdSV, suppression of polarographic maxima, potentiometry, and amperometry.[128] Nonbiodegradable surfactants can cause serious water pollution and destruction of water flora and fauna. Electrochemical techniques (potentiometry, amperometry, tensammetry), some electrocapillary measurements and biosensors applied for the detection of surfactants were reviewed by Kauffmann *et al.*[129] Another widely studied group of organic species are cyclodextrins. Their electrochemical behavior and analytical determination with emphasis on the polarography, voltammetry, and tensammetry was reviewed.[130] Attention was also paid to the electrochemical reactivity of homocysteine and cysteine at mercury electrodes.[131]

VII. EXAMPLES OF DETERMINATION OF INORGANIC SUBSTANCES

Polarography and voltammetry are widely used for the determination of traces of inorganic species,[132,133] and they have been applied successfully for trace measurements of metals in complexes too. Polarographic and voltammetric methods are often selective to the oxidation states of metals, which is usually not the case with other methods. When assessing the possibilities of polarographic techniques in the inorganic field, the ability to follow chemical equilibria should be mentioned as well. An interesting comparison of advanced electroanalytical and spectrometric techniques can be found in tutorial review.[175]

The sensitivity can be greatly enhanced by using stripping techniques. Voltammetry with preliminary analyte accumulation on the electrode, which ensures lower detection limits (see Figure 1), is probably used the most frequently. A survey of inorganic applications of preconcentration techniques can be found in the literature.[18,19] These methods utilise the ability of many metals to dissolve in and to form an amalgam with mercury. For trace element determination in waters, ASV was until recently the most important version of stripping voltammetry used and is still used extensively. This technique enables determination of metals with the reduction potential more negative than that of mercury and more positive than that of the major reducible ion in the supporting electrolyte (hydrogen ions, or ions of the base electrolyte) (see Figure 2). However, there are many inorganic compounds that cannot be electrochemically deposited as an amalgam. Therefore, AdSV, which uses nonelectrolytic adsorptive preconcentration had been used increasingly. AdSV has been often used for determination of trace elements in aquatic systems (in sea waters, etc.)[134,135,136,137] and in ores, metals, and alloys.[138,139] This method became very popular since its introduction in the mid-1980s.[19,71,140,141] The ability to determine several metals simultaneously in one scan represents a major advantage of AdSV. Simultaneous assay of molybdenum, uranium, vanadium, and antimony can be cited as an example of such an analysis.[142] Extremely low detection limits of stripping techniques are demonstrated by selected examples in Table 6. Bond's review[143] encompasses the author's 25 years' experience in developing polarographic, stripping voltammetric, and adsorptive stripping voltammetric methods of analysis in on-line, on-stream, and off-line modes for the determination of elements such as Cd, Pb, Ge, Sb (oxidation states (III) and (V)), Co, Ni, Zn, Fe (oxidation states (II) and (III)), Tl, As (total) and Cu in zinc plant electrolyte. The state of the art and prospects of flow-injection analysis (FIA) for environmental monitoring (natural and effluent water, atmospheric air, precipitation, soil, etc.) using catalytic reactions (including catalytic polarographic currents) and catalytic effects of Cu(II), Mn(II), Co(II), Hg(II), Fe(II, III), Se(IV), V(IV, V), Mo(VI), Cr(III, VI), iodide, bromide, fluoride, chloride, and carbonate ions in FIA redox reactions were reviewed.[144] The application of two-component analysis methods, differentiation of signals, and orthogonal function to the resolution of partially overlapping differential pulse voltammetric (DPV) and cathodic stripping voltammetric (DPCSV) peaks was demonstrated on a binary system of tin(II) and lead(II) and applied successfully to the simultaneous determination of both metals in canned soft drinks and drinking water.[145] Differential pulse anodic stripping voltammetry of copper in dichloromethane was successfully applied to the analysis of human hair.[146] Flow injection method for preconcentration and polarographic determination of copper in water with LOD of 9.5 ng/ml, and a sampling rate of 15 samples/h was validated by analysis of certified reference materials.[147]

Voltammetry has been applied extensively in speciation studies involving metal-organic (including macromolecules) interactions.[160] This has included both solution and adsorption studies. Hundreds of useful references can be found in reviews on polarographic determination of stability constants[161] and kinetics of reduction of metal complexes.[162] Stripping techniques can be applied to the determination of traces of various elements in high purity materials,[163] of precious metals,[164] of cobalt in zinc plant electrolyte,[165] etc. Polarographic tailor-made speciation and quantitation methods for sulfite, thiosulphite, polythionate, sulfidic and polysulfidic sulfur in synthetic fuels from coal conversion processes had been proposed by Jordan *et al.*[166]

Contemporary developments in this area concentrate on applications of stripping techniques to flowing systems,[167] potentiometric stripping analysis of inorganic substances,[22] the use of mercury film electrodes,[31,174] mercury film microelec-

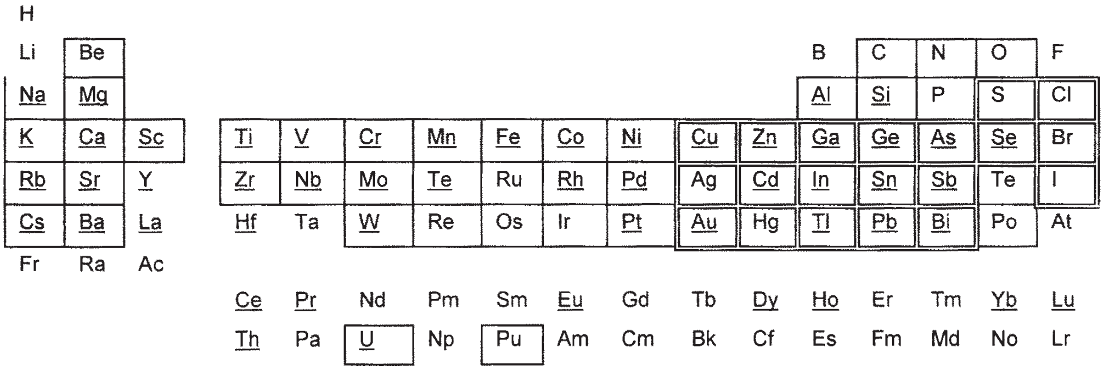


FIGURE 2. Elements determinable by various polarographic and voltammetric methods. (Elements determined by DC polarography are in full lined boxes, by ASV in double boxes, and by AdSV are underlined.)

TABLE 6
Selected Examples of Stripping Voltammetry at HMDE

Analyte	*Technique*	*Supporting electrolyte*	*Reagent*	*Application*	*LOD*	*Ref.*
Al	adsorptive LS CSV	0.2 M acetate buffer, pH 4.5	solochrome violet RS	in snow samples	5.10^{-9} M	148
As	LS CSV	0.18 M H_2SO_4 with 50 µg/mL Se(IV)	- - -	in orchard leaves	3.10^{-8} M	149
Cu,Cd,Pb	adsorptive DP CSV	UV-irradiated sea-water, 0,01M HEPES pH 7.5	8-hydroxy-quinoline	simultaneous detection in sea water	~10^{-10} M	150
Mo	adsorptive DP CSV	UV-irradiated sea water, acidified with HCl, pH 3	8-hydroxy-quinoline	- - -	1.10^{-10} M	151
Se	adsorptive DP CSV	HCl, pH 1.6	$Cu(I)_2Se$ complex	in sea water	1.10^{-11} M	152
Fe	adsorptive DP CSV	0.1 M acetate buffer pH 5.1	Solochrome violet RS	- - -	~10^{-8} M	153
Ti	adsorptive DP CSV	acidified and UV-irradiated sea water, pH 3-3.3	mandelic acid	catalytic effect	7.10^{-12} M	154
Zn	adsorptive DP CSV	75 mM BES, pH 7.1	APD	- - -	3.10^{-11} M	155
Br^-, Cl^-, I^-	DP CSV	0.1 M perchloric acid in 1:1 $EtOH/H_2O$	- - -	analysis of mixture	Cl^- 5.10^{-6} M Br^- 5.10^{-7} M I^- 6.10^{-8} M	156
CN^-	ASV	0.1 M KNO_3, $CuSO_4$	- - -	in presence of Cu (II), formation of insoluble CuCN on electrode surface	1.10^{-10} M	157
I^-	DP CSV	0.01 M HNO_3 - 0,05 % ascorbic acid	- - -	- - -	~10^{-9} M	158
S^{2-}	CSV	0.1 M NaOH	- - -	- - -	3.10^{-8} M	159

trodes,[168] the research on new applications of ultramicroelectrodes.[27] These trends are well illustrated by batch and flow *in situ* determination of uranium by SW AdSV on MFE or HMDE, which represents a sensitive and fast method for its analysis in different matrices.[169] The list could be continued by the combination of polarographic techniques with catalytic hydrogen waves,[170] applications of various new decomposition techniques (high-pressure ashing) for ASV,[171] by determination of elements without sample pre-treatment by multimode determination of elements,[22] and by polarography and voltammetry of ultrasmall inorganic colloids (tin and titanium dioxides yielding diffusion currents),[172] etc.

In addition to the many advantages of polarographic and voltammetric methods, there are also a few interferences and drawbacks. These include the overlay of stripping peaks of other species present in the sample, the presence of oxygen and its removal from flowing solutions, or just simply a reluctance to using mercury as an electrode material because of its toxicity. In the case of the latter it should be noted that there are many compounds (e.g., solvents) that are much more dangerous then mercury when not used properly and are still commonly used in modern analytical laboratories.

VIII. CONCLUSIONS

An analytical chemist should be able to choose the best analytical method for the determination of a given analyte in a given matrix. It was the aim of this article to show that for some analytes and some types of matrices, polarographic and voltammetric methods at mercury electrodes may be the "best method" and can successfully compete with more widespread separation and spectrometric techniques. Moreover, in many other cases modern polarographic and voltammetric techniques can be among "fit for the purpose" methods. Lower investment and running costs, speed, sensitivity, universality, and wide applicability speaks in favor of polarographic techniques despite their limited selectivity. To increase the use of polarography in modern analytical laboratories would require an improvement in education in this field and to pay more attention to the validation of newly developed methods. Then polarographic and voltammetric methods will play a useful role in analytical laboratories even into the third millennium.

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