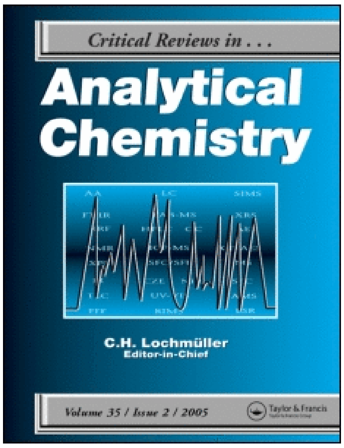

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Mercury Electrodes-Possibilities and Limitations in Environmental Electroanalysis

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Mercury Electrodes–Possibilities and Limitations in Environmental Electroanalysis

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Recent developments in the use of polarography and voltammetry at mercury electrodes in environmental analysis are reviewed and their combination with preliminary separation and pre-concentration using liquid or solid phase extraction is discussed. Attention is focused on ecotoxic nitrated polycyclic aromatic hydrocarbons, heterocyclic compounds, and pesticides. Advantages and limitations of mercury electrodes are critically evaluated and some recent applications of these techniques developed in our laboratory are given.

Keywords Mercury electrodes, polarography, voltammetry, environmental analysis, nitrated polycyclic aromatic hydrocarbons, heterocyclic compounds, pesticides, review

INTRODUCTION

The invention of polarography in 1922 by Professor Heyrovský represented a qualitative change in electroanalytical chemistry which at that time was restricted to potentiometry and controlled current electrolysis. The sensitivity of polarographic methods of analysis, enabling determination of electroactive species in concentrations down to about 10^{-5} M, was superior to most other contemporary techniques. During the 1950s and 1960s, DC polarography (DCP) was one of the five most frequently used analytical techniques. Later, with the advance of spectrometric and separation methods for the determination of organic compounds, DCP lost its importance (1). Renaissance of polarography was based on methods effectively eliminating the charging current and thus enabling to reach much lower limit of detection (LOD). Square wave polarography (SWP) and differential pulse polarography (DPP), and their voltammetric variants at a hanging mercury drop electrode (HMDE), namely square wave voltammetry (SWV) and differential pulse voltammetry (DPV), opened new possibilities in trace analysis. These methods can be combined with the stripping analysis, in which prior accumulation of the analyte on the electrode surface leads to the increased sensitivity by about three orders of magnitude (2). Even though very successful, HMDE, consisting of a renewable drop of mercury at the end of a fine capillary, has some drawbacks mentioned below. Some of these disadvantages can be successfully eliminated by using a mercury film electrode (MFE), prepared by coating a suitable substrate with a thin film of metallic mercury (3).

The sensitivity of the above-mentioned methods (LOD from 10^{-6} to 10^{-11} M) is sufficient for routine environmental electroanalysis, whereas the selectivity is limited by the width of the potential window of the relevant mercury electrode. However, their selectivity can be increased using preliminary separation with liquid-liquid (LLE) or solid phase (SPE) extraction or column, paper, or thin layer chromatography. The combination of modern polarographic and voltammetric techniques with a preconcentration and/or separation step enables the use of mercury electrodes for solving many problems in contemporary environmental analytical chemistry (4–8).

The aim of this review is to show that modern polarographic and voltammetric techniques at mercury electrodes can be successfully used for the determination of trace amounts of various genotoxic and ecotoxic organic environmental pollutants. The extent of this review makes it impossible to quote all papers dealing with polarographic or voltammetric determination of these compounds. Thus, only selected examples demonstrating the applicability of these methods are given, focused on genotoxic nitrated polycyclic aromatic hydrocarbons (NPAHs), heterocyclic compounds, and pesticides.

MERCURY ELECTRODES

The species to be determined at mercury electrodes must be electroactive (i.e., must undergo electroreduction or

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Dedicated to the memory of Professor Jaroslav Heyrovský on the occasion of the 50th Anniversary of the Nobel Prize for polarography.

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electrooxidation within the available potential windows), or must react with Hg ions, or must be catalytically active or be adsorbed on mercury. The list of organic functional groups reducible or oxidizable on mercury electrodes can be found in review (6). The possibility to determine electro-inactive compounds after their conversion into electroactive ones is rarely used in recent environmental analysis. The electroactive species must be soluble in a solvent which is conductive and interfering materials must be absent. Mercury enables reaching negative potentials down to –2.5 V and thus following numerous reductions occurring in this potential range. On the other hand the dissolution of mercury at about +0.4 V prevents reaching more positive potentials. Hence mercury electrodes are not suitable for monitoring oxidizable species (9).

There are several types of mercury electrodes, dropping mercury electrode (DME), hanging mercury drop electrode (HMDE), and mercury film electrode (MFE) being the most frequently used. Their fundamental technical parameters are well known (6, 10). DME and HMDE have been used successfully in countless applications involving the reduction of organic and inorganic electroactive compounds. The DME is now less frequently used, being replaced by HMDE. Nevertheless, the advantages of DME, such as simplicity, reliability, and renewable surface, can be successfully used in many cases of environmental electroanalysis, especially in combination with DPP. The main disadvantages of DME (high consumption of mercury and higher charging current) are eliminated by using HMDE as the most frequently used mercury electrode with high reproducibility, low consumption of mercury, and the possibility of adsorptive or electrolytic accumulation of analytes on its surface. Of course, even HMDE has some drawbacks. It is bulky, requires a mercury reservoir and regular maintenance of the capillary, and incorporates complicated electronics and mechanics for precise drop generation and disposal. Another serious problem, which is becoming increasingly important, is the very use of metallic mercury. The potential risks of poisoning, contamination, and disposal associated with the use of mercury have led some countries to complete ban of mercury (11, 12). Moreover, HMDE, unlike solid electrodes, is mechanically unstable (i.e., the mercury drops are easily dislodged) so that it is not particularly suitable for on-site analysis (e.g., shipboard operations that involve vibrations) or for flow-through applications (where the electrode is subject to high flow rates). Finally, HMDE is not the ideal substrate for permanent modification by chemical reagents or permselective coatings that improve the analytical properties (e.g., selectivity and sensitivity). Even though in principle it is possible to modify the surface of HMDE, such procedures have been used only occasionally due to the electrode sensitivity to mechanical handling and to its very principle of operation (one drop for each measurement) (3, 10).

MFEs have come into use in order to address some of these limitations: they can be of fairly small size, do not require any ancillaries, provide a larger surface-to-volume ratio, are mechanically more stable than mercury drops, and offer great scope for different cell configurations (e.g., rotating electrodes and flow-through designs) and for chemical modification of their surface. Additionally, since the preparation of MFEs requires only minute quantities of mercury, the consumption of metallic mercury is minimized. Traditional limitations of MFEs lie with their lower precision and reproducibility, limited potential range and difficulty in preparing, cleaning, and reactivating the mercury film (3, 10).

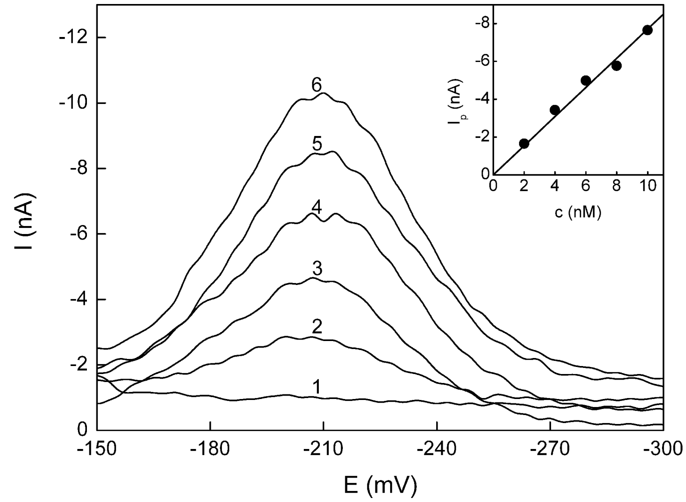

FIG. 1. Adsorptive stripping DC voltammograms of 2-aminoanthraquinone at HMDE in BR buffer pH 2 medium, $t_{acc} = 600$ s, $E_{acc} = -50$ mV, polarization rate 20 mV/s, c(2-aminoanthraquinone) = (1) M, (2) 2×10^{-9} M, (3) 4×10^{-9} M, (4) 6×10^{-9} M, (5) 8×10^{-9} M, (6) 1×10^{-8} M. The corresponding calibration straight line is in the inset.

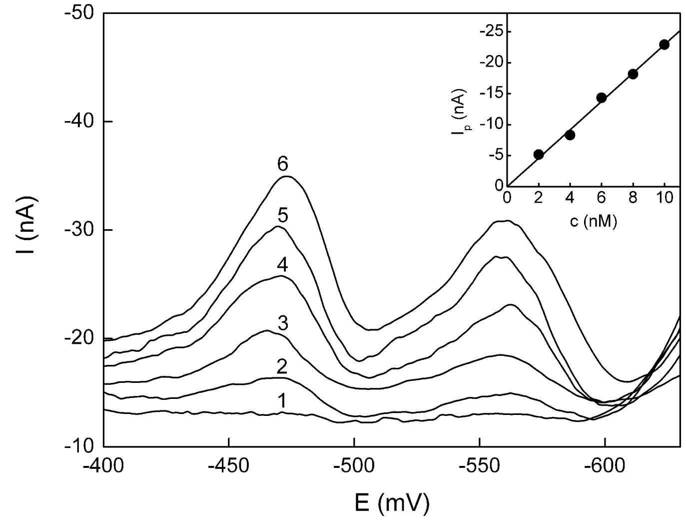

FIG. 2. DP voltammograms of 2,7-dinitro-9-fluorenone at HMDE in BR buffer pH 11—methanol (1:1) after SPE from 0.5 l of spiked river water, polarization rate 10 mV/s, c(2,7-dinitro-9-fluorenone) in spiked river water: (1) 0 M, (2) 2×10^{-9} M, (3) 4×10^{-9} M, (4) 6×10^{-9} M, (5) 8×10^{-9} M, (6) 1×10^{-8} M. The corresponding calibration straight line is in the inset.

TABLE 1
Polarographic and voltammetric determination of selected genotoxic nitro and carbonyl derivatives of polycyclic aromatic hydrocarbons

Analyte	Technique/electrode	Supporting electrolyte	E_{acc} (mV)	t_{acc} (s)	LOD (M)	Ref.
2,2′-Dinitrobiphenyl	DCTP/DME	BR buffer pH 6—methanol (1:1)	—	—	6×10^{-7}	(22)
	DPP/DME	BR buffer pH 6—methanol (1:1)	—	—	2×10^{-7}	
		0.01 M NaOH—methanol (1:1)	—	—	1×10^{-7}	
	DPV/HMDE	BR buffer pH 11—methanol (1:1)	—	—	1×10^{-7}	
		0.01 M NaOH—methanol (1:1)	—	—	6×10^{-8}	
	DPV/HMDE (direct determination in DW)	0.01 M NaOH	—	—	2×10^{-7}	
	DPV/HMDE (direct determination in RW)	0.01 M NaOH	—	—	2×10^{-7}	
	DPV/HMDE (SPE from 100 ml of DW)	0.01 M NaOH—methanol (1:1)	—	—	2×10^{-8}	
	DPV/HMDE (SPE from 100 ml of DW)	0.01 M NaOH—methanol (1:1)	—	—	2×10^{-8}	
	DPV/HMDE (SPE from 100 ml of RW)	0.01 M NaOH—methanol (1:1)	—	—	3×10^{-8}	
2,7-Dinitrofluorene	DCTP/DME	BR buffer pH 2—methanol (1:1)	—	—	2×10^{-6}	(4, 21)
	DPP/DME	BR buffer pH 2—methanol (1:1)	—	—	2×10^{-7}	
	DPV/HMDE	BR buffer pH 12—methanol (1:1)	—	—	1×10^{-8}	
	AdSV/HMDE	BR buffer pH 3—methanol (9:1)	0	60	2×10^{-8}	
	AdSV/HMDE	BR buffer pH 3—methanol (9:1)	0	300	4×10^{-9}	
2,7-Dinitro-9-fluorenone	DCTP/DME	BR buffer pH 2, 6, or 11—methanol (1:1)	—	—	1×10^{-6}	(15, 21)
	DPP/DME	BR buffer pH 6 or 11—methanol (1:1)	—	—	1×10^{-7}	
	DPV/HMDE	BR buffer pH 11—methanol (1:1)	—	—	2×10^{-8}	
	AdSV/HMDE	BR buffer pH 11—methanol (9:1)	–300	60	4×10^{-9}	
	DPV/HMDE (direct determination in DW)	0.01 M NaOH	—	—	2×10^{-8}	
	DPV/HMDE (SPE from 500 ml of DW)	BR buffer pH 11—methanol (1:1)	—	—	2×10^{-9}	
	DPV/HMDE (SPE from 500 ml of RW)	BR buffer pH 11—methanol (1:1)	—	—	4×10^{-9}	
1,3-Dinitronaphthalene	DCTP/DME	BR buffer pH 2, 5, or 12—methanol (1:1)	—	—	2×10^{-6}	(23)
	DPP/DME	BR buffer pH 2 or 12—methanol (1:1)	—	—	1×10^{-7}	
	DPV/HMDE	BR buffer pH 2, 5, or 12—methanol (1:1)	—	—	3×10^{-7}	
	AdSV/HMDE	BR buffer pH 12	–200	45	2×10^{-8}	
		BR buffer pH 12	–200	120	2×10^{-9}	
1,5-Dinitronaphthalene	DCTP/DME	0.01 M NaOH—methanol (1:1)	—	—	2×10^{-6}	(24)
	DPP/DME	0.01 M NaOH—methanol (1:1)	—	—	1×10^{-7}	
	DPV/HMDE	0.01 M NaOH—methanol (1:1)	—	—	1×10^{-7}	
	AdSV/HMDE	0.01 M NaOH—methanol (1:1)	–250	30	2×10^{-8}	

(*Continued on next page*)

TABLE 1
Polarographic and voltammetric determination of selected genotoxic nitro and carbonyl derivatives of polycyclic aromatic hydrocarbons (Continued)

Analyte	Technique/electrode	Supporting electrolyte	E_{acc} (mV)	t_{acc} (s)	LOD (M)	Ref.
1,8-Dinitronaphthalene	DCTP/DME	0.01 M NaOH—methanol (1:1)	—	—	2×10^{-6}	(25)
	DPP/DME	0.01 M NaOH—methanol (1:1)	—	—	4×10^{-7}	
	DPV/HMDE	0.01 M NaOH—methanol (1:1)	—	—	4×10^{-7}	
	AdSV/HMDE	0.01 M NaOH—methanol (1:1)	–450	120	2×10^{-8}	
9-Nitroanthracene	DCTP/DME	BR buffer pH 4—methanol (1:1)	—	—	1×10^{-6}	(26, 27)
	DPP/DME	BR buffer pH 4—methanol (1:1)	—	—	2×10^{-7}	
	DPV/HMDE	BR buffer pH 9—methanol (1:1)	—	—	2×10^{-7}	
	AdSV/HMDE	BR buffer pH 7—methanol (9:1)	–140	180	2×10^{-9}	
	DPV/HMDE (LLE with hexane from 4 l of DW)	BR buffer pH 9—methanol (1:1)	—	—	5×10^{-10}	
	DPV/HMDE (LLE with hexane from 4 l of RW)	BR buffer pH 9—methanol (1:1)	—	—	2×10^{-10}	
2-Nitrobiphenyl	DCTP/SMDE	BR buffer pH 12—methanol (1:1)	—	—	3×10^{-7}	(28, 29)
	DPP/SMDE	BR buffer pH 12—methanol (1:1)	—	—	2×10^{-7}	
	DPV/HMDE	BR buffer pH 12—methanol (1:1)	—	—	3×10^{-8}	
	AdSV/HMDE	0.01 M NaOH—methanol (100:1)	–400	60	2×10^{-8}	
		0.01 M NaOH—methanol (100:1)	–400	180	3×10^{-9}	
3-Nitrobiphenyl	DCTP/SMDE	BR buffer pH 12—methanol (1:1)	—	—	3×10^{-7}	(28, 29)
	DPP/SMDE	BR buffer pH 12—methanol (1:1)	—	—	3×10^{-8}	
	DPV/HMDE	BR buffer pH 12—methanol (1:1)	—	—	3×10^{-8}	
	AdSV/HMDE	0.01 M NaOH—methanol (100:1)	–400	300	2×10^{-8}	
		0.01 M NaOH—methanol (100:1)	–400	600	2×10^{-9}	
	DPV/HMDE (direct determination in DW)	0.01 M NaOH—methanol (1:1)	—	—	2×10^{-8}	
	DPV/HMDE (LE with hexane from 100 ml of DW)	BR buffer pH 12—methanol (1:1)	—	—	2×10^{-9}	
4-Nitrobiphenyl	DCTP/SMDE	BR buffer pH 12—methanol (1:1)	—	—	3×10^{-7}	(28, 29)
	DPP/SMDE	BR buffer pH 12—methanol (1:1)	—	—	3×10^{-8}	
	DPV/HMDE	BR buffer pH 12—methanol (1:1)	—	—	3×10^{-8}	
	AdSV/HMDE	0.01 M NaOH—methanol (100:1)	–400	600	2×10^{-9}	
3-Nitrofluoranthene	DCTP/DME	BR buffer pH 3—methanol (1:9)	—	—	3×10^{-6}	(30)
	DPP/DME	BR buffer pH 3—methanol (1:9)	—	—	1×10^{-7}	
	DPV/HMDE	BR buffer pH 3 or 12—methanol (1:9)	—	—	3×10^{-8}	
		0.01 M NaOH—methanol (1:9)	—	—	3×10^{-8}	
	AdSV/HMDE	BR buffer pH 12—methanol (1:1)	–200	500	2×10^{-8}	
		0.01 M NaOH—methanol (1:1)	–200	500	2×10^{-8}	
		0.01 M NaOH—methanol (9:1)	–200	1200	5×10^{-9}	
	DPV/HMDE (LE with hexane from 100 ml of DW)	BR buffer pH 3—methanol (1:9)	—	—	4×10^{-9}	
	DPV/HMDE (LE with hexane from 10 ml of RW)	BR buffer pH 3—methanol (1:9)	—	—	3×10^{-8}	

TABLE 1
Polarographic and voltammetric determination of selected genotoxic nitro and carbonyl derivatives of polycyclic aromatic hydrocarbons (Continued)

Analyte	Technique/electrode	Supporting electrolyte	E_{acc} (mV)	t_{acc} (s)	LOD (M)	Ref.
	DPV/HMDE (SPE from 500 ml of DW)	BR buffer pH 3—methanol (1:9)	—	—	4×10^{-10}	
	DPV/HMDE (SPE from 500 ml of RW)	BR buffer pH 3—methanol (1:9)	—	—	2×10^{-9}	
2-Nitrofluorene	DCTP/DME	BR buffer pH 12—methanol (1:1)	—	—	4×10^{-6}	(4, 21)
	DPP/DME	BR buffer pH 12—methanol (1:1)	—	—	4×10^{-7}	
	DPV/HMDE	BR buffer pH 12—methanol (9:1)	—	—	4×10^{-8}	
	AdSV/HMDE	BR buffer pH 12—methanol (9:1)	–300	60	2×10^{-8}	
		BR buffer pH 12—methanol (9:1)	–300	600	3×10^{-9}	
2-Nitro-9-fluorenone	DCTP/DME	BR buffer pH 4—methanol (1:1)	—	—	1×10^{-6}	(21)
	DPP/DME	BR buffer pH 4—methanol (1:1)	—	—	2×10^{-7}	
	DPV/HMDE	BR buffer pH 11—methanol (1:1)	—	—	2×10^{-8}	
	AdSV/HMDE	BR buffer pH 11—methanol (1:1)	–200	180	4×10^{-9}	
1-Nitronaphthalene	DCTP/DME	0.01 M NaOH—methanol (1:1)	—	—	1×10^{-6}	(31)
	DPP/DME	0.01 M NaOH—methanol (1:1)	—	—	1×10^{-7}	
	DPV/HMDE	0.01 M NaOH—methanol (1:1)	—	—	2×10^{-7}	
		0.01 M NaOH—methanol (9:1)	—	—	3×10^{-8}	
	AdSV/HMDE	0.001 M LiOH	–400	300	2×10^{-9}	
	DPV/HMDE (direct determination in DW)	0.01 M NaOH	—	—	2×10^{-8}	
	DPV/HMDE (direct determination in RW)	0.1 M NaOH	—	—	3×10^{-8}	
	DPV/HMDE (SPE from 100 ml of DW)	0.01 M NaOH—methanol (9:1)	—	—	2×10^{-9}	
	DPV/HMDE (SPE from 1 l of DW)	0.01 M NaOH—methanol (9:1)	—	—	2×10^{-10}	
	DPV/HMDE (SPE from 100 ml of RW)	0.01 M NaOH—methanol (9:1)	—	—	2×10^{-9}	
2-Nitronaphthalene	DCTP/DME	BR buffer pH 8—methanol (1:1)	—	—	2×10^{-6}	(32)
	DPP/DME	BR buffer pH 8—methanol (1:1)	—	—	2×10^{-7}	
	DPV/HMDE	0.01 M NaOH—methanol (1:1)	—	—	3×10^{-7}	
		0.01 M NaOH—methanol (9:1)	—	—	2×10^{-8}	
	AdSV/HMDE	0.001 M LiOH	–400	120	2×10^{-9}	
	DPV/HMDE (direct determination in DW)	0.01 M NaOH	—	—	2×10^{-8}	
	DPV/HMDE (direct determination in RW)	0.01 M NaOH	—	—	4×10^{-8}	
	DPV/HMDE (LE with hexane from 100 ml of DW)	0.01 M NaOH—methanol (9:1)	—	—	5×10^{-9}	
	DPV/HMDE (LE with hexane from 1 l of DW)	0.01 M NaOH—methanol (9:1)	—	—	4×10^{-10}	
	DPV/HMDE (SPE from 100 ml of DW)	0.01 M NaOH—methanol (9:1)	—	—	3×10^{-9}	

(*Continued on next page*)

TABLE 1
Polarographic and voltammetric determination of selected genotoxic nitro and carbonyl derivatives of polycyclic aromatic hydrocarbons (Continued)

Analyte	Technique/electrode	Supporting electrolyte	E_{acc} (mV)	t_{acc} (s)	LOD (M)	Ref.
	DPV/HMDE (SPE from 1 l of DW)	0.01 M NaOH—methanol (9:1)	—	—	3×10^{-10}	
	DPV/HMDE (SPE from 100 ml of RW)	0.01 M NaOH—methanol (9:1)	—	—	3×10^{-9}	
1-Nitropyrene	DCTP/DME	BR buffer pH 2 or 13—methanol (1:9)	—	—	3×10^{-6}	(4, 33)
	DPP/DME	BR buffer pH 2—methanol (1:9)	—	—	4×10^{-7}	
		BR buffer pH 13—methanol (1:9)	—	—	3×10^{-7}	
	DPV/HMDE	BR buffer pH 2—methanol (1:1)	—	—	1×10^{-7}	
		BR buffer pH 12—methanol (1:1)	—	—	6×10^{-8}	
	AdSV/HMDE	BR buffer pH 2—methanol (99:1)	–200	600	1×10^{-9}	
2-Aminoanthraquinone	DCTP/DME	BR buffer pH 6—methanol (1:1)	—	—	5×10^{-6}	(20)
	DPP/DME	BR buffer pH 6—methanol (1:1)	—	—	4×10^{-6}	
	DCV/HMDE	BR buffer pH 6—methanol (1:1)	—	—	6×10^{-7}	
	DPV/HMDE	BR buffer pH 2—methanol (1:1)	—	—	2×10^{-7}	
		BR buffer pH 6—methanol (1:1)	—	—	4×10^{-7}	
	AdS-DCV/HMDE	BR buffer pH 2—methanol (99:1)	–50	60	2×10^{-8}	
		BR buffer pH 2—methanol (99:1)	–50	600	3×10^{-9}	
	AdS-DPV/HMDE	BR buffer pH 2—methanol (99:1)	–50	60	3×10^{-8}	
9-Fluorenone	DCTP/DME	BR buffer pH 10—methanol (1:1)	—	—	3×10^{-6}	(21)
	DPP/DME	BR buffer pH 7—methanol (1:1)	—	—	5×10^{-7}	
	DPV/HMDE	BR buffer pH 3—methanol (1:1)	—	—	2×10^{-8}	

DW–drinking water; RW–river water.

POLAROGRAPHIC AND VOLTAMMETRIC TECHNIQUES

The well arranged overview of the most widely used polarographic and voltammetric techniques, including their potential programs, can be found in our previous review (6). The original DCP at DME is nowadays displaced by more sensitive pulse techniques. Nevertheless, there are some situations in which even now the classical DCP can offer some advantages—limiting currents in a given solution for a chosen electrode depend only on the concentration of the electroactive species, number of transferred electrons, and diffusion coefficient of the electroactive species and are not affected by the rate of electrode reaction. Thus, comparison of limiting currents enables a rapid determination of the number of transferred electrons. The more sensitive pulse variation—DPP at DME—represents a modern technique for environmental analysis, especially due to LOD around 10^{-7} M and a renewable surface enabling analysis in matrices causing electrode surface passivation. SWV at HMDE and DPP at HMDE give LOD around 10^{-8} M, particularly when the oxidation–reduction process is reversible (9). These methods can be combined with the stripping analysis, in which prior accumulation of the analyte on the electrode surface leads to the increased sensitivity. Anodic stripping voltammetry (ASV) is a well known method, employed mainly for determination of traces of heavy metal ions. In cathodic stripping voltammetry (CSV), analytes are accumulated at the electrode via reaction with mercury ions formed by previous dissolution of mercury at positive potentials, forming low soluble compounds. Surface active organic compounds (and complexes of some metals) can be adsorbed at the electrode surface using adsorptive stripping voltammetry (AdSV) (13). In this technique, the analyte is concentrated by adsorption on the electrode surface, and subsequently stripped off in reduction or oxidation scan (2). AdSV belongs to the most sensitive and frequently used analytical methods; however, its use in environmental analysis is limited because it is less robust and more prone to interferences from surface active substances and other compounds likely to be present in environmental matrices. Thus, it should be used mainly for analysis of relatively clean samples (e.g., of drinking water) or of samples after preliminary clean-up or separation. Another limitation is that not all electroactive compounds are adsorbed at mercury electrodes. AdSV determination of organic genotoxic compounds was reviewed recently (14). Extremely high sensitivity of AdSV at HMDE is demonstrated by Figure 1.

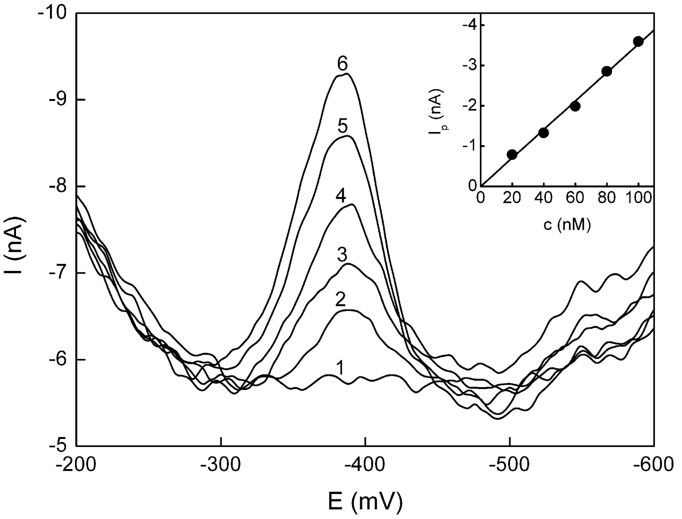

FIG. 3. Adsorptive stripping voltammograms of 6-methyl-5-nitroquinoline at HMDE in BR buffer pH 5 – methanol (99:1) medium, $t_{acc} = 30$ s, $E_{acc} = -200$ mV, polarization rate 20 mV/s, c(6-methyl-5-nitroquinoline) = (1) 0 M, (2) 2×10^{-8} M, (3) 4×10^{-8} M, (4) 6×10^{-8} M, (5) 8×10^{-8} M, (6) 1×10^{-7} M. The corresponding calibration straight line is in the inset.

ENVIRONMENTAL MATRICES

The sensitivity of polarographic and voltammetric techniques at mercury electrodes is above-average for the determination of various environmental pollutants (6). However, the selectivity of these techniques is limited by the width of the potential window. For the determination in simple matrices (e.g., drinking water, rain water, or snow), the direct determination can be used. The development of polarographic/voltammetric determination is then simplified to finding optimal conditions. In dependence on solubility of the determined compound, the suitable solvent is chosen (deionized water or mixture of linear low molecular alcohols with water are usually used in the case of most environmental pollutants). Electrochemical behavior of electroactive organic compounds depends on pH so that optimum pH value of supporting electrolyte is important. Optimal conditions applied to direct determination of organic pollutant in drinking, well, rain, or river water can then lead to LODs similar to those in deionized water.

In the case of more complicated matrices (e.g. river, sea or waste water, soil, ice etc.), the preliminary separation step is usually required. This step can be simultaneously used for analyte pre-concentration, too. LLE or SPE are the most frequently used techniques. Ten-fold to thousand-fold pre-concentration is attainable by proper choice of optimal sorbent and eluent (in SPE), or optimal extraction liquid (in LLE), extraction recovery playing an important role. An example of the use of SPE is depicted in Figure 2. The LOD of 2,7-dinitro-9-fluorenone by DPV and AdSV at HMDE is 2×10^{-8} M and 4×10^{-9}M, respectively. The SPE recoveries from spiked deionized, drinking, and river water are about 95, 95, and 82%, respectively, the pre-concentration of the analyte being hundred-fold (15). Thus, further decrease of LOD of DPV at HMDE is possible using the SPE as a pre-concentration step.

High performance liquid chromatography (HPLC) belongs to powerful separation techniques in environmental analysis of liquid samples, although it is much more expensive than LLE or SPE. In combination with electrochemical detection, we obtain very sensitive and selective methods for the determination of a wide group of electrochemically active organic compounds. Nevertheless, HPLC in combination with polarographic or voltammetric detection using mercury electrodes is not often used (8). Newly developed electrode materials are preferred, e.g., boron-doped diamond, solid amalgams, carbon pastes, or graphite composites (5, 16, 17).

PRACTICAL APPLICATIONS

Generally, environmental pollutants can be divided into three main groups: organic compounds, inorganic compounds, and microorganisms. Pesticides, solvents, PAHs and their derivatives, dyes, and surfactants are the organic pollutants commonly found in air, water, or soil. Even though electroanalytical methods are sensitive and inexpensive, in the area of environmental pollutants they are not too often used. However, the only prerequisite for voltammetric determination is the presence of reducible or oxidizable moieties. Thus, the research in polarographic and voltammetric determination of genotoxic pollutants in environmental samples should further continue.

The practical applications of polarographic and/or voltammetric techniques at mercury electrodes reviewed in this article are focused on trace amounts of electrochemically active nitro derivatives of PAHs (NPAHs), heterocyclic compounds and their nitro derivatives, and on "almost omnipresent" pesticides and agrochemicals.

Nitro and Carbonyl Derivatives of Polycyclic Aromatic Hydrocarbons

Representatives of this relatively new class of environmental carcinogens (18) are either directly emitted from combustion sources (e.g., diesel or gasoline engines) or formed from their parent PAH in atmosphere. They are more mutagenic and/or carcinogenic than their parent PAHs, so that their monitoring is very important (19). They are easily electrochemically reducible and thus are suitable candidates for the application of modern polarographic and voltammetric methods on mercury electrodes. The same is valid for carbonyl derivatives of PAHs, namely 2-aminoanthraquinone (20) and 9-fluorenone (21). Methods developed in UNESCO Laboratory of Environmental Electrochemistry (Prague, Czech Republic) for the determination of these compounds in the last decade are summarized in Table 1.

Heterocyclic Compounds

Until recently, there was little interest in heterocyclic compounds in the environment, probably because of their low

TABLE 2
Polarographic and voltammetric determination of selected genotoxic heterocyclic compounds

Analyte	Technique/electrode	Supporting electrolyte	E_{acc} (mV)	t_{acc} (s)	LOD (M)	Ref.
6-Methyl-5-nitroquinoline	DCTP/DME	BR buffer pH 4—methanol (1:1)	—	—	1×10^{-6}	(37)
	DPP/DME	BR buffer pH 4—methanol (1:1)	—	—	2×10^{-7}	
	DPV/HMDE	BR buffer pH 5—methanol (1:1)	—	—	2×10^{-7}	
	AdSV/HMDE	BR buffer pH 5—methanol (9:1)	–200	30	2×10^{-8}	
		BR buffer pH 5—methanol (99:1)	–200	30	2×10^{-8}	
		0.01 M NaOH—methanol (99:1)	–200	30	2×10^{-8}	
	DPV/HMDE (direct determination in DW)	BR buffer pH 5—methanol (1:1)	—	—	3×10^{-6}	
	DPV/HMDE (direct determination in RW)	BR buffer pH 5—methanol (1:1)	—	—	5×10^{-7}	
	AdSV/HMDE (direct determination in DW)	BR buffer pH 5—methanol (99:1)	–200	30	2×10^{-8}	
	DPV/HMDE (LE with hexane from 1 l of DW) [a]	BR buffer pH 5—methanol (1:1)	—	—	4×10^{-9}	
	DPV/HMDE (LE with hexane from 1 l of drinking water) [b]	BR buffer pH 5—methanol (95:5)	—	—	2×10^{-10}	
	DPV/HMDE (LE with hexane from 1 l of RW)[b]	BR buffer pH 5—methanol (95:5)	—	—	2×10^{-9}	
6-Methyl-5-nitrouracil	DCTP/DME	BR buffer pH 6	—	—	2×10^{-6}	(37)
	DPP/DME	BR buffer pH 6	—	—	2×10^{-7}	
	DPV/HMDE	BR buffer pH 7	—	—	2×10^{-7}	
	DPV/HMDE (direct determination in DW)	BR buffer pH 7 (9:1)	—	—	3×10^{-7}	
	DPV/HMDE (direct determination in RW)	BR buffer pH 7—methanol (9:1)	—	—	3×10^{-7}	
	DPV/HMDE (SPE from 10 ml of DW)	BR buffer pH 7	—	—	4×10^{-8}	
	DPV/HMDE (SPE from 100 ml of RW)	BR buffer pH 7	—	—	6×10^{-8}	
5-Nitrobenzimidazole	DCTP/DME	BR buffer pH 2 or 7	—	—	2×10^{-6}	(38)
		BR buffer pH 12	—	—	3×10^{-6}	
	DPP/DME	BR buffer pH 2, 7 or 12	—	—	5×10^{-7}	
	DCV/HMDE	BR buffer pH 5	—	—	4×10^{-7}	
	DPV/HMDE	BR buffer pH 4	—	—	3×10^{-8}	
	DPV/HMDE (direct determination in DW)	BR buffer pH 4	—	—	5×10^{-8}	
	DPV/HMDE (direct determination in DW)	0.01 M NaOH (9:1)	—	—	4×10^{-8}	
5-Nitroindazole	DCTP/DME	BR buffer pH 2 or 12—methanol (1:1)	—	—	2×10^{-6}	(39)
	DPP/DME	BR buffer pH 2 or 12—methanol (1:1)	—	—	2×10^{-7}	
	DPV/HMDE	0.01 M HCl—methanol (1:1)	—	—	2×10^{-7}	
		0.01 M NaOH—methanol (1:1)	—	—	2×10^{-7}	

TABLE 2
Polarographic and voltammetric determination of selected genotoxic heterocyclic compounds (Continued)

Analyte	Technique/electrode	Supporting electrolyte	E_{acc} (mV)	t_{acc} (s)	LOD (M)	Ref.
	AdSV/HMDE	0.1 M H_3PO_4	–75	60	2×10^{-7}	
		0.01 M NaOH	0	180	1×10^{-8}	
	DPV/HMDE (direct determination in DW)	0.02 M NaOH—methanol (1:1)	—	—	1×10^{-7}	
	DPV/HMDE (direct determination in RW)	0.02 M NaOH—methanol (1:1)	—	—	2×10^{-7}	
	DPV/HMDE (SPE from 100 ml of DW)	0.01 M NaOH—methanol (1:1)	—	—	2×10^{-8}	
	DPV/HMDE (SPE from 500 ml of DW)	0.01 M NaOH—methanol (1:1)	—	—	2×10^{-9}	
	DPV/HMDE (SPE from 100 ml of RW)	0.01 M NaOH—methanol (1:1)	—	—	2×10^{-8}	
	DPV/HMDE (SPE from 500 ml of RW)	0.01 M NaOH—methanol (1:1)	—	—	2×10^{-9}	
5-Nitroquinoline	DCTP/DME	BR buffer pH 3	—	—	9×10^{-7}	(15)
	DPP/DME	BR buffer pH 3	—	—	9×10^{-8}	
	DPV/HMDE	0.18 M NaOH	—	—	2×10^{-8}	
	DPV/HMDE (direct determination in DW)	0.2 M NaOH	—	—	2×10^{-8}	
	DPV/HMDE (direct determination in RW)	0.2 M NaOH	—	—	7×10^{-9}	
	DPV/HMDE (SPE from 100 ml of DW)	0.2 M NaOH—methanol (9:1)	—	—	3×10^{-9}	
	DPV/HMDE (SPE from 100 ml of RW)	0.2 M NaOH—methanol (9:1)	—	—	1×10^{-9}	
8-Nitroquinoline	DCTP/DME	BR buffer pH 5—methanol (1:1)	—	—	2×10^{-6}	(40)
	DPP/DME	BR buffer pH 5—methanol (1:1)	—	—	1×10^{-7}	
	DPV/HMDE	BR buffer pH 4—methanol (1:1)	—	—	1×10^{-7}	
	AdSV/HMDE	BR buffer pH 10—methanol (9:1)	–250	40	1×10^{-8}	
		0.002 M LiOH—methanol (9:1)	–250	40	2×10^{-8}	
	DPV/HMDE (direct determination in DW)	BR buffer pH 4—methanol (9:1)	—	—	9×10^{-8}	
	DPV/HMDE (direct determination in RW)	BR buffer pH 4—methanol (9:1)	—	—	1×10^{-7}	
	DPV/HMDE (SPE from 100 ml of DW)	BR buffer pH 4—methanol (1:1)	—	—	1×10^{-8}	
	DPV/HMDE (SPE from 200 ml of DW)	BR buffer pH 4—methanol (1:1)	—	—	2×10^{-9}	
	DPV/HMDE (SPE from 100 ml of RW)	BR buffer pH 4—methanol (1:1)	—	—	2×10^{-8}	
Quinazoline	DCTP / DME	BR buffer pH 6 or 10	—	—	1×10^{-6}	(41)
	DPP / DME	BR buffer pH 6	—	—	2×10^{-7}	
	DCV / HMDE	BR buffer pH 6 or 10	—	—	2×10^{-7}	
	DPV / HMDE	BR buffer pH 6	—	—	2×10^{-7}	

[a] substance after evaporation dissolved in 10 ml of supporting electrolyte; [b] substance after evaporation dissolved in 1 ml of supporting electrolyte; DW—drinking water; RW—river water.

TABLE 3
Polarographic and voltammetric determination of selected pesticides

Analyte	Used as	Chemical class	Technique/ electrode	Matrix [recovery (%)]	LOD (M)	Ref.
Ametryne	Herbicide	Triazine	DCP/DME	Buffered aqueous solution	—[a]	(44)
			DPP/DME	Buffered aqueous solution	—[a]	
Amitraz	Insecticide	Formamidine	AdSV/HMDE	BR buffer pH 10.1—ethanol (8:2)	2×10^{-9}	(45)
				Soil [91–96%]	—[b]	
				DW and WW [90–97%]	—[b]	
Anilazine	Fungicide	Triazine	DPP/DME	BR buffer pH 2.0	1×10^{-7}	(46)
				RW [96%]	—[b]	
				soil [98%]	—[b]	
Atrazine	Herbicide	Triazine	DCP/DME	Buffered aqueous solution	—[a]	(47)
			DPP/DME	Buffered aqueous solution	—[a]	
			ACP/SMDE	1 M KCl	—[a]	(48)
Buprofezin	Insect growth regulator	Thiadiazine	AdSV/HMDE	BR buffer pH 7.1—ethanol (4:1)	7×10^{-9}	(49)
				Soil [90–93%]	—[b]	
				DW [99%]	—[b]	
				WW [97%]	—[b]	
Butralin	Herbicide	2,6-Dinitroaniline	DPP/DME	BR buffer pH 4.0	6×10^{-8}	(50)
				Grains, soils, water samples	—[c]	
Chloridazon	Herbicide	Pyridazinone	DPV/HMDE	Citric acid pH 2.3	3×10^{-8}	(51)
Cyfluthrin	Insecticide	Pyrethroid	DPP/DME	BR buffer pH 3.0—methanol (6:4)	2×10^{-8}	(52)
				Formulations [99–100%]	—[b]	
				Grains [99–100%]	—[b]	
				Soils [98–100%]	—[b]	
				DW [93–98%]	—[b]	
				Well water [92–95%]	—[b]	
Cypermethrin	Insecticide	Pyrethroid	DCP/DME	Buffered aqueous solution	—[a]	(53)
			DPP/DME	Buffered aqueous solution	—[a]	
			DPP/DME	Agricultural formulations, food grains and soil	—[c]	
Dialifos	Insecticide	Organophosphorus	AdSV/MFE-Au	BR buffer pH 2.0	2×10^{-8}	(54)
				soil [92–97%]	—[b]	
2,4-Diamino-1,3,5-triazine	Herbicide	Triazine	DCP/DME	Buffered aqueous solution	—[a]	(55)
			DPP/DME	Buffered aqueous solution	—[a]	
Dichlorvos	Insecticide, breakdown product, impurity	Organophosphorus	SWV/HMDE	0.5 M Na_2SO_4	1×10^{-8}	(56)
				River water	3×10^{-8}	
Dimethametryn	Herbicide	Triazine	DCP/DME	Buffered aqueous solution	—[a]	(44)
			DPP/DME	Buffered aqueous solution	—[a]	
Diquat	Herbicide	Bipyridylium	AdSV/HMDE	Drinking water	3×10^{-8}	(57)
				Soil	3×10^{-8}	
2,6-Dimethoxy-4-chloro-1,3,5-triazine	Herbicide	Triazine	DCP/DME	Buffered aqueous solution	—[a]	(58)

TABLE 3
Polarographic and voltammetric determination of selected pesticides (Continued)

Analyte	Used as	Chemical class	Technique/ electrode	Matrix [recovery (%)]	LOD (M)	Ref.
			DPP/DME	Buffered aqueous solution	—^{a}	
Dinobuton	Insecticide, fungicide	Dinitrophenol derivative	DPP/DME	Universal buffer pH 6.0	—^{a}	(59)
				Formulations [99–100%]	—^{b}	
				Spiked distilled water [94–97%]	—^{b}	
Dinocap	Fungicide, insecticide	Dinitrophenol derivative	DCTP/DME	BR buffer pH 2.0—methanol (1:1)	1×10^{-6}	(60)
			DPP/DME	BR buffer pH 2.0—methanol (1:1)	5×10^{-7}	
			DPV/HMDE	BR buffer pH 7.0—methanol (1:1)	2×10^{-7}	
Ethion	Insecticide	Organophosphorus	LSSV/HMDE	BR buffer pH 8.4	2×10^{-8}	(61)
				Vegetable and fruit samples	—^{c}	
Fenitrothion	Insecticide	Organophosphorus	SWV/HMDE	BR buffer pH 10.5	2×10^{-8}	(62)
				Formulations [98–109%]	—^{b}	
			AdS-SWV/HMDE	RW [85–99%]	6×10^{-9}	(63)
Flumethrin	Insecticide	Pyrethroid	DCP/DME	Buffered aqueous solution	—^{a}	(64)
			DPP/DME	BR buffer pH 3.0	2×10^{-8}	
				Formulations [99%]	—^{b}	
				Grains [98–100%]	—^{b}	
				Soil [99%]	—^{b}	
				DW [98–99%]	—^{b}	
				Well water [99%]	—^{b}	
Imidacloprid	Insecticide	Chloro-nicotinyl	DPP/DME	BR buffer pH 8.0	4×10^{-8}	(65)
				Formulations [99–102%]	—^{b}	
			AdS-SWV/HMDE	BR buffer pH 7.2	2×10^{-8}	(66)
				RW [89–104%]	—^{b}	
Isopropalin	Herbicide	2,6-Dinitroaniline	DPP/DME	BR buffer pH 4.0	2×10^{-8}	(50)
				Grains, soils, water samples	—^{c}	
Malathion	Insecticide	Organophosphorus	DCP/DME	0.1 M buffer (NH_4Cl + NH_4OH) pH 9.0	—^{c}	(67)
			DPP/DME			
			DPP/DME	Vegetables, soil, fruits and soft drinks		
2-Methyl-4,6-dinitrophenole	Insecticide, fungicide, herbicide	Dinitrophenol derivative	DCTP/DME	BR buffer pH 10.0—methanol (9:1)	1×10^{-6}	(68, 69)
			DPP/DME	BR buffer pH 7.0—methanol (9:1)	1×10^{-7}	
			DPV/HMDE	BR buffer pH 6.0—methanol (9:1)	1×10^{-8}	
				DW [94%]	2×10^{-9}	
				RW [73%]	2×10^{-9}	
			AdSV/HMDE	BR buffer pH 6.0	1×10^{-9}	

(*Continued on next page*)

TABLE 3
Polarographic and voltammetric determination of selected pesticides (Continued)

Analyte	Used as	Chemical class	Technique/ electrode	Matrix [recovery (%)]	LOD (M)	Ref.
Methylparathion	Insecticide, nematicide	Organophosphorus	DPP/DME	0.01 M $CaCl_2$—pH 6.8	2×10^{-8}	(70)
				Soil suspensions	8×10^{-8}	
Mevinphos	Insecticide	Organophosphorus	DPP/DME	Insecticidal formulations	1×10^{-9}	(71)
				Grains and soil samples	— [c]	
Parathion	Insecticide	Organophosphorus	DCP/DME	Buffered aqueous solution	— [a]	(72)
Pendimethalin	Herbicide	2,6-Dinitroaniline	DPP/DME	Buffered water–acetone (3:1) solution	2×10^{-8}	(73)
				Formulations, grains, soils, water	— [c]	
Propazine	Herbicide	Triazine	DCP/DME	Buffered aqueous solution	— [a]	(47, 74)
			DPP/DME	Buffered aqueous solution	— [a]	
Pymetrozine	Insecticide	Triazine	DPP/DME	BR buffer pH 2.0	5×10^{-7}	(75)
				Formulations [97–101%]	— [b]	
				Lake water [93–102%]	— [b]	
				Orange juice [96–103%]	— [b]	
Simazine	Herbicide	Triazine	DCP/DME	Buffered aqueous solution	— [a]	(76)
			DPP/DME	Buffered aqueous solution	— [a]	
Simetryn	Herbicide	Triazine	DCP/DME	Buffered aqueous solution	— [a]	(44)
			DPP/DME	Buffered aqueous solution	— [a]	
Terbutylazine	Algaecide, herbicide, microbiocide	Triazine	ACP/SMDE	1 M KCl	— [a]	(48)
Tetrachlorvinphos	Insecticide	Organophosphorus	DPP/DME	Insecticidal formulations	1×10^{-9}	(71)
				Grains and soil samples	— [c]	
Thiamethoxam	Fungicide, insecticide	—	DPP/DME	BR buffer pH 8	1×10^{-7}	(77)
				Formulations [86–95%]	— [b]	
Thiazopyr	Herbicide	Pyridinecarboxylic acid	DPP/DME	BR buffer pH 7.0	3×10^{-7}	(78)
				Soil samples [94–99%]	— [b]	
				Fruit juice [97–99%]	— [b]	
Thifensulfuron methyl	Herbicide	Sulfonylurea	DPP/DME	BR buffer pH 3.0	4×10^{-7}	(79)
				Soil [103%]	3×10^{-7}	
				Orange juice [102%]	1×10^{-6}	
Triflumizole	Fungicide	Azole	DPP/DME	BR buffer pH 2.0	7×10^{-9}	(80)
				Formulations [101–104%]	— [b]	
				Soil [101–103%]	— [b]	
				Lake water [101–106%]	— [b]	
Zinc dimethyldithiocarbamate	Fungicide, microbiocide, dog and cat repellent	Dithiocarbamate, inorganic-zinc	DPP/DME	Acetonitrile [in thye presence of $Cu(ClO_4)_2$]	— [c]	(81)

[a] the value of LOD was not investigated; [b] the recovery value is mentioned only; [c] the value of LOD was not obtainable; DW—drinking water; RW—river water; WW—waste water.

concentrations one or two orders of magnitude lower than those of their homocyclic analogues (34). However, the first studies focused on biological effects and toxicity of heterocyclic compounds have started discussions on their possible human health and ecological risks. These compounds are a major fraction in biomass burning aerosols (35). The most studied group of these "new environmental pollutants" is a group of polycyclic aromatic nitrogen-containing heterocycles which are mutagenic and/or carcinogenic. Heteroaromatic compounds with a π–electron deficit are polarographically reducible and can be determined using modern polarographic and voltammetric techniques in aqueous and/or aqueous-methanolic solutions (36). The example of sensitive AdSV at HMDE determination of genotoxic 6-methyl-5-nitroquinoline use is depicted in Figure 3. Another selected polarographic and voltammetric determinations of environmentally important heterocyclic compounds at mercury electrodes are summarized in Table 2.

Pesticides and Agrochemicals

Pesticide is a term used in a broad sense for chemicals, synthetic or natural, that are used for the control of insects, fungi, bacteria, weeds, nematodes, rodents, and other pests (42). These compounds and the products derived from them by degradation or metabolism give rise to residues that may spread through the environment. Many pesticides contain electroactive groups and thus voltammetry can be used for their determination. However, despite the fact that many agrochemicals are directly reducible at DME, relatively few polarographic determinations appeared in recent literature (43).

Several recent examples of the use of mercury electrodes for determination of pesticides or agrochemicals in various environmental matrices are summarized in Table 3.

CONCLUSIONS

The limited extent of this review makes it impossible to quote all papers dealing with recently published polarographic or voltammetric determination of environmental pollutants. To obtain general information about another important groups of environmental pollutants (organic and inorganic as well), e.g., inorganic carcinogens, heavy metals, organic dyes, or pharmaceuticals, the reader is referred to reviews and monographs (4–8, 10, 14, 36, 82–84).

It was the aim of this review 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, high speed (an analysis can be routinely carried out in less than 3 minutes, if necessary, within fractions of a second), sensitivity, universality, and wide applicability speaks in favor of voltammetric techniques despite their limited selectivity. To increase the use of polarography in modern analytical laboratories it is necessary to improve education in this field and to pay more attention to the validation of newly developed methods. Then polarographic and voltammetric methods at mercury electrodes will play a useful role in environmental monitoring even more than 50 years after the Nobel Prize for polarography.

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ABBREVIATIONS

ACP	Alternating current polarography
AdSV	Adsorptive stripping voltammetry
BR buffer	Britton–Robinson buffer
DCP	Direct current polarography
DCTP	Direct current tast polarography
DCV	Direct current voltammetry
DME	Classical dropping mercury electrode
DPP	Differential pulse polarography
DPV	Differential pulse voltammetry
$\mathbf{E}_{\mathrm{acc}}$	Potential of accumulation
HMDE	Hanging mercury drop electrode
HPLC	High performance liquid chromatography
GCPE	Glassy carbon paste electrode
GCE	Glassy carbon electrode
LLE	Liquid-liquid extraction
LOD	Limit of determination
LSSV	Linear sweep stripping voltammetry
MFE	Mercury film electrode
MFE-Au	Mercury film electrode at gold substrate
MFE-GC	Mercury film electrode at glassy carbon substrate
NPAH	Nitrated polycyclic aromatic hydrocarbon
PAH	Polycyclic aromatic hydrocarbon
SMDE	Static mercury drop electrode
SPE	Solid phase extraction
SWV	Square wave voltammetry
$\mathbf{t}_{\mathrm{acc}}$	Time of accumulation

REFERENCES

1. P. Zuman, Current examples of practical and fundamental applications of DC polarography. *J. Solid State Electrochem.* 10 (2006):841–851.
2. R. Kalvoda, Is polarography still attractive? *Chem. Anal. (Warsaw)* 52 (2007):869–873.
3. A. Economou and P. R. Fielden, Mercury film electrodes: Developments, trends and potentialities for electroanalysis. *Analyst* 128 (2003):205–212.
4. J. Barek, M. Pumera, A. Muck, M. Kaderabkova, and J. Zima, Polarographic and voltammetric determination of selected nitrated polycyclic aromatic hydrocarbons. *Anal. Chim. Acta* 393 (1999):141–146.

5. J. Barek, V. Mejstrik, A. Muck, and J. Zima, Polarographic and voltammetric determination of chemical carcinogens. *Crit. Rev. Anal. Chem.* 30 (2000):37–57.
6. J. Barek, A. G. Fogg, A. Muck, and J. Zima, Polarography and voltammetry at mercury electrodes. *Crit. Rev. Anal. Chem.* 31 (2001):291–309.
7. V. Vyskocil, J. Barek, I. Jiranek, and J. Zima, Polarographic and voltammetric determination of genotoxic substances in drinking water using mercury electrodes, in *Progress on Drinking Water Research*, eds. M. H. Lefebvre and M. M. Roux (Nova Science Publishers, New York, 2009), Ch. 5, 171–198.
8. K. Rajeshwar and J. G. Ibanez, *Environmental Electrochemistry: Fundamentals and Applications in Pollution Sensors and Abatement* (Academic Press, London, 1997).
9. P. Zuman, Role of mercury electrodes in contemporary analytical chemistry. *Electroanalysis* 12 (2000):1187–1194.
10. J. Wang, *Analytical Electrochemistry*, 3rd ed. (John Wiley & Sons, Hoboken, NJ, USA, 2006).
11. E. Gustafsson, Swedish experiences of the ban on products containing mercury. *Water, Air, Soil Pollut.* 80 (1995):99–102.
12. A. S. Boyd, D. Seger, S. Vannucci, M. Langley, J. L. Abraham, and L. E. King, Mercury exposure and cutaneous disease. *J. Am. Acad. Dermatol.* 43 (2000):81–90.
13. R. Kalvoda, Adsorptive stripping voltammetry and/or chronopotentiometry. Comparison and assessment. *Electroanalysis* 12 (2000):1207–1210.
14. J. Barek, K. Peckova, and V. Vyskocil, Adsorptive stripping voltammetry of environmental carcinogens. *Curr. Anal. Chem.* 4 (2008):242–249.
15. V. Vyskocil, I. Jiranek, J. Barek, K. Peckova, and J. Zima, Are mercury electrodes still useful sensors? Polarographic and voltammetric determination of polarographically reducible environmental carcinogens, in *Sensing in Electroanalysis*, Vol. 2, eds. K. Vytras and K. Kalcher (University of Pardubice, Pardubice, Czech Republic, 2007), 105–119.
16. A. Danhel, K. K. Shiu, B. Yosypchuk, J. Barek, K. Peckova, and V. Vyskocil, The use of silver solid amalgam working electrode for determination of nitrophenols by HPLC with electrochemical detection. *Electroanalysis* 21 (2009):303–308.
17. K. Peckova, K. Jandova, L. Maixnerova, G. M. Swain, and J. Barek, Amperometric determination of aminobiphenyls using HPLC-ED with boron-doped diamond electrode. *Electroanalysis* 21 (2009):316–324.
18. J. C. Moreira, and J. Barek, Analysis of carcinogenic nitrated polycyclic aromatic hydrocarbons — a review. *Quim. Nova* 18 (1995):362–367.
19. B. Zielinska, and S. Samy, Analysis of nitrated polycyclic aromatic hydrocarbons. *Anal. Bioanal. Chem.* 386 (2006):883–890.
20. K. Peckova, H. F. Ayyildiz, M. Topkafa, H. Kara, M. Ersoz, and J. Barek, Polarographic and voltammetric determination of trace amounts of 2-aminoanthraquinone. *Chem. Anal. (Warsaw)* 52 (2007):989–1001.
21. V. Vyskocil, P. Bologa, K. Peckova, and J. Barek, Polarographic and voltammetric determination of selected genotoxic fluorene derivatives using traditional mercury electrodes. *Abstract of the Modern Analytical Chemistry 2008 Conference*, Prague, Czech Republic (2008):108–112.
22. P. Rysanek, V. Vyskocil, J. Barek, K. Peckova, and J. Zima, Polarographic and voltammetric determination of 2,2′-dinitrobiphenyl, in *Sensing in Electroanalysis*, vol. 3, eds. K. Vytras, K. Kalcher, and I. Svancara (University of Pardubice, Pardubice, Czech Republic, 2008), 177–187.
23. K. Shanmugam, J. Barek, and A. Zima, Polarographic and voltammetric determination of trace amounts of 1,3-dinitronaphthalene. *Chem. Anal. (Warsaw)* 49 (2004):765–776.
24. K. Shanmugam, J. Barek, and J. Zima, Polarographic and voltammetric determination of submicromolar concentrations of genotoxic 1,5-dinitronaphthalene. *Collect. Czech. Chem. Commun.* 69 (2004):2021–2035.
25. K. Shanmugam, Polarographic and voltammetric determination of genotoxic dinitronaphthalenes. PhD Thesis, Charles University in Prague, Department of Analytical Chemistry, Prague, 2004.
26. J. Barek, M. Kaderabkova, V. Mejstrik, and J. Zima, Polarographic and voltammetric determination of trace amounts of 9-nitroanthracene. *Electroanalysis* 13 (2001):1265–1269.
27. J. Barek, M. Kaderabkova, J. C. Moreira, and J. Zima, Extraction-voltammetric determination of nanomolar concentrations of 9-nitroanthracene. *Chem. Anal. (Warsaw)* 50 (2005):37–46.
28. R. Stepan, J. Barek, V. Mejstrik, and J. Zima, Voltammetric determination of carcinogenic nitrobiphenyls at a hanging mercury drop electrode. *Sensors* 3 (2003):43–60.
29. R. Stepan, J. Barek, V. Mejstrik, J. C. Moreira, and J. Zima, Polarographic and voltammetric determination of carcinogenic nitrobiphenyls at a static and hanging mercury drop electrode. *Anal. Lett.* 37 (2004):2753–2770.
30. K. Cizek, J. Barek, and J. Zima, Polarographic and voltammetric determination of trace amounts of 3-nitrofluoranthene. *Collect. Czech. Chem. Commun.* 71 (2006):1571–1587.
31. K. Peckova, J. Barek, and J. Zima, Determination of trace amounts of 1-nitronaphthalene by modern polarographic and voltammetric methods using mercury electrodes. *Chem. Listy* 95 (2001):709–712.
32. K. Peckova, J. Barek, J. C. Moreira, and J. Zima, Polarographic and voltammetric determination of trace amounts of 2-nitronaphthalene. *Anal. Bioanal. Chem.* 381 (2005):520–525.
33. J. Barek, J. Zima, J. C. Moreira, and A. Muck, Polarographic and voltammetric determination of 1-nitropyrene. *Collect. Czech. Chem. Commun.* 65 (2000):1888–1896.
34. T. Nielsen, K. Siigur, C. Helweg, O. Jorgensen, P. E. Hansen, and U. Kirso, Sorption of polycyclic aromatic compounds to humic acid as studied by high-performance liquid chromatography. *Environ. Sci. Technol.* 31 (1997):1102–1108.
35. E. A. J. Bleeker, S. Wiegman, P. de Voogt, M. Kraak, H. A. Leslie, E. de Haas, and W. Admiraal, *Reviews of Environmental Contamination and Toxicology* (Springer, New York, 2002).
36. J. Barek, J. Cvacka, A. Muck, V. Quaiserova, and J. Zima, Electrochemical methods for monitoring of environmental carcinogens. *Fresenius. J. Anal. Chem.* 369 (2001):556–562.
37. N. Fantova, Polarographic and voltammetric determination of 6-methyl-5-nitrouracil and 6-methyl-5-nitroquinoline. *Diploma Thesis*, Charles University in Prague, Department of Analytical Chemistry, Prague, 2001.
38. D. Deylova, Voltammetric determination of 5-nitrobenzimidazole. *Diploma Thesis*, Charles University in Prague, Department of Analytical Chemistry, Prague, 2008.
39. P. Simunkova, Polarographic and voltammetric determination of 5-nitroindazole. *Diploma Thesis*, Charles University in Prague, Department of Analytical Chemistry, Prague, 2004.

40. J. Kolarova, Polarographic and voltammetric determination of 8-nitroquinoline. *Diploma Thesis*, Charles University in Prague, Department of Analytical Chemistry, Prague, 2002.
41. J. Hladikova, V. Vyskocil, K. Peckova, and J. Barek, Polarographic and voltammetric determination of quinazoline — the structural unit of anticancer drugs, in *Sensing in Electroanalysis*, Vol. 3, eds. K. Vytras, K. Kalcher, and I. Svancara (University of Pardubice, Pardubice, Czech Republic, 2008), 165–175.
42. A. M. Jimenez and M. J. Navas, Chemiluminescent methods in agrochemical analysis. *Crit. Rev. Anal. Chem.* 27 (1997):291–305.
43. E. M. Garrido, C. Delerue-Matos, J. Lima, and A. M. O. Brett, Electrochemical methods in pesticides control. *Anal. Lett.* 37 (2004):1755–1791.
44. M. J. Higuera, R. M. Galvin, J. M. R. Mellado, and M. R. Montoya, EC(EE) processes in the reduction of some 2-methylthio-4,6-di(alkylamino)-1,3,5-triazines on mercury electrodes. *Electrochem. Commun.* 4 (2002):30–35.
45. M. S. Ibrahim, M. S. El-Maazawi, K. M. Al-Magboul, and M. M. Kamal, Determination of amitraz pesticide by adsorptive stripping voltammetry on the hanging mercury drop electrode. *Mikrochim. Acta* 137 (2001):215–220.
46. H. Mercan and R. Inam, Determination of the fungicide anilazine in soil and river water by differential pulse polarography. *Clean: Soil, Air, Water* 36 (2008):913–919.
47. M. J. Higuera, M. R. Montoya, R. M. Galvmn, and J. M. R. Mellado, Some aspects on the electrochemical behaviour atrazine and propazine on mercury electrodes. *Bull. Electrochem.* 19 (2003):513–520.
48. R. Sokolova, M. Hromadova, and L. Pospisil, Adsorption of s-triazine pesticides, terbutylazine and atrazine: Environmental risk parallels differences in compact film formation. *J. Electroanal. Chem.* 552 (2003):53–58.
49. M. S. Ibrahim, K. M. Al-Magboul, and M. M. Kamal, Voltammetric determination of the insecticide buprofezin in soil and water. *Anal. Chim. Acta* 432 (2001):21–26.
50. M. Sreedhar and S. J. Reddy, Electrochemical reduction and differential pulse polarographic determination of butralin and isopropalin in environmental samples at a mercury electrode. *Bull. Chem. Soc. Jpn.* 75 (2002):2155–2159.
51. M. Zimpl, M. Kotoucek, K. Lemr, J. Vesela, and J. Skopalova, Electrochemical reduction of chloridazon at mercury electrodes, and its analytical application. *Fresenius. J. Anal. Chem.* 371 (2001):975–982.
52. M. Sreedhar, M. T. Reddy, K. Balaji, and J. S. Reddy, Electrochemical reduction behaviour of the synthetic pyrethroid insecticide cyfluthrin and its determination in formulations and environmental samples. *Int. J. Environ. Anal. Chem.* 86 (2006):757–765.
53. N. Y. Sreedhar, K. Samatha, and D. Sujatha, An evaluation of electrochemical techniques applied in the determination of cypermethrin in formulations, food grains and soil. *Fresenius Environ. Bull.* 9 (2000):774–782.
54. S. Morais, O. Tavares, and C. Delerue-Matos, Voltammetric determination of dialifos in soils with a mercury film ultramicroelectrode. *Anal. Lett.* 38 (2005):1275–1288.
55. R. Perez, R. M. Galvin, J. M. R. Mellado, and M. R. Montoya, A contribution to the study of the electroreduction of 2,4-diamino-1,3,5-triazine on mercury electrodes. *J. Electrochem. Soc.* 149 (2002):E306-E310.
56. R. T. S. Oliveira and S. A. S. Machado, Quantification of the pesticide dichlorvos by square wave voltammetry in pure and natural waters. *Quim. Nova* 27 (2004):911–915.
57. B. B. Prasad and B. Arora, Trace analysis of 1,10-phenanthroline based herbicide in water and soil samples. *Ann. Chim.* 92 (2002):1135–1142.
58. J. M. R. Mellado, M. R. Montoya, and R. M. Galvin, The reduction of 2,6-dimethoxy-4-chloro-1,3,5-triazine on mercury electrodes in aqueous solutions in relation with the reduction of s-triazine herbicides. *Electroanalysis* 16 (2004):1972–1976.
59. N. Y. Sreedhar, K. Samatha, and D. Sujatha, An electrochemical approach to the determination of dinobuton: A study of water samples. *Analyst* 125 (2000):1645–1648.
60. J. Fischer, Electrochemical determinations of biologically active organic compounds. PhD Thesis, Charles University in Prague, Department of Analytical Chemistry, Prague, 2007.
61. P. Qiu, Y. N. Ni, and S. Kokot, Determination of pesticide ethion by linear sweep stripping voltammetry. *Chem. Res. Chin. Univ.* 23 (2007):14–17.
62. L. Z. Melgar and S. A. S. Machado, Determination of fenitrothion in commercial formulations by square wave voltammetry and UV-Vis spectroscopy. *J. Braz. Chem. Soc.* 16 (2005):743–748.
63. T. Galeano-Diaz, A. Guiberteau-Cabanillas, A. Espinosa-Mansilla, and M. D. Lopez-Soto, Adsorptive stripping square wave voltammetry (Ad-SSWV) accomplished with second-order multivariate calibration — Determination of fenitrothion and its metabolites in river water samples. *Anal. Chim. Acta* 618 (2008):131–139.
64. M. Sreedhar and S. J. Reddy, Electrochemical reduction and determination of flumethrin in environmental samples. *Fresenius Environ. Bull.* 11 (2002):371–376.
65. A. Navalon, R. El-Khattabi, A. Gonzalez-Casado, and J. L. Vilchez, Differential-pulse polarographic determination of the insecticide imidacloprid in commercial formulations. *Mikrochim. Acta* 130 (1999):261–265.
66. A. Guiberteau, T. Galeano, N. Mora, P. Parrilla, and F. Salinas, Study and determination of the pesticide imidacloprid by square wave adsorptive stripping voltammetry. *Talanta* 53 (2001):943–949.
67. K. Thakur and K. S. Pitre, Analysis of organophosphate pesticide (Malathion) in natural origin and industrial samples using DCP and DPP methods. *Bull. Electrochem.* 22 (2006):149–153.
68. J. Fischer, J. Barek, and J. Zima, Determination of trace amounts of 2-methyl-4,6-dinitrophenol using modern polarographic and voltammetric methods at mercury electrodes. *Chem. Listy* 97 (2003):114–118.
69. P. Jirik, J. Fischer, and J. Barek, Extraction polarographic determination of trace amounts of 2-methyl-4,6-dinitrophenol. *Chem. Listy* 99 (2005):600–604.
70. G. M. Castanho, C. M. P. Vaz, and S. A. S. Machado, Electroanalytical procedure for the determination of methylparathion in soil suspensions and its application for sorption studies with Brazilian soils. *J. Braz. Chem. Soc.* 14 (2003):594–600.
71. G. Madhavi, J. Damodar, S. K. Mohan, and S. J. Reddy, Determination of organophosphorous pesticides by differential pulse polarography. *Bull. Electrochem.* 15 (1999):535–538.
72. M. Z. A. Rafiquee, H. S. Rathore, S. K. Gangwar, and D. Kabir-ud, Polarographic study on parathion in micellar media. *J. Indian Chem. Soc.* 82 (2005):329–332.

73. M. Sreedhar, J. Damodar, N. Venkata, V. Jyothi, and S. R. J. Reddy, Polarographic behavior and determination of pendimethalin in formulations, and environmental samples. *Bull. Chem. Soc. Jpn.* 73 (2000):2477–2480.
74. M. J. Higuera, M. R. Montoya, and J. M. R. Mellado, On the electroreduction of 4-chloro-2,6-diisopropylamino-s-triazine (propazine) on mercury electrodes. *Electrochem. Commun.* 1 (1999):184–189.
75. H. Mercan, E. Yilmaz, and R. Inam, Determination of insecticide pymetrozine by differential pulse polarography/application to lake water and orange juice. *J. Hazard. Mater.* 141 (2007):700–706.
76. M. J. Higuera, M. R. Montoya, R. M. Galvin, and J. M. R. Mellado, A contribution to the study of the electroreduction of 2-chloro-4,6-di(ethylamino)-1,3,5-triazine (simazine) on mercury electrodes. *J. Electroanal. Chem.* 474 (1999):174–181.
77. V. Guzsvany, M. Kadar, F. Gaal, K. Toth, and L. Bjelica, Rapid differential pulse polarographic determination of thiamethoxam in commercial formulations and some real samples. *Microchim. Acta* 154 (2006):321–328.
78. H. Mercan and R. Inam, Differential pulse polarographic behaviour of thiazopyr herbicide and application to its determination in fruit juice and soil samples. *Int. J. Environ. Anal. Chem.* 88 (2008):879–890.
79. R. Inam, T. Sarigul, E. Z. Gulerman, and N. Uncu, Polarographic determination of herbicide thifensulfuron methyl/application to agrochemical pesticide, soil, and fruit juice. *Int. J. Environ. Anal. Chem.* 86 (2006):1135–1149.
80. R. Inam, E. Z. Gulerman, and T. Sarigul, Determination of triflumizole by differential pulse polarography in formulation, soil and natural water samples. *Anal. Chim. Acta* 579 (2006):117–123.
81. D. K. Sharma, S. Kumar, C. Chauhan, and A. Gupta, A pulse polarographic method for the analysis of zinc dithiocarbamates. *Indian J. Chem. Sect A-Inorg. Bio-Inorg. Phys. Theor. Anal. Chem.* 46 (2007):1121–1124.
82. P. Zanello, *Inorganic Electrochemistry: Theory, Practice and Application* (The Royal Society of Chemistry, Cambridge, 2003).
83. R. Kalvoda, Environmental electroanalytical chemistry — contemporary trends and prospects. *Crit. Rev. Anal. Chem.* 30 (2000):31–35.
84. A. Ambrosi, R. Antiochia, L. Campanella, R. Dragone, and I. Lavagnini, Electrochemical determination of pharmaceuticals in spiked water samples. *J. Hazard. Mater.* 122 (2005):219–225.