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Silver Amalgam Electrodes – A Look Back at the Last Five Years of Their Development and Applications

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Abstract: Different types of silver amalgam electrodes have been introduced as modern and promising replacements for traditional mercury electrodes. Advantages and possibilities of these novel electrode materials were highlighted and demonstrated at a number of sensitive voltammetric and amperometric (HPLC, flow injection analysis) methods developed in our UNESCO Laboratory of Environmental Electrochemistry in the last five years. The determined analytes were hazardous organic chemical carcinogens and genotoxic environmental pollutants, pesticides, antitumor, antibiotic and antivirotic drugs, and explosives containing electrochemically reducible nitro, nitroso, azido, and oxo groups.

Keywords: Voltammetry; Amperometry; Silver amalgam electrodes; Review.

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Introduction

Even in the golden age of fascinating possibilities of modern spectrometric and separation methods, modern electroanalytical methods play their irreplaceable role [1,2]. Modern voltammetric methods in a batch arrangement and amperometric methods in a flowing arrangement can provide valuable contribution, especially in the monitoring of biologically active organic compounds important in the term of human health and environmental protection. This fact is proved by a number of reviews originated in our UNESCO Laboratory of Environmental Electrochemistry [3-18]. The main advantages of electroanalytical methods are: Low running and investment costs, high sensitivity, acceptable selectivity, easy miniaturization and automatization, and last but not least easy portability of lightweight analytical instruments enabling their use under the field conditions. The crucial point in the practical success of modern voltammetric and amperometric methods is the choice of a suitable working electrode. Such electrode is the heart of the whole instrument and predestines the parameters of analytical determination (such as a spectrum of amenable analytes, sensitivity and selectivity, validity, limits of detection and quantification), simultaneously with the pertinent complications, especially those connected with the passivation of the working electrode.

One of the most suitable electrode materials for the determination and detection of electrochemically reducible organic compounds is mercury [2,3,8,14]. Nevertheless, even this almost ideal electrode material exhibits certain disadvantages such as a mechanical instability complicating the use of mercury in flowing systems and in field measurements. Certain complications are also connected with not entirely substantiated fears of the toxicity of mercury [19] which, however, does not play important role if laboratory measurements are performed in the correct way.

Therefore, our Laboratory has paid the attention to the utilization of different types of silver amalgam electrodes for voltammetric and amperometric determinations of biologically active organic compounds. A number of results, obtained during the elaboration of the BSc, MSc, and PhD Theses and during the secondary school students' research within the framework of their Secondary school special activity [20] and within the framework of the projects *Way to the Science* (in Czech: “Cesta k vědě”) [21] and *Open Science II* (“Otevřená věda II”) [22], is reviewed in this contribution.

Silver Amalgam Electrodes

Design, study and use of new types of electrodes represent a significant part of research of electrochemical instrumentation. In polarography, voltammetry and related techniques, mercury drop electrodes took their outstanding position, especially due to the excellent quality and renewability of its surface [3]. Searching for alternatives to mercury electrodes exhibiting an analogous electrochemical behavior represents an important contribution to recent research.

In the framework of this research in the past five years, attention had been focused on a new type of electrodes [23,24]. They were made of silver solid amalgam as a follow-up of previously published findings on amalgamated silver wire or disc [25-27]. At that time, the current results of the research of metal solid amalgam electrodes as well as the possibilities of their use were published [23,24,28]. The main intention was to introduce electrodes based on nontoxic solid amalgams with useful properties (simple handling and their mechanical hardiness, high sensitivity and reproducibility, and reasonable selectivity) enabling their application as substitutes of hanging mercury drop electrode (HMDE). Favorable results of this research resulted in commercial introduction of the first types of such silver solid amalgam electrodes [23].

These eminently useful working electrodes can be prepared in every laboratory. The silver solid amalgam electrodes are prepared using a drawn-out glass tube, whose tip is packed with a fine silver powder, amalgamated by liquid mercury and connected to an electric contact [23,29,30]. In this manner, the mechanically stable and nontoxic amalgam is formed [29,31-33]. Silver solid amalgam thus formed can be mechanically polished, e.g., using water suspension of 0.3 μm alumina, to provide a polished silver solid amalgam electrode (p-AgSAE) [4]. For analytical purposes, a mercury meniscus modified silver solid amalgam electrode (m-AgSAE) [4] is more suitable. This electrode can be prepared by mere immersing of p-AgSAE into a small volume of liquid mercury for 15 s. The m-AgSAE provides somewhat lower noise and a better repeatability of the response. With respect to the limited range of this contribution, we refer to reviews [4,9,15,30,34-36], where the detailed information regarding preparation, properties, classification and practical applications of such nontraditional electrode material are described.

Other types of silver amalgam electrodes, e.g., silver solid amalgam paste electrodes with an organic pasting liquid (AgSA-PE) [30,37] or silver amalgam paste electrodes (AgA-PE) [30,38,39], silver amalgam composite electrodes [5,40,41], or single crystal silver

amalgam microelectrodes (SCAgAE) [15] represent interesting possibilities and alternatives. SCAgAE allows measuring in one drop of solution or construction of miniaturized cylindric electrochemical detectors.

For a survey of voltammetric and amperometric methods developed at silver solid (m-AgSAE or p-AgSAE) and paste (AgSA-PE or AgA-PE) amalgam electrodes in our UNESCO Laboratory of Environmental Electrochemistry in the last five years, see Table I. The determined analytes were hazardous organic chemical carcinogens and genotoxic environmental pollutants, pesticides, antitumor, antibiotic and antivirotic drugs, and explosives containing electrochemically reducible nitro, nitroso, azido, and oxo groups.

Silver Solid Amalgam Electrodes

A nontoxic dental amalgam electrode developed by Trondheim research group was found to be suitable for voltammetric determination of zinc, cadmium, lead, thallium, copper, nickel, and cobalt [42]. The same research group has shown that nontoxic silver-based electrodes containing 4 % of bismuth, mercury, or lead dioxide exhibit a high hydrogen overvoltage making them suitable for voltammetric determination of electrochemically reducible metals [43]. Working electrodes based on nontoxic solid amalgams developed by a Prague research group [31] can be used either as liquid mercury-free p-AgSAE or as m-AgSAE or mercury film covered silver solid amalgam electrode (MF-AgSAE) [36] after modification of p-AgSAE surface by a mercury meniscus or mercury film, respectively. Those electrodes exhibit a high hydrogen overvoltage, in some cases comparable with that of the HMDE [31]. In contrast to common solid electrodes, m-AgSAE has an ideally smooth liquid surface which eliminates the necessity of its mechanical surface regeneration. Practically nontoxic m-AgSAE has a good mechanical stability, enables simple handling and regeneration including an electrochemical pretreatment of its surface, etc. In absence of specific interactions between the analyte and silver from silver solid amalgam, the voltammetric peak potentials on the m-AgSAE and HMDE are nearly the same [31,44]. High sensitivity of differential pulse voltammetry at m-AgSAE is demonstrated by Fig. 1 [45].

Thanks to these qualities, the use of silver solid amalgam electrode is possible even in flow systems (Fig. 2) [46] such as high performance liquid chromatography (HPLC-ED) [47] or flow injection analysis with electrochemical detection (FIA-ED) [48,49].

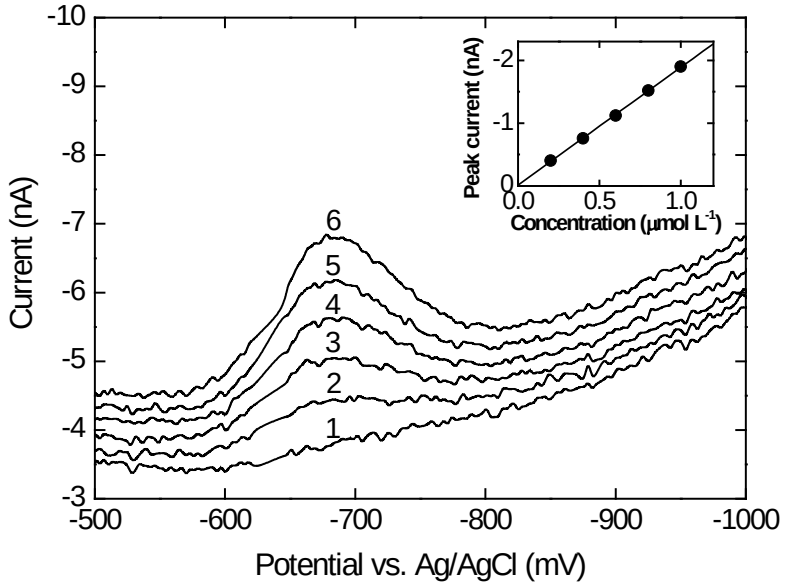

Figure 1. DP voltammograms of 2-nitrobiphenyl at the m-AgSAE in 0.01 mol L^{-1} – methanol (9:1) medium; concentrations measured: 0 (1), 0.2 (2), 0.4 (3), 0.6 (4), 0.8 (5), and 1.0 (6) μmol L^{-1}; regeneration potentials, $E_{1,reg}$ = 0 mV and $E_{2,reg}$ = –1800 mV; polarization rate, 20 mV s^{-1}. The corresponding calibration straight line is given in the inset.

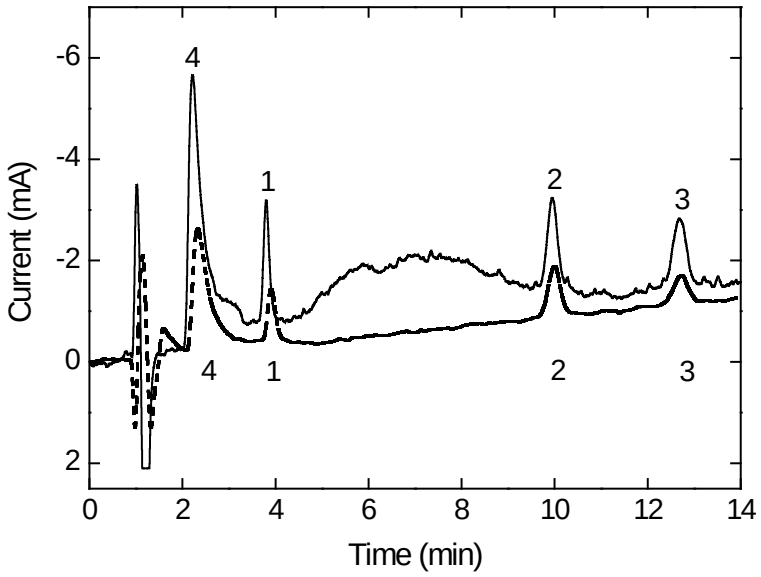

Figure 2. Chromatograms of a mixture of acifluorfen (1), nitrofen (2), oxyfluorfen (3) (all of concentration 1×10^{-4} mol L^{-1}), and dissolved oxygen (4) obtained using amperometric detection at the p-AgSAE in wall-jet arrangement (solid line) and at a silver solid amalgam tubular detector (dashed line). Separation column: LiChrospher® 100 RP-18 (Merck, Germany). Mobil phase: 0.01 mol L^{-1} HCl / acetonitrile (40/60; v/v); detection potential, –1300 mV; flow rate, 1 mL min^{-1}; injection volume, 20 μL.

Silver Solid Amalgam Paste Electrodes and Silver Amalgam Paste Electrodes

Powdered solid amalgam can be used for the preparation of paste electrodes [37] similar to classical carbon paste electrodes [7] using the same pasting liquids (mineral oil, silicone oil, paraffin oil, or tricresylphospahte). However, the ratio between powdered silver amalgam and pasting liquid is approximately 20:1 as compared with approximately a 1:1 ratio for carbon paste electrodes. Electrode surface renewal is the same – paste is pushed out of the electrode body by a piston and wiped off by wet paper. The potential window for such a polished AgSA-PE is comparable with other silver solid amalgam electrodes [4]. However, the hydrogen overvoltage in alkaline medium is lower which can be connected with oxygen dissolved in pasting liquid or adsorbed on silver amalgam particles.

The hydrophobic nature of the above mentioned pasting liquids sometimes retards electrode kinetics. However, there is a limited interval of silver and mercury ratio in which this mixture has the paste consistency for a long time and can be used for the preparation of paste electrode [50]. Amalgams containing 15 – 18 % (w/w) of silver relatively quickly solidify and if the content of silver is below 10 % (w/w) the amalgam is liquid. Therefore, the optimum content of silver in the amalgam paste is 10 – 12 % (w/w). The paste and the electrode can be prepared as follows [50]: A mixture of mercury and 10 – 15 % (w/w) of fine silver powder (particle size 2 – 3.5 μm) is vigorously mixed for 60 s in a compact dental amalgams preparation unit. A Teflon® holder with a movable piston, designed for carbon paste electrodes, is filled with silver amalgam paste. Before use, about 1 mm layer of paste is pressed out and discarded, and a new surface is smoothed on a glass plate. Depending on the silver content, a smoothed surface can resemble either mercury film electrode (10 – 12 % (w/w) of silver) or solid electrode (more than 12 % (w/w) of silver). In the first case, better reproducibility can be achieved [4].

Silver amalgam paste can also be used for the preparation of disposable paste electrodes [38,39]. A small amount of the silver amalgam paste prepared as described above is put inside the small commercially available plastic pipette tip (hole size 600 ± 25 μm), an electrical connection with the steel wire is made, and then the amalgam surface is smoothed on glass surface. According to our experience, thus prepared electrode can be used for several days when electrochemical regeneration is used. However, it can be disposed of after one measurement, e.g., for analysis of biological samples to prevent cross contamination [4].

Single Crystal Silver Amalgam Electrodes

Crystallic silver amalgam has been studied for its crystal morphology since 1930. Depending on amalgam composition, the silver amalgam crystallizes in three crystal structures (phases): Space-centered cubic (γ) with 29 – 32.5 % (w/w) of silver, hexagonal (β) with 33 – 48 % (w/w) of silver, and face-centered cubic (α) with more than 48 % (w/w) of silver (Fig. 3A) [51,52]. All these phases make needle like crystals. The crystallic silver amalgam can be prepared by stepwise addition of silver nitrate solution into deionized water containing a drop of metallic mercury.

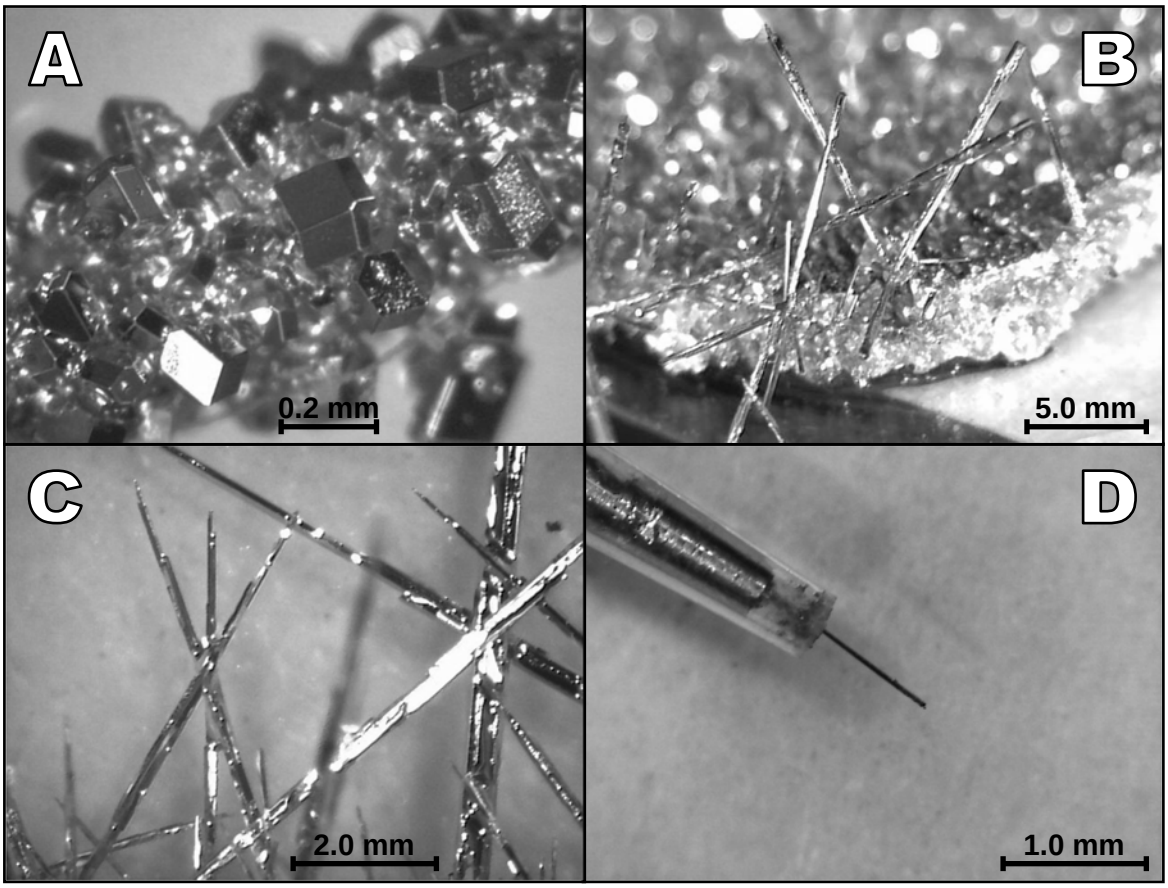

Figure 3. Face-centered cubic (α phase), hexagonal (β phase), and space-centered cubic (γ phase) structures of the crystals of silver amalgam (A), a growing of the needle crystals of silver amalgam (B), a detail of well-shaped needle crystals of silver amalgam (C), and prepared single crystal silver amalgam microelectrode (D) (all photographed using Microscope Camera, Digitus, Taiwan).

The silver amalgam crystals growing on the mercury surface (Fig. 3B) have variable composition (Ag_xHg_y, 50 – 75 % of mercury) such as already found in silver amalgam minerals [52]. A thin silver wire stuck into a mercury drop provides more and better shaped needle crystals [51]. Amalgam must be cleaned from nitrate salts of mercury (colorless crystals of $Hg_2(NO_3)_2 \cdot 2H_2O$ and yellow $Hg(NO_3)_2 \cdot H_2O$) by decanting of mother liquor and repeated dissolving by perchloric acid solution and finally cleaned by deionized water [53]. Otherwise, it would contaminate supporting electrolytes during voltammetric measurements and block the usage of silver amalgam.

Well-shaped needle crystals of silver amalgam (Fig. 3C) can be used for the construction of single crystal silver amalgam microelectrodes (SCAgAE) (Fig. 3D) – an ideally smooth electrode surface, small proportions and potential of hydrogen overvoltage similar to mercury electrodes are its main advantages. Contact between the crystal and silver wire is mediated by silver amalgam paste (Ag(s) in Hg(l) ~15 % of silver (w/w)) sucked into 10 μL plastic pipette tip. Crystal sticks out from narrowed part of tip and it is isolated by film of polystyrene (~30 mg of polystyrene dissolved in 1 mL of 1,2-dichloroethane). Variable sizes of single amalgam crystals should provide possible applications such as voltammetric determinations in microvolumes, amperometric detection in flow systems (capillary and/or microcolumn flow injection analysis (FIA), sequential injection analysis (SIA), HPLC, or capillary zone electrophoresis (CZE)) and detectors for lab-on-chip devices [15,53,54].

Conclusions

A huge diversity of problems currently solved by modern analytical chemistry requires great diversity of approaches, methods and materials used for finding optimal solutions. Although the advantages and possibilities of current spectrometric and separation methods are fascinating, we can certainly declare that modern electrochemical and electroanalytical methods may represent a competitive alternative; especially, if they are using novel electrode materials and progressive approaches. Even now, silver amalgam electrodes can be used in a number of analytical applications and we can surely outlook their promising perspectives.

As it has been shown, nontoxic silver solid amalgam electrodes, especially those covered with mercury meniscus (m-AgSAE), have found broad analytical applications in both batch and flowing system determinations.

Table I. *A survey of compounds determined voltammetrically and amperometrically using different types of silver amalgam electrodes.*

Compound	Working electrode	Technique	Medium / Matrix	LDR [a] [μmol L^{-1}]	L_Q [b] [μmol L^{-1}]	Ref.
			CHEMICAL CARCINOGENS			
2-Amino-6-nitrobenzothiazole	m-AgSAE	DCV	BR buffer pH 4.0 – methanol (9:1)	0.2 – 100	0.7	[55]
		DPV	BR buffer pH 10.0 – methanol (9:1)	0.2 – 100	0.4	[55]
	p-AgSAE	DCV	BR buffer pH 10.0 – methanol (9:1)	2 – 100	3	[55]
		DPV	BR buffer pH 3.0 – methanol (9:1)	2 – 100	3	[55]
2-Amino-9-fluorenone	m-AgSAE	DPV	BR buffer pH 4.0 – methanol (9:1)	0.1 – 100	0.2	— [c]
2,7-Dinitrofluorene	m-AgSAE	DCV	BR buffer pH 8.0 – methanol (1:1)	0.2 – 10	0.3	[56]
		DPV	BR buffer pH 8.0 – methanol (1:1)	0.2 – 10	0.2	[56]
		DPV	DW – BR buffer pH 8.0 (9:1)	0.2 – 1	0.3	[56]
		DPV	RW – BR buffer pH 8.0 (9:1)	0.2 – 1	0.5	[56]
2,7-Dinitro-9-fluorenone	m-AgSAE	DCV	BR buffer pH 4.0 – methanol (1:1)	0.2 – 10	0.5	[56]
		DPV	BR buffer pH 4.0 – methanol (1:1)	0.1 – 10	0.2	[56]
		DPV	DW – BR buffer pH 4.0 (9:1)	0.2 – 1	0.3	[56]
		DPV	RW – BR buffer pH 4.0 (9:1)	0.2 – 1	0.4	[56]
1,3-Dinitronaphthalene	m-AgSAE	DPV	BR buffer pH 10.0 – methanol (1:1)	1 – 100	2	[57]
	AgSA-PE	DPV	BR buffer pH 6.0 – methanol (1:1)	1 – 100	1	[58]
1,5-Dinitronaphthalene	m-AgSAE	DPV	BR buffer pH 10.0 – methanol (1:1)	1 – 100	1	[57]
	AgSA-PE	DPV	BR buffer pH 12.0 – methanol (1:1)	1 – 100	2	[58]
1,8-Dinitronaphthalene	m-AgSAE	DPV	BR buffer pH 10.0 – methanol (1:1)	0.25 – 100	0.5	[57]
	AgSA-PE	DPV	BR buffer pH 8.0 – methanol (1:1)	1 – 100	1	[58]

Table I. (*continued*)

Compound	Working electrode	Technique	Medium / Matrix	LDR [a] [μmol L^{-1}]	L_Q [b] [μmol L^{-1}]	Ref.
9-Fluorenone	m-AgSAE	DCV	BR buffer pH 8.0 – methanol (1:1)	0.8 – 40	0.9	[59]
		DPV	BR buffer pH 10.0 – methanol (1:1)	0.8 – 20	0.5	[59]
5-Nitrobenzimidazole	m-AgSAE	DCV	BR buffer pH 8.0	0.2 – 100	0.3	[60]
		DPV	BR buffer pH 8.0	0.2 – 100	0.6	[60]
	p-AgSAE	DCV	BR buffer pH 8.0	0.2 – 100	0.8	[60]
		DPV	BR buffer pH 8.0	0.2 – 100	0.5	[60]
	AgA-PE	DCV	BR buffer pH 7.0	0.2 – 100	0.2	[61]
		DPV	BR buffer pH 5.0	0.2 – 100	0.2	[61]
2-Nitrobiphenyl	m-AgSAE	DCV	BR buffer pH 6.0 – methanol (1:1)	0.2 – 100	0.4	[45]
		DPV	BR buffer pH 8.0 – methanol (1:1)	0.2 – 100	0.3	[45]
4-Nitrobiphenyl	m-AgSAE	DCV	0.25 mol L^{-1} acetate buffer pH 4.8 – methanol (7:3)	0.4 – 100	0.2	[45]
		DCV	DW – 0.25 mol L^{-1} acetate buffer pH 4.8 (9:1)	0.1 – 1	0.2	[45]
		DPV	0.25 mol L^{-1} acetate buffer pH 4.8 – methanol (7:3)	0.4 – 100	0.2	[45]
		DPV	DW – 0.25 mol L^{-1} acetate buffer pH 4.8 (9:1)	0.1 – 1	0.2	[45]
3-Nitrofluoranthene	m-AgSAE	DPV	0.01 mol L^{-1} NaOH – methanol (1:9)	0.4 – 10	0.4	[62]
		AdSDPV	0.01 mol L^{-1} NaOH – methanol (1:1)	0.02 – 1	0.03	[62]
2-Nitrofluorene	m-AgSAE	DCV	BR buffer pH 10.0 – methanol (1:1)	1 – 100	2	[56]
		DPV	BR buffer pH 10.0 – methanol (1:1)	0.2 – 100	0.2	[56]
		AdSDPV	1×10^{-4} mol L^{-1} LiOH – methanol (1:1)	0.001 – 0.1	0.002	[56]
		DPV	DW – BR buffer pH 10.0 (9:1)	0.2 – 1	0.2	[56]
		DPV	RW – BR buffer pH 10.0 (9:1)	0.2 – 1	0.4	[56]

Table I. *(continued)*

Compound	Working electrode	Technique	Medium / Matrix	LDR [a] [μmol L^{-1}]	L_Q [b] [μmol L^{-1}]	Ref.
2-Nitro-9-fluorenone	m-AgSAE	DCV	BR buffer pH 8.0 – methanol (1:1)	0.4 – 10	0.5	[56]
		DPV	BR buffer pH 9.0 – methanol (1:1)	0.2 – 10	0.4	[56]
		DPV	DW – BR buffer pH 9.0 (9:1)	0.2 – 1	0.4	[56]
		DPV	RW – BR buffer pH 9.0 (9:1)	0.2 – 1	0.5	[56]
5-Nitroquinoline	m-AgSAE	DCV	0.05 mol L^{-1} $Na_2B_4O_7$ pH 9.0	0.4 – 100	0.5	[48]
		DPV	0.05 mol L^{-1} $Na_2B_4O_7$ pH 9.0	0.2 – 100	0.3	[48]
		FIA-ED (WJ)	0.05 mol L^{-1} $Na_2B_4O_7$ pH 9.0	2 – 100	3	[48]
		FIA-ED (WJ)	DW – 0.05 mol L^{-1} $Na_2B_4O_7$ pH 9.0	2 – 100	4	[48]
		FIA-ED (WJ)	RW – 0.05 mol L^{-1} $Na_2B_4O_7$ pH 9.0	2 – 100	2	[48]
6-Nitroquinoline	m-AgSAE	DCV	BR buffer pH 7.0	0.4 – 100	0.6	[48]
		DPV	0.01 mol L^{-1} NaOH	0.2 – 100	0.3	[48]
4-Nitroindane	m-AgSAE	DCV	BR buffer pH 5.0 – methanol (1:1)	0.1 – 100	0.1	[63]
		DPV	BR buffer pH 9.0 – methanol (1:1)	0.1 – 100	0.1	[63]
1-Nitronaphthalene	m-AgSAE	DPV	BR buffer pH 7.0 – methanol (9:1)	0.2 – 100	0.3	[64]
		DPV	DW – BR buffer pH 7.0 (9:1)	0.4 – 1	0.5	[64]
		DPV	RW – BR buffer pH 7.0 (9:1)	0.8 – 10	0.8	[64]
2-Nitronaphthalene	m-AgSAE	DPV	BR buffer pH 7.0 – methanol (9:1)	0.4 – 100	0.5	[64]
		DPV	DW – BR buffer pH 7.0 (9:1)	0.4 – 1	0.5	[64]
		DPV	RW – BR buffer pH 7.0 (9:1)	0.6 – 10	0.7	[64]
1-Nitropyrene	m-AgSAE	DCV	0.01 mol L^{-1} NaOH – methanol (3:7)	1 – 100	3	[65]
		DPV	0.01 mol L^{-1} NaOH – methanol (3:7)	0.1 – 100	0.6	[65]

Table I. (*continued)*

Compound	Working electrode	Technique	Medium / Matrix	LDR [a] [μmol L^{-1}]	L_Q [b] [μmol L^{-1}]	Ref.
			PESTICIDES			
Acifluorfen	m-AgSAE	DPV	BR buffer pH 12.0 – methanol (1:1)	1 – 100	3	[66]
Bifenox	m-AgSAE	DPV	BR buffer pH 9.0 – methanol (1:9)	0.1 – 100	0.3	[67]
2,4-Dinitrophenol	m-AgSAE	DPV	BR buffer pH 4.0	0.1 – 100	2	[68]
	p-AgSAE	DPV	BR buffer pH 5.0	0.1 – 100	3	[68]
	p-AgSAE	HPLC-ED (TL)	0.05 mol L^{-1} phosphate buffer pH 6.0 – methanol (7:3)	10 – 2500	5	[47]
		HPLC-ED (WJ)	0.05 mol L^{-1} phosphate buffer pH 6.0 – methanol (7:3)	25 – 2500	10	[47]
2-Methoxy-5-nitrophenol	p-AgSAE	HPLC-ED (TL)	0.05 mol L^{-1} phosphate buffer pH 6.0 – methanol (7:3)	10 – 2500	10	[47]
		HPLC-ED (WJ)	0.05 mol L^{-1} phosphate buffer pH 6.0 – methanol (7:3)	25 – 2500	25	[47]
2-Methyl-4,6-dinitrophenol	m-AgSAE	DPV	BR buffer pH 4.0	0.2 – 10	0.2	[69]
Nitrofen	m-AgSAE	DPV	BR buffer pH 3.0 – methanol (1:1)	0.6 – 10	0.9	[66]
2-Nitrophenol	m-AgSAE	DPV	BR buffer pH 8.0	1 – 100	1	[68]
	p-AgSAE	DPV	BR buffer pH 5.0	1 – 100	1	[68]
	m-AgSAE	DPV after SPE	BR buffer pH 8.0 – methanol (4:6) (SPE from DeW)	0.02 – 1	0.02	[68]
		DPV after SPE	BR buffer pH 8.0 – methanol (4:6) (SPE from DW)	0.02 – 1	0.02	[68]
	p-AgSAE	HPLC-ED (TL)	0.05 mol L^{-1} phosphate buffer pH 6.0 – methanol (7:3)	10 – 2500	10	[47]
		HPLC-ED (WJ)	0.05 mol L^{-1} phosphate buffer pH 6.0 – methanol (7:3)	25 – 2500	25	[47]
4-Nitrophenol	m-AgSAE	DPV	BR buffer pH 6.0	1 – 100	1	[68]
	p-AgSAE	DPV	BR buffer pH 6.0	1 – 100	3	[68]
	AgA-PE	DPV	BR buffer pH 3.0	0.2 – 100	0.3	[38]

Table I. (*continued)*

Compound	Working electrode	Technique	Medium / Matrix	LDR [a] [μmol L^{-1}]	L_Q [b] [μmol L^{-1}]	Ref.
4-Nitrophenol	p-AgSAE	HPLC-ED (TL)	0.05 mol L^{-1} phosphate buffer pH 6.0 – methanol (7:3)	10 – 2500	10	[47]
		HPLC-ED (WJ)	0.05 mol L^{-1} phosphate buffer pH 6.0 – methanol (7:3)	25 – 2500	25	[47]
Oxyfluorfen	m-AgSAE	DPV	BR buffer pH 12.0 – methanol (1:1)	0.2 – 10	0.3	[66]
Pendimethalin	m-AgSAE	DPV	BR buffer pH 7.0 – methanol (1:1)	0.2 – 10	0.3	[62]
			DRUGS			
Azidothymidine	m-AgSAE	DPV	0.05 mol L^{-1} $Na_2B_4O_7$ pH 9.0	0.4 – 1500	0.4	[70]
	p-AgSAE	DPV	0.05 mol L^{-1} $Na_2B_4O_7$ pH 9.0	0.6 – 1500	0.6	[70]
Carmustine	m-AgSAE	DCV	BR buffer pH 7.0	2 – 100	0.8	[49]
		DPV	BR buffer pH 7.0	2 – 100	0.7	[49]
		FIA-ED (WJ)	BR buffer pH 7.0	6 – 100	7	[49]
Flutamide	m-AgSAE	DCV	BR buffer pH 7.0 – methanol (9:1)	2 – 100	5	[71]
		DPV	BR buffer pH 7.0 – methanol (9:1)	2 – 100	3	[71]
Lomustine	m-AgSAE	DCV	0.05 mol L^{-1} acetate buffer pH 4.0 – methanol (9:1)	2 – 100	3	[49]
		DPV	0.05 mol L^{-1} acetate buffer pH 4.0 – methanol (9:1)	2 – 100	2	[49]
Metronidazole	m-AgSAE	DPV	BR buffer pH 10.0	0.2 – 100	0.3	[72]
4-Nitro-3-(trifluoromethyl)aniline	m-AgSAE	DCV	BR buffer pH 8.0 – methanol (9:1)	0.4 – 100	0.3	[73]
		DPV	BR buffer pH 8.0 – methanol (9:1)	0.8 – 100	0.7	[73]
Nizatidine	m-AgSAE	DCV	BR buffer pH 3.0	0.2 – 100	0.3	— [d]
		DPV	BR buffer pH 3.0	0.2 – 100	0.3	— [d]
Ornidazole	m-AgSAE	DPV	BR buffer pH 10.0	0.2 – 100	0.4	[72]

Table I. (*continued)*

Compound	Working electrode	Technique	Medium / Matrix	LDR [a] [μmol L^{-1}]	L_Q [b] [μmol L^{-1}]	Ref.
Streptozotocin	m-AgSAE	DCV	BR buffer pH 6.0	0.2 – 100	0.4	[49]
		DPV	BR buffer pH 6.0	0.2 – 100	0.2	[49]
			EXPLOSIVES			
Picric acid	AgA-PE	DPV	BR buffer pH 2.0	0.2 – 100	0.06	[74]
		DPV	DW – BR buffer pH 2.0 (9:1)	0.2 – 1	0.1	[74]
		DPV	RW – BR buffer pH 2.0 (9:1)	0.2 – 1	0.1	[74]
			ENVIRONMENTAL POLLUTANTS			
Diallyl phthalate	m-AgSAE	DPV	0.1 mol L^{-1} TMAB in methanol	2 – 100	4	[75]
Dibutyl phthalate	m-AgSAE	DPV	0.1 mol L^{-1} TMAB in methanol	2 – 100	2	[75]
Didecyl phthalate	m-AgSAE	DPV	0.1 mol L^{-1} TMAB in methanol	2 – 100	4	[75]
Diethyl phthalate	m-AgSAE	DPV	0.1 mol L^{-1} TMAB in methanol	2 – 100	3	[75]
Maleic acid	AgA-PE	DPV	BR buffer pH 2.0	2 – 100	2	[39]
		DPV	DW – BR buffer pH 2.0 (1:1)	2 – 100	3	[39]
		DPV	RW – BR buffer pH 2.0 (1:1)	20 – 100	7	[39]

Legend: [a] – linear dynamic range; [b] – limit of quantification; [c] – T. Moravec, V. Vyskočil, J. Barek: unpublished results; [d] – J. Koštejn, D. Deýlová, V. Vyskočil, J. Barek: unpublished results.

They can, in many cases, successfully substitute mercury electrodes; especially, in field applications and in the measurements in flowing streams, being also useful for the investigation of electrochemical properties of various biologically important systems. A polished silver solid amalgam electrode (p-AgSAE) can be used when the work with liquid mercury is not desirable or even forbidden. Composite silver amalgam electrodes, which under certain circumstances behave as an array of microelectrodes, can be very useful as well as silver amalgam paste electrodes (AgSA-PE and AgA-PE) with an extremely easy renewability of their surface. Based on the shown examples, it can be stated that silver amalgam electrodes are not only able to substitute for a hanging mercury drop electrode (HMDE) but they also offer new possibilities which cannot be realized with mercury electrodes. Undoubtedly, further research in this field will reveal further possibilities and practical applications of this nontraditional electrode material. At present, very promising results were obtained with solid amalgam microelectrodes based on single silver amalgam crystals [15,53,54].

Abbreviations & Symbols Used

AdSDPV	adsorptive stripping differential pulse voltammetry
AgA-PE	silver amalgam paste electrode
AgSA-PE	silver solid amalgam paste electrode
BR pufr	Britton–Robinson buffer
DCV	direct current voltammetry
DeW	spiked deionized water
DPV	differential pulse voltammetry
DW	spiked drinking water
FIA-ED	flow injection analysis with electrochemical detection
HMDE	hanging mercury drop electrode
HPLC-ED	high performance liquid chromatography with electrochemical detection
LDR	linear dynamic range
L_Q	limit of quantification
m-AgSAE	mercury meniscus modified silver solid amalgam electrode
p-AgSAE	polished silver solid amalgam electrode
RW	spiked river water
SCAgAE	single crystal silver amalgam microelectrodes
SPE	solid phase extraction
TL	thin layer arrangement
TMAB	tetramethylammonium bromide
WJ	wall-jet arrangement

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