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Voltammetric and Amperometric Determination of Biologically Active Organic Compounds Using Various Types of Silver Amalgam Electrodes

Jiří Barek[1*], **Jan Fischer**[1], **Josino C. Moreira**[2], and **Joseph Wang**[3]

[1] *Charles University in Prague, Faculty of Science, University Research Centre UNCE "Supramolecular Chemistry", Department of Analytical Chemistry, UNESCO Laboratory of Environmental Electrochemistry, Albertov 6, CZ-128 43 Prague, Czech Republic.*
[2] *National School of Public Health, FIOCRUZ, Rua Leopoldo Bulhoes, 1480 - Manguinhos, Rio de Janeiro, Brazil.*
[3] *University of California San Diego (UCSD), La Jolla, Department of Nanoengineering, 9500 Gilman Drive 0448, CA 92093-0448, USA.*

Abstract: In this paper, possibilities of various types of silver amalgam electrodes for determination of micromolar and submicromolar concentrations of various electrochemically reducible biologically active organic compounds are reviewed. Attention is paid to the use of polished and mercury meniscus modified silver solid amalgam electrodes, silver amalgam paste electrodes both with and without pasting liquids, single crystal silver amalgam electrodes, composite silver amalgam electrodes, and porous silver amalgam electrodes. Main focus is on voltammetric application of above mentioned electrodes. However, their application in flowing systems (high performance liquid chromatography and flow injection analysis with electrochemical detection) is briefly discussed as well. The compatibility of various types of silver amalgam electrodes with preliminary separation based on solid phase extraction is demonstrated on determination of nanomolar concentrations of environmentally important compounds in model samples of drinking and river waters.

Keywords: Silver solid amalgam electrodes; Silver amalgam paste electrodes; Single crystal silver amalgam electrodes; Composite silver amalgam electrodes; Porous silver amalgam electrodes; Differential pulse voltammetry; Amperometry; Biologically active compounds.

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*) Author to whom correspondence should be addressed. E-mail: barek@natur.cuni.cz

Introduction

The best available electrode for voltammetric determination of electrochemically reducible organic compounds is undoubtedly hanging mercury drop electrode (HMDE) [1]. Broad potential window in cathodic region, easy surface renewal eliminating problems with its passivation, user-friendliness, easy operability and possibility of chemical and/or biological modification are unsurpassed. In combination with differential pulse voltammetry (DPV) limits of quantitation (Lq) in micromolar and submicromolar concentration range can be easily achieved. Adsorptive stripping voltammetry (AdSV) based on adsorptive accumulation of analyte on HMDE surface can reach the limit of quantitation in the nanomolar and subnanomolar concentration range [2].

However, mercury has two disadvantages. It is mechanically relatively unstable and thus not suitable for field measurements and for measurements in flowing systems. Moreover, due to toxic effects of mercury [3], there are increasing legal obstacles of its use it analytical laboratories although we are convinced that most of those fears is unsubstantiated. Although recent European Regulations (REACH and Directive 2007/S1/CE of 25th September 2007) do not explicitly forbid the use of mercury as electrode material, there is an increasing pressure to substitute it whenever and wherever possible. Therefore, there is an intensive search for alternative "green" voltammetric sensors. Bismuth [4], antimony [5], lead [6], selenium [7], and tin [8] film sensors were successfully used for determination of trace metals. However, for organic compounds, the electrodes based on silver-amalgam materials seem to be most frequently used [9,10].

Overview of Silver Amalgam Electrodes

The advantages of silver amalgam electrodes can be summarized as follows:

- broad potential window in cathodic region comparable with HMDE,
- low noise and reasonably low charging current,
- possibility of mechanical, chemical or electrochemical renewal of their surface,
- mechanical stability making them suitable for field measurements and/or measurements,
- in flowing systems,
- possibility of chemical and/or biological modification.

Several types of silver amalgam electrodes suitable for monitoring of biologically active and electrochemically reducible compounds were developed and/or subsequently applied in our laboratory [10,11].

Solid silver amalgam electrodes can be easily prepared; they are mechanically stable and user friendly. Polished silver solid amalgam electrode (p-AgSAE) does not contain any liquid mercury. However, it is more prone to passivation and its mechanical pretreatment, polishing and reactivation in the case of passivation is more complicated and time consuming. Moreover, signal reproducibility on p-AgSAE is worse than on so called mercury meniscus modified silver solid amalgam electrode (m-AgSAE), the surface of which can be easily renewed either mechanically (old meniscus is wiped off and after short polishing a new one is formed) or electrochemically by a series of suitable potential cleaning pulses. Even thou corresponding cleaning potentials are usually found by trial and error method, it is relatively simple task. Therefore, m-AgSAE is the electrode of choice in most cases of monitoring of organic compounds, which can be seen in Table I (given overleaf; see pp. 42-44).

Paste silver amalgam electrodes [12-15] can minimize problems with passivation in the same way as carbon past electrodes do, i.e. by simple renewal of electrode surface by wiping off the upper layer of the paste. We have developed two types of paste silver amalgam electrodes. First one - without organic pasting liquid - is prepared from pure silver amalgam containing 11 % of silver which has a consistence of paste and can be filed into glass tube, Teflon body or plastic pipette tip to fabric this type of electrode. Second type with organic pasting liquid is prepared by dispersing solid amalgam powder in a suitable organic pasting liquid [mineral oil (44:1), paraffin oil (20:1), silicone oil (15:1), or tricresylphosphate (11:1)] in the same was as carbon paste electrodes are prepared.

Single crystal silver amalgam electrode [16] fabricated from miniature individual crystal of solid amalgam is suitable for measurements in micro volumes or in flow systems inside narrow capillaries. However, it is rather difficult to construct as it requires some experience and therefore, it is more suitable for research and scientific purposes than for routine operations.

Silver solid amalgam tubular electrode [17] is suitable for amperometric detection in flowing system (HPLC-ED or FIA-ED). It actually works in amperometric regime and behaves like a ring electrode because only narrow part of the electrode body at the end of the solid amalgam tube has corresponding potential because of potential drop along the tube.

Silver amalgam porous electrode [18] is convenient tool for amperometric detection in flow-through regime and/or for fabrication of chemically or enzymatically modified

reactors serving for conversion of an analyte before proper amperometric detection which can be based either on detection of product or on detection of oxygen consumed in thus realized enzymatic reaction.

Overview of Determinable Biologically Active Organic Substances

We have developed quite a number of methods of determination of micro and submicromolar concentrations of various types of biologically active and electrochemically reducible organic substances using voltammetry and/or amperometry at above discussed silver amalgam electrodes. These methods can be classified from several points of view.

Obviously the most important pre-requisite is the presence of a suitable functional group electrochemically reducible in the potential window provided by aforementioned silver amalgam electrodes. From this point of view silver amalgam electrodes are suitable for determination of azo, nitro, nitroso, and peroxo compounds, compounds containing quinoid moiety, conjugated carbonyl bonds and heterocyclic moiety. It can be foreseen that silver amalgam electrodes will be applicable also for other, so far not investigated, substances containing these moieties.

From the point of view of the use of tested analytes and/or their occurrence in various samples, determined substances can be divided into environmental pollutants, markers of exposition, markers of illness, drugs and their metabolites, pesticides and products of their transformation, dyes and products of their transformation, explosives and products of their transformation, etc. Again, it can be reasonably expected that many other analytes from above mentioned groups will be determinable using these electrodes.

Alternatively, we can classify newly developed methods on the basis of applied technique as methods based o differential pulse voltammetry, adsorptive stripping voltammetry, flow injection with amperometric detection, and HPLC with amperometric detection. This classification also involves the distinction between batch and continuous measurements.

From the point of view the analyzed matrix most of the so far developed methods are focused on drinking and river water in the case of environmental samples, urine and blood in the case of biological samples, and tablets or other pharmaceutical formulations in the case of drugs. In the case of more complex matrix, methods used for preliminary separation and/or

preconcentration can be used as another criterion for classification. In this context, liquid-liquid extraction and solid phase extraction is most frequently used in combination with silver amalgam electrodes.

The intent of this detailed classification of so-far developed method was to give the reader an overview enabling him to find in a concise way further possible application(s) of those very promising electrodes.

Conclusions

This paper demonstrates possibilities of various types of silver amalgam electrodes for voltammetric and amperometric determination of trace amounts of electrochemically reducible biologically active organic compounds. For routine voltammetric determination, m-AgSAE is probably the best available silver amalgam electrode which in many cases can serve as a suitable non-toxic and user friendly alternative to superior HMDE. Silver amalgam paste electrodes with easily renewable surface can be successfully used in the case of problems with working electrode passivation. Single crystal silver solid amalgam electrodes represent useful tools when electrode and sample miniaturization is requested. Porous amalgam electrodes offer interesting possibilities for detection in flowing systems and for preparation of enzyme modified electrodes and/or reactors. We believe that silver amalgam electrodes can be useful tools in electroanalytical laboratories both for practical applications and for fundamental research purposes.

Abbreviations

AB	acetate buffer
AdSDPV	adsorptive stripping differential pulse voltammetry
AgA-PE	silver amalgam paste electrode
BB	borate buffer
BR	Britton-Robinson buffer
SCAgAE	single crystal silver amalgam electrode
CV	cyclic voltammetry
DCV	direct current voltammetry

Table I. *List of biologically active organic compounds determined by different types of silver amalgam electrodes in UNESCO Laboratory of Environmental Electrochemistry at Charles University in Prague between the years 2008-2014.*

CAS#	Compound	Working electrode	Technique	Medium	Concentration range from L_Q (mol L^{-1})	Ref.
86-00-0	2-nitrobiphenyl	m-AgSAE	DCV	MeOH - LiOH pH 12.0 (1:9)	0.2 - 100	[19]
		m-AgSAE	DPV	MeOH - LiOH pH 12.0 (1:9)	0.1 - 10	[19]
		m-AgSAE	CV	MeOH - BR pH 2.1; 7.0; 13.1 (3:7)	100 [a]	[19]
88-89-1	2,4,6-trinitrophenol	p-AgSA-CE	DPV	BR pH 2.0	0.25 - 100	[20,21]
		p-AgSA-CE	DCV	BR pH 2.0	0.055 - 100	[20,21]
		m-AgSAE	DCV	BR pH 2.0	0.11 - 100	[22]
		m-AgSAE	DPV	BR pH 2.0	0.12 - 100	[22]
		m-AgSAE	CV	MeOH - BR pH 2; 8; 12 (1:9)	100 [a]	[22]
91-19-0	quinoxaline	m-AgSAE	DCV	BR pH 13.0	0.82 - 100	[23]
		m-AgSAE	DCV	BR pH 13.0	0.039 - 100	[23]
92-93-3	4-nitrobiphenyl	m-AgSAE	CV	MeOH - BR pH 2.1; 7.0; 13.1 (3:7)	100 [a]	[19,24]
94-52-0	5-nitrobenzimidazol	AgA-PE	DCV	BR pH 7.0	0.6 - 100	[25]
		AgA-PE	DPV	BR pH 5.0	0.2 - 100	[25]
		AgA-PE	DCV	BR pH 7.0	1.2 - 100	[26]
		AgA-PE	DPV	BR pH 7.0	1.2 - 100	[26]
101-05-3	anilazine	m-AgSAE	DPV	MeOH - BR pH 2.0 (1:9)	0.61 - 100	[27]
		m-AgSAE	AdSDPV	MeOH - BR pH 2.0 (1:9)	0.5 - 10	[27]
118-96-7	2,4,6-trinitrotoluene	m-AgSAE	DCV	MeOH - BR pH 4.0 (1:9)	0.54 - 100	[22]
		m-AgSAE	DPV	MeOH - BR pH 4.0 (1:9)	0.46 - 100	[22]
		m-AgSAE	CV	MeOH - BR pH 2; 8; 12 (1:9)	100 [a]	[22]
154-93-8	carmustine	m-AgSAE	DCV	BR pH 7.0	0.83 - 100	[28,29]
		m-AgSAE	DPV	BR pH 7.0	0.71 - 100	[28,29]
		m-AgSAE	FIA-ED	BR pH 7.0	7.2 - 100	[28,29]

CAS#	Compound	Working electrode	Technique	Medium	Concentration range from L_Q (mol L^{-1})	Ref.
154-93-8	carmustine	m-AgSAE	HPLC-ED	MeOH - BR pH 3.0 (4:6)	4.4 - 100	[28,29]
		p-AgSAE	HPLC-ED	MeOH - BR pH 3.0 (4:6)	4.6 - 100	[28,29]
		MF-AgSAE	HPLC-ED	MeOH - BR pH 3.0 (4:6)	7.1 - 100	[28,29]
393-11-3	4-nitro-3-trifluoromethyl aniline	m-AgSAE	DCV	MeOH - BR pH 8.0 (9:1)	0.33 - 100	[30]
		m-AgSAE	DPV	MeOH - BR pH 8.0 (9:1)	0.65 - 100	[30]
439-14-5	diazepam	m-AgSAE	DCV	MeOH - NaOH pH 13.0 (1:9)	6.6 - 100	[31]
		m-AgSAE	DPV	MeOH - NaOH pH 13.0 (1:9)	1 - 100	[31]
474-25-9	chenodeoxycholic acid	m-AgSAE	DPV	MeOH - BB pH 9.1 (1:9)	140 - 300	[32]
		m-AgSAE	DPV	MeOH - BR pH 4.0 (1:9)	16 - 100	[32]
602-38-0	1,8-dinitronaphthalene	AgSA-PE	DPV	MeOH-BR pH 8.0 (1:1)	1 - 100	[33,34]
		AgSA-PE	CV	MeOH-BR pH 8.0 (1:1)	50 [a]	[33,34]
605-71-0	1,5-dinitronaphthalene	AgSA-PE	DPV	MeOH-BR pH 12.0 (1:1)	1 - 100	[33,34]
		AgSA-PE	CV	MeOH-BR pH 12.0 (1:1)	50 [a]	[33,34]
606-37-1	1,3-dinitronaphthalene	AgSA-PE	DPV	MeOH-BR pH 6.0 (1:1)	1 - 100	[33,34]
		AgSA-PE	CV	MeOH-BR pH 6.0 (1:1)	50 [a]	[33,34]
607-34-1	5-nitroquinoline	m-AgSAE	CV	BR pH 2.0;7.0; NaOH pH 12.0	100 [a]	[35,36]
		m-AgSAE	DCV	BR pH 7.0	0.5 - 100	[35,36]
		m-AgSAE	DPV	NaOH pH 12.0	0.3 - 100	[35,36]
		m-AgSAE	FIA-ED	BB pH 9.0	5.4 - 100	[35,36]
		m-AgSAE	HPLC-ED	MeOH - BB pH 7.0 (85:15)	9.2 - 100	[35,36]
607-57-8	2-nitrofluorene	m-AgSAE	HPLC-ED	MeOH - BB pH 7.0 (85:15)	17 - 100	[35,36]
		p-AgSA-CE	DCV	MeOH - BR pH 5.0 (1:1)	3.7 - 100	[37,38]
		p-AgSA-CE	DCV	MeOH - BR pH 11.0 (1:1)	6 - 100	[37,38]
		p-AgSA-CE	DPV	MeOH - BR pH 5.0 (1:1)	3.4 - 100	[37,38]
		p-AgSA-CE	DPV	MeOH - BR pH 11.0 (1:1)	3 - 100	[37,38]
613-50-3	6-nitroquinoline	m-AgSAE	CV	BR pH 2.0;7.0; NaOH pH 12.0	100 [a]	[35,36]

CAS#	Compound	Working electrode	Technique	Medium	Concentration range from L_Q (mol L^{-1})	Ref.
613-50-3	6-nitroquinoline	m-AgSAE	DCV	BR pH 7.0	0.6 - 100	[35,36]
		m-AgSAE	DPV	NaOH pH 12.0	0.3 - 100	[35,36]
		m-AgSAE	FIA-ED	BB pH 9.0	6.2 - 100	[35,36]
636-93-1	2-methoxy-5-nitrophenol	m-AgSAE	DCV	BR pH 2.0	1.7 - 100	[39]
		m-AgSAE	DCV	BR pH 6.0	5.4 - 100	[39]
		m-AgSAE	DPV	BR pH 2.0	3.4 - 100	[39]
		m-AgSAE	DPV	BR pH 6.0	1.3 - 100	[39]
		m-AgSAE	AdSDPV	BR pH 2.0	0.36 - 1	[40]
		m-AgSAE	DPV	BR pH 6.0	1.3 - 100	[40]
		m-AgSAE	CV	BR pH 2.0; 6.0; 10.0	100 [a]	[40]
892-21-7	3-nitrofluoranthene	m-AgSAE	HPLC-ED	MeOH - BB pH 7.0 (85:15)	33 - 100	[35,36]
1088-11-5	nordiazepam	m-AgSAE	DCV	MeOH - BR pH 10.0 (1:9)	5.5 - 100	[31]
		m-AgSAE	DPV	MeOH - BR pH 10.0 (1:9)	1.7 - 100	[31]
3034-38-6	5-nitroimidazole	m-AgSAE	DCV	BR pH 7.0	1 - 100	[41]
		m-AgSAE	DPV	BR pH 10.0	1.5 - 100	[41]
3096-57-9	2-aminofluoren-9-one	m-AgSAE	DCV	MeOH - BR pH 4.0 (1:9).	0.2 - 10	[42,43]
		m-AgSAE	DPV	MeOH - BR pH 4.0 (1:9).	0.1 - 10	[42,43]
		m-AgSAE	AdSDPV	BR pH 4.0	0.01 - 0.1	[42,43]
		m-AgSAE	CV	MeOH-BR pH 2.0; 7.0; 13.0 (3:7)	100 [a]	[42,43]
5522-43-0	1-nitropyrene	m-AgSAE	HPLC-ED	MeOH - BB pH 7.0 (85:15)	28 - 100	[35,36]
7496-02-8	6-nitrochrysene	m-AgSAE	DCV	MeOH - BR pH 9.0 (1:1)	0.1 - 10	[44]
		m-AgSAE	DPV	MeOH - BR pH 9.0 (1:1)	0.05 - 10	[44]
16773-42-5	ornidazol	m-AgSAE	DCV	BR pH 8.0	0.15 - 100	[45]
		m-AgSAE	DPV	BR pH 8.0	0.23 - 100	[45]
		m-AgSAE	CV	BR pH 3.0; 8.0; 12.0	100 [a]	[45]
34701-14-9	4-nitroindan	m-AgSAE	DCV	MeOH - BR pH 5.0 (1:1)	0.1 - 100	[46,47]

CAS#	Compound	Working electrode	Technique	Medium	Concentration range from L_Q (mol L^{-1})	Ref.
34701-14-9	4-nitroindan	m-AgSAE	DPV	MeOH - BR pH 9.0 (1:1)	0.1 - 100	[46,47]
		m-AgSAE	CV	MeOH - BR pH 3.0; 8.0; 12.0 (1:1)	100 [a]	[46,47]
49866-87-7	difenzoquat	m-AgSAE	DPV	BR pH 11, gelatin	0.61 - 100	[48]
72178-02-0	fomesafen	m-AgSAE	DPV	MeOH - BR pH 8.0 (1:1)	1 - 100	[49]
		m-AgSAE	DPV	MeOH - PB pH 2.0 (3:7)	10 - 100	[50]
99616-64-5	metronidazole	p-AgSA-CE	DCV	BR pH 4.0	2.4 - 100	[37,51]
		p-AgSA-CE	DPV	BR pH 4.0	4.3 - 100	[37,51]
		m-AgSAE	DCV	BR pH 8.0	0.32 - 100	[45]
		m-AgSAE	DPV	BR pH 8.0	0.19 - 100	[45]
		m-AgSAE	CV	BR pH 3.0; 8.0; 12.0	100 [a]	[45]

[a] Method was not used for analytical application.

DPV	differential pulse voltammetry
FIA-ED	flow injection analysis with electrochemical (amperometric) detection
HPLC-ED	high performance liquid chromatography with electrochemical (amperometric) detection
m-AgSAE	mercury meniscus modified silver solid amalgam electrode
MeOH	methanol
MF-AgSAE	mercury film modified silver solid amalgam electrode
mM	mmol L^{-1}
p-AgSA-CE	polished silver solid amalgam composite electrode
p-AgSAE	polished silver solid amalgam electrode
PB	phosphate buffer
TBAC	tetrabutylammonium chloride

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