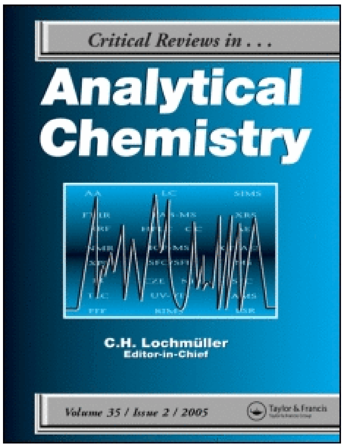

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Analytical Applications of Solid and Paste Amalgam Electrodes

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The review describes working and reference electrodes based on solid and/or paste amalgams and their application for voltammetric, amperometric, and potentiometric determination of both inorganic and organic analytes. Attention is paid to their preparation, pre-treatment and possible modification, and their application in classical voltammetric arrangements, in flowing systems (HPLC-ED, FIA-ED), and in adsorptive transfer stripping voltammetry. The review confirms that amalgam electrodes can successfully substitute mercury electrodes and, in some special cases, offer possibilities not available to mercury electrodes.

Keywords Voltammetry, solid amalgam electrode, paste amalgam electrode, reference amalgam electrode, amperometric amalgam detector, potentiometry

INTRODUCTION

There is no doubt that, even today, mercury introduced by Professor Heyrovský is the best electrode material because of easily renewable and atomically smooth surface and large cathodic window. However, there is a tendency to avoid the use of mercury because of unsubstantiated fears of its toxicity and because of its low mechanical stability complicating the use of mercury electrodes in flowing systems and in portable devices. In an extensive review published in this journal (1), it was clearly shown that amalgam electrodes (AE) can, in many cases, successfully substitute mercury electrodes. Extensive development in the field of amalgam electrodes and their practical applications prompted us to prepare this review covering the period 2002–2008. In addition to the description of solid amalgam electrodes (SAE or Me SAE where Me is Ag, Au, Cu, Ir, etc.) not mentioned in previous review, attention will be paid to composite and paste amalgam electrodes, and their possible modification broadening their practical applications. Amalgam reference electrodes will be briefly mentioned as well. It will be shown that in some cases it is possible to exploit properties of amalgam-forming metal to construct amalgam electrodes offering possibilities not available to pure mercury electrodes.

PREPARATION AND GENERAL CHARACTERIZATION OF AMALGAM ELECTRODES

Amalgam can be liquid, paste, or solid depending on mercury-metal ratio. The classification of amalgam electrodes is depicted in Figure 1. Liquid amalgams have been used in polarography and voltammetry for decades and the term "amalgam polarography" was introduced (2). Practical realization of liquid amalgam electrodes is identical to mercury electrodes, only liquid amalgam is used instead of mercury. A detailed description of liquid amalgam electrodes is out of the scope of this review. However, it should be stressed that mercury film or mercury meniscus prepared at the surface of solid amalgam is rapidly converted into saturated amalgam of the metal contained in electrode material. Solid and paste amalgam working electrodes (WE) can be classified according to the state of their surface as follows:

- **polished**—solid amalgam electrode not containing liquid mercury (p-MeSAE), the surface of which was mechanically polished;
- **film modified**—polished MeSAE covered by mercury film (MF-MeSAE);
- **meniscus modified**—polished MeSAE covered by mercury meniscus (m-MeSAE);
- **composite**—WE based on fine amalgam powder dispersed in a solid polymer (MeSA-CE);
- **paste with pasting liquid**—WE based on fine amalgam powder dispersed in a suitable pasting liquid (MeSA-PE);

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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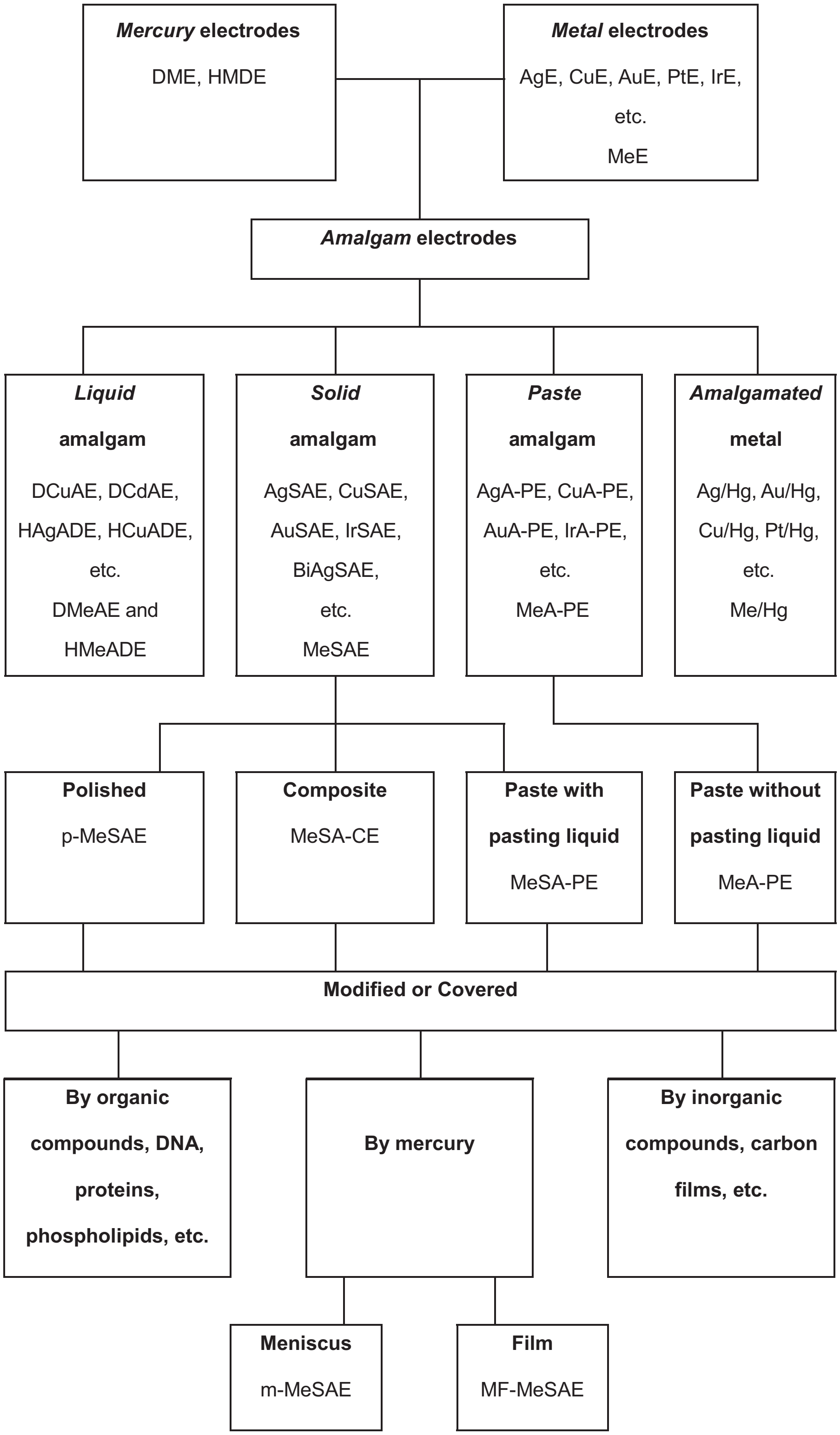

FIG. 1. Classification of amalgam electrodes.

- **paste without pasting liquid**—WE based on paste amalgam with relatively low content of a metal (MeA-PE).

Liquid Mercury Free Polished Solid Amalgam Electrode (p-MeSAE)

p-MeSAE are closely connected to electrodes based on amalgamated metals [Ag (3–7), Au (8, 9), Pt (9, 10), Ir (11, 12), Cu (6, 13, 14)]. MeSAE can be easily polished using emery paper followed by wet alumina. They contain a relatively high content of metal (in the case of AgSAE it is 20% of Ag or even more) and they can be easily prepared by thorough mixing of corresponding aliquots of mercury and metal powder (15, 16). However, thus prepared amalgams are frequently porous, which can be a disadvantage unless we want to prepare a porous electrode. According to our experience it is better to use the procedure described in (1, 17–19) which is very reliable and thus prepared electrodes do not change their properties for at least 10 years.

MeSAEs can be prepared as follows: a fine powder of the given metal (Ag, Au, etc.) is pressed into the bottom part of the tube with an appropriate inner diameter so that the height of the formed column amounts to 0.5–1 cm. The platinum wire (ϕ 0.1 mm) serving as a contact is introduced into the upper part of the column. The bottom of the tube is dipped into a small bottle with 0.5 mL of dry liquid mercury until the whole metal powder column is wetted by mercury (usually just a few minutes). The mercury soaks between the fine particles and within a couple of hours forms a phase of a compact solid amalgam. The bottle with mercury must be hermetically closed. The upper part of the platinum wire is connected with the electrical contact and upper part of the tube is closed by a lid. The bottom of the tube is first rubbed smooth on a soft emery paper and subsequently polished with a wet alumina. The silver solid amalgam obtained in this way was studied by x-ray diffraction, AFM, and electron microscopy (20). It has been proved that the amalgam has a crystalline structure. Based on the comparison with the database of standards, it can be said that all diffraction lines correspond to silver amalgam (Ag_2Hg_3). On the amalgam surface no different phases and no pores were observed. It was shown that the material did not contain liquid mercury and it was verified that mercury did not evaporate from the solid amalgam (20). Some metals (Cu, Bi, Pt, etc.) are usually covered by a layer of oxides or of other compounds which prevents their amalgamation. In that case it is necessary first to remove this layer and only then to saturate the metal powder with mercury. For metals which are well soluble in mercury [Cd—10%, Ga—3,6%, In—70%, Tl—43%, etc. (21)] we recommend another procedure of the SAE's preparation. First, a "skeleton" of the silver powder should be prepared and then this powder should be saturated by a concentrated liquid amalgam of the metal. Such electrodes will contain silver as well but because of its low electrochemical activity the

TABLE 1
Range of working potentials of different electrodes in selected supporting electrolytes

Electrode (disc diameter, mm; electrode surface, mm^2)	Potential range, V					
	0.1M $HClO_4$	0.1M HCl	0.2M acetate buffer, pH 4.8	0.05M Na_2EDTA, 0.2M acetate buffer, pH 4.8	0.05M $Na_2B_4O_7$, pH 9.2	0.1M NaOH
HMDE (1.01 mm^2)	−1.19 . . . +0.44	−1.27 . . . +0.11	−1.70 . . . +0.31	−1.55 . . . +0.09	−1.98 . . . +0.15	−1.97 . . . −0.07
PtE (0.40; 0.13)	−0.32 . . . +1.37	−0.30 . . . +1.11	−0.51 . . . +1.28	−0.51 . . . +1.05	−0.77 . . . +1.16	−0.96 . . . +0.85
AuE (0.40; 0.13)	−0.54 . . . +1.69	−0.55 . . . +0.93	−0.91 . . . +1.49	−0.84 . . . +0.75	−1.39 . . . +1.15	−1.62 . . . +0.81
AgE (0.40; 0.13)	−0.64 . . . +0.39	−0.81 . . . +0.08	−0.99 . . . +0.36	−0.99 . . . +0.35	−1.20 . . . +0.38	−1.41 . . . +0.19
CuE (0.60; 0.28)	−0.95 . . . +0.02	−0.80 . . . −0.12	−0.99 . . . −0.01	−0.97 . . . −0.04	−1.17 . . . +0.97	−1.34 . . . −0.19
p-AgSAE (0.70; 0.38)	−1.12 . . . +0.45	−1.12 . . . +0.11	−1.51 . . . +0.31	−1.45 . . . +0.11	−1.88 . . . +0.16	−1.96 . . . −0.06
*MF-AgSAE (0.52; 0.21)	−1.28 . . . +0.44	−1.19 . . . +0.11	−1.47 . . . +0.31	−1.47 . . . +0.10	−1.82 . . . +0.15	−2.07 . . . −0.06
m-AgSAE (0.54; 0.46)	−1.11 . . . +0.44	−1.12 . . . +0.12	−1.39 . . . +0.30	−1.39 . . . +0.10	−1.92 . . . +0.15	−1.99 . . . −0.06
m-AuSAE (0.40; 0.25)	−1.12 . . . +0.45	−1.11 . . . +0.12	−1.47 . . . +0.31	−1.45 . . . +0.11	−1.90 . . . +0.16	−1.91 . . . −0.05
m-IrSAE (0.67; 0.71)	−1.01 . . . +0.43	−1.01 . . . +0.12	−1.32 . . . +0.29	−1.34 . . . +0.10	−1.63 . . . +0.15	−1.72 . . . −0.06
m-CdAgSAE (0.53; 0.41)	−1.07 . . . −0.66	−1.06 . . . −0.69	−1.29 . . . −0.68	−1.29 . . . −0.73	−1.93 . . . −0.69	−1.93 . . . −0.84
m-CuSAE (0.48; 0.36)	−1.17 . . . +0.06	−1.18 . . . −0.07	−1.44 . . . −0.03	−1.43 . . . −0.13	−1.75 . . . +0.95	−1.86 . . . −0.24
m-BiAgSAE (0.70; 0.77)	−0.97 . . . −0.02	−0.96 . . . −0.09	−1.25 . . . −0.18	−1.29 . . . −0.17	−1.84 . . . −0.29	−1.82 . . . −0.48
AgSA-CE (2.9 mm)	−1.09 . . . +0.45	−1.07 . . . +0.15	−1.34 . . . +0.45	−1.33 . . . +0.45	−1.63 . . . +0.52	−1.85 . . . +0.17
AgSA-PE (3.0 mm)	−1.04 . . . +0.36	−0.90 . . . +0.21	−1.15 . . . +0.38	−1.09 . . . +0.36	−1.50 . . . +0.24	−1.45 . . . +0.30
AgA-PE (0.60; 0.57)	−1.15 . . . +0.43	−1.18 . . . +0.11	−1.67. . . +0.30	−1.58. . . +0.10	−1.85 . . . +0.15	−1.95 . . . −0.07
AgA-PE (2.0; 3.14)	−1.24 . . . +0.48	−1.24 . . . +0.15	−1.47 . . . +0.36	−1.46 . . . +0.15	−1.90 . . . +0.21	−1.83 . . . +0.01

Experimental results obtained by DCV; saturated calomel reference electrode; scan rate 0.02 V/s; the potential limits correspond to 1 μA current level for the electrodes with diameter less than 1 mm and 20 μA for larger electrodes; air oxygen was removed by nitrogen. *mercury film thickness $l = 1.92$ μm.

properties of AE, in most cases, will be decided by the metal of the highest activity (Table 1). The range of working potentials of the p-AgSAE is shown in Table 1, which demonstrates that the hydrogen overvoltage of this electrode is the largest among the electrodes not containing liquid mercury.

Mercury Film Covered Solid Amalgam Electrode (MF-MeSAE)

On the polished surface of a solid amalgam, a liquid mercury film can be easily deposited electrochemically. Mercury easily wets solid amalgam and forms an ideally smooth and homogeneous liquid surface in contrast with, e.g., glassy carbon which is not wetted by mercury and thus micro droplets of mercury are formed on its surface. Optimum conditions for mercury film deposition are as follows: 0.01M $HgCl_2$ in 1M KI and applied potential −200 mV vs. saturated calomel electrode (SCE). A detailed procedure for preparation of the film with exactly defined thickness can be found in (22, 23). The thickness depends on the time of deposition and on the electrode area. A 60-second deposition at p-AgSAE with 0.5 mm diameter gives about 1-μm film thickness, with which it is possible to work for approximately one day; afterwards, a new film must be prepared. A simple electrolytic device described in (22, 23) decreases the risk of environment contamination with toxic Hg(II) ions and 0.2 mL of 0.01M $HgCl_2$ in 1M KI is sufficient for multiple (e.g., 100 times) film deposition. ASV of Tl(I) on thus-prepared MF-AgSAE confirmed its analytical potential. Peak current density was higher for MF-AgSAE as compared with p-AgSAE or m-AgSAE while the peak width, important for good resolution, was the lowest from the above-mentioned electrodes. It has been found that the thinner the mercury film is the more negative the peak potential, which is valid for mercury films on different substrates and theoretically substantiated (24).

Mercury Meniscus Covered Solid Amalgam Electrode (m-MeSAE)

By immersing a p-MeSAE into liquid mercury, a mercury meniscus is formed at its surface which is not visually changed for several months. However, it is recommended to repeat the amalgamation once per week to prevent deterioration of sensitivity or reproducibility. (Into a 5 mL bottle, 0.5 mL of metallic mercury and 2 mL of deionized water are introduced; the lower end of p-MeSAE is dipped into the mercury layer and agitated intensively for about 15 seconds. Then the electrode is rinsed with water and checked by means of a lens to determine whether a meniscus of mercury has been formed). The m-MeSAE is the most reliable and most similar to the hanging mercury drop electrode (HMDE) so that most analytical applications published so far are using this electrode (Table 2). The above-described procedure for meniscus forming is simple and fast. However, it does not guarantee that the new meniscus will give the same response as the previous one, which is partially connected with possible passivation of old meniscus and partially with a different area of the new meniscus. The problem of electrode reproducibility is addressed (as with many other solid electrodes) by standard addition technique.

Composite Electrodes From Silver Solid Amalgam Powder (AgSA-CE)

Solid composite electrodes are composed at least from one insulating phase (ceresin wax, Teflon®, polyethylene, epoxide, metacrylate resin, etc.) and one conducting phase (various forms of carbon, powdered metals, powdered amalgams, etc.); eventually they can contain some other additives (25–27). These electrodes have quite attractive electrochemical, physical, and mechanical properties (28); they are stable, mechanically resistant and durable, they can be easily polished, and the conductivity of composite materials is comparable with the conductivity of metallic conductors. They are frequently applied for stripping voltammetry of metals. Solid amalgam can be easily powderized and thus used as a conductive phase of composite electrodes. The optimum procedure for the preparation of silver solid amalgam composite electrode (29, 30) is as follows: AgSA freshly prepared by mixing of the silver particles (size 5–10 μm) with liquid mercury (final composition of such AgSA: Ag 40% and Hg 60%, crystalline form Ag_2Hg_3) was powdered in agate grinding mortar and let to solidify for one day at room temperature. After that the formed amalgam was powdered once again to very fine form. An appropriate amount of solid amalgam powder was added to the epoxy resin and the mixture was thoroughly homogenized. The composite mixture was pressed into the electrode body (90 mm-long glass tube of 2.9 mm-inner diameter, the height of the mixture column was 8–10 mm). The electric contact of the electrode was realized by copper wire inserted into soft composite mixture. After solidification of the electrode material (1 day), the electrode surface was brushed by emery paper of various granulation and at the end it was gently polished by alumina paste of various granulation (up to 0.05 mm). Thus prepared and polished, p-AgSA-CE can be eventually modified (similarly as p-AgSAE) in various ways (e.g., by electrolytic deposition of the mercury film on the solid surface to prepare MF-AgSAE-CE or by formation of a mercury meniscus by dipping the electrode shortly in the liquid mercury to prepare m-AgSA-CE). Optical microscopic studies of AgSA-CE revealed that the active part of thus prepared electrode surface looks like an array of small electrodes from AgSA. After electrolytic formation of mercury film it can be seen that the active surface of the electrode is not homogenous. The amalgam particles are of various sizes; it is possible to differentiate the microparticles covered with relatively large amounts of mercury as well as with a thin layer of mercury film (the crystalline structure of the amalgam is recognizable or not) and it is possible to recognize the particles uncovered by mercury. The electrolytic formation of Hg-film on the electrode seems to be a very simple and effective way to determine the ratio between conducting and non-conducting particles at the surface of the composite WE.

TABLE 2

The use of solid and paste amalgam electrodes for the study and determination of different substances

Substance	Electrode/technique	Supporting electrolyte	L_Q	Ref.
Cu^{2+}	m-AgSAE/ASV	0.4 M acetate buffer (pH 4.8)	$3\cdot10^{-4}$ mg/L	(44)
Cu^{2+}	p-AgSAE/ASV	0.01 M HNO_3	$1\cdot10^{-2}$ mg/L	(20)
Cu^{2+}	AgA-PE/ASV	0.1 M acetate buffer (pH 4.8)	$2\cdot10^{-2}$ mg/L	(35)
Cu^{2+}	AgSA-CE/DPV	0.1 M acetate buffer (pH 4.8)	0.2 mg/L	(29)
Pb^{2+}	m-AgSAE/ASV	0.4 M acetate buffer (pH 4.8)	$7\cdot10^{-4}$ mg/L	(44)
Pb^{2+}	p-AgSAE/ASV	0.01 M HNO_3	$1\cdot10^{-2}$ mg/L	(20)
Pb^{2+}	m-CuSAE/ASV	0.2 M acetate buffer (pH 4.8)	$2\cdot10^{-3}$ mg/L	(45)
Pb^{2+}	AgA-PE/ASV	0.1 M acetate buffer (pH 4.8)	$9\cdot10^{-3}$ mg/L	(35)
Pb^{2+}	AgSA-CE/DPV	0.1 M acetate buffer (pH 4.8)	$3\cdot10^{-2}$ mg/L	(29)
Cd^{2+}	m-AgSAE/ASV	0.4 M acetate buffer (pH 4.8)	$1\cdot10^{-3}$ mg/L	(44)
Cd^{2+}	p-AgSAE/ASV	0.01 M HNO_3	$1\cdot10^{-2}$ mg/L	(20)
Cd^{2+}	m-CuSAE/ASV	0.2 M acetate buffer (pH 4.8)	$2\cdot10^{-3}$ mg/L	(45)
Cd^{2+}	AgA-PE/ASV	0.1 M acetate buffer (pH 4.8)	$2\cdot10^{-2}$ mg/L	(35)
Cd^{2+}	AgSA-CE/DPV	0.1 M acetate buffer (pH 4.8)	$2\cdot10^{-2}$ mg/L	(29)
Zn^{2+}	m-AgSAE/ASV	0.4 M acetate buffer (pH 4.8)	$9\cdot10^{-4}$ mg/L	(44)
Zn^{2+}	p-AgSAE/ASV	0.01 M HNO_3	$5\cdot10^{-3}$ mg/L	(20)
Tl^{+}	m-AgSAE/ASV	0.4 M acetate buffer (pH 4.8)	$4\cdot10^{-4}$ mg/L	(44)
Ni^{2+}	m-AgSAE/AdSV	0.1 M [$NH_4Cl + NH_3$] (pH 9.8), 0.001% dimethylglyoxime	$9\cdot10^{-4}$ mg/L	(47)
Fe^{3+}	m-AgSAE/DPV	0.35 M NaOH, 3% triethanolamine, 0.01 M Na_2EDTA	0.20 mg/L	(47)
Fe^{3+}	p-AgSAE/ASV	0.1 M NaOH, 1.5% triethanolamine	0.01 mg/L	(48)
Mn^{2+}	m-CuSAE/CSV	0.05 M $Na_2B_4O_7$ (pH 9.2)	0.03 mg/L	(45)
Mn^{2+}	R-AgSAE/ASV	0.05 M NH_4Cl	$1\cdot10^{-3}$ mg/L	(49)
IO_3^-	m-AgSAE/DPV	0.1 M NaOH	0.14 mg/L	(43)
IO_3^-	p-AgSAE/DPV	0.1 M NaOH	0.34 mg/L	(43)
IO_3^-	AgA-PE/DPV	0.1 M NaOH	0.03 mg/L	(35)
IO_3^-	AgSA-CE/DPV	0.1 M NaOH	0.2 mg/L	(29)
NO_3^-	m-AgSAE/DPV	0.02 M $CeCl_3$	1.2 mg/L	(19, 47)
NO_3^-	p-AgSAE/DPV	0.04 M $CeCl_3$	3.2 mg/L	(20)
SCN^-	p-AgSAE/DPV	0.1 M acetate buffer (pH 4.6)	0.3 mg/L	(20)
SCN^-	p-AgSAE/CSV	0.1 M acetate buffer (pH 4.6)	$5\cdot10^{-4}$ mg/L	(20)
Adenine	m-CuSAE/CSV	0.05 M $Na_2B_4O_7$ (pH 9.2)	$6\cdot10^{-9}$ mol/L	(47)
Adenine	p-AgSAE/CSV	0.005 M NaOH, 0.4 mg/L Cu^{2+}	$3\cdot10^{-9}$ mol/L	(50)
Adenine	AgSA-CE/CSV	0.005 M NaOH, 0.4 mg/L Cu^{2+}	$5\cdot10^{-8}$ mol/L	(29)
Guanine	p-AgSAE/CSV	0.005 M NaOH, 0.4 mg/L Cu^{2+}	$7\cdot10^{-9}$ mol/L	(50)
Adenosine detection of phase transients	*PtSAE, *CuSAE, *AgSAE chronoamperometric and capacitance measurements	0.1 M NaCl	—	(51, 52)
Oligonucleotides (acid hydrolyzed): 80-mer (Adenine$_{80}$) 10-mer (Adenine$_{10}$)	*AuSAE/CSV	0.05 M $Na_2B_4O_7$ 50 μM Cu(II)	$5\cdot10^{-9}$ mol/L	(53)

(*Continued on next page*)

TABLE 2
The use of solid and paste amalgam electrodes for the study and determination of different substances (Continued)

Substance	Electrode/technique	Supporting electrolyte	L_Q	Ref.
Oligonucleotides: tensammetric responses, homopurine ODN lengths, contain of purine units in ODNs	*PtSAE/ACV *CuSAE/ACV *AuSAE/ACV *AgSAE/ACV	0.3 M NaCl, 50 mM Na_2HPO_4	—	(54)
Calf thymus ssDNA (acid-treated)	m-CuSAE/CSV	0.005 M NaOH	$4 \cdot 10^{-9}$ mol/L	(55)
Plasmid DNA pSP64(acid-treated)	p-AgSAE/CSV	0.005 M NaOH, 0.4 mg/L Cu^{2+}	$7 \cdot 10^{-9}$ mol/L	(50)
Calf thymus ssDNA	p-AgSAE/CSV	0.005 M NaOH, 0.4 mg/L Cu^{2+}	$6 \cdot 10^{-9}$ mol/L	(50)
DNA-Os,bipy	m-AgSAE/AdSV, catalyt	0.1 M acetate buffer (pH 4.7)	$2 \cdot 10^{-4}$ mg/L	(56)
DNA-Os,bipy	m-AgSAE/AdTSV, catalyt	0.1 M acetate buffer (pH 4.7)	$2 \cdot 10^{-3}$ mg/L	(56)
Calf thymus ssDNA; redox DNA responses	p-AgSAE/CV/AdSV/AdTSV MF-AgSAE/CV/AdSV/ AdTSV	0.3 M ammonium formiate, 50 mM phosphate buffer, pH 6.9	—	(57)
Calf thymus ssDNA, supercoiled linear and suprcoiled denatured DNA; tensammetric DNA responses	p-AgSAE/ACV MF-AgSAE/ACV	0.3 M NaCl, 50 mM Na_2HPO_4	—	(57)
Covalently closed circular supercoiled DNA; detecting DNA damage	p-AgSAE/ACV/AdTS ACV MF-AgSAE/ACV/AdTS ACV	0.3 M NaCl, 50 mM Na_2HPO_4	—	(57)
Covalently closed circular supercoiled DNA; detecting of enzymatic and chemical DNA damage	m-AgSAE/ACV/AdTS ACV	0.3 M NaCl, 50 mM Na_2HPO_4	—	(57)
Cysteine	m-AgSAE/CSV	0.05 M $Na_2B_4O_7$ (pH 9.2)	$9 \cdot 10^{-9}$ mol/L	(59)
Cysteine	m-CuSAE/CSV	0.05 M $Na_2B_4O_7$ (pH 9.2)	$3 \cdot 10^{-8}$ mol/L	(59)
Cysteine	m-AgSAE/Brdička reaction MF-AgSAE/Brdička reaction p-AgSAE/Brdička reaction	0.1 M ammonium buffer (pH 9.8) 1 mM $Co(NO_3)_2$	$1 \cdot 10^{-7}$ mol/L $2 \cdot 10^{-7}$ mol/L $5 \cdot 10^{-8}$ mol/L	(60)
Cystine	m-CuSAE/CSV	0.05 M $Na_2B_4O_7$ (pH 9.2)	$5 \cdot 10^{-9}$ mol/L	(18)
Phytochelatin PC2	m-CuSAE/CSV	0.05 M $Na_2B_4O_7$ (pH 8.1)	$9 \cdot 10^{-9}$ mol/L	(46)
Phytochelatin PC3	m-CuSAE/CSV	0.05 M $Na_2B_4O_7$ (pH 8.1)	$6 \cdot 10^{-9}$ mol/L	(46)
Phytochelatin PC3	m-AgSAE/Brdička reaction	0.1 M ammonium buffer (pH 9.8) 1 mM $Co(NO_3)_2$	$6 \cdot 10^{-8}$ mol/L	(60)
Glutathione	m-CuSAE/CSV	0.05 M $Na_2B_4O_7$ (pH 8.1)	$1 \cdot 10^{-8}$ mol/L	(46)
Glutathione	m-AgSAE/Brdička reaction MF-AgSAE/Brdička reaction p-AgSAE/Brdička reaction	0.1 M ammonium buffer (pH 9.8) 1 mM $Co(NO_3)_2$	$1 \cdot 10^{-5}$ mol/L $1 \cdot 10^{-5}$ mol/L $6 \cdot 10^{-8}$ mol/L	(60)
Ascorbic acid	m-AgSAE/DPV p-AgSAE/DPV AgA-PE/DPV	0.1 M acetate buffer (pH 4.8)	0.3 mg/L 0.8 mg/L 0.6 mg/L	(35)
Ascorbic acid	AgSA-CE/DPV	0.1 M acetate buffer (pH 4.8)	$2 \cdot 10^{-6}$ mol/L	(29)

TABLE 2
The use of solid and paste amalgam electrodes for the study and determination of different substances (Continued)

Substance	Electrode/technique	Supporting electrolyte	L_Q	Ref.
Ethanol	m-CuSAE/DPV	0.2 M NaOH	0.5%	(61)
1-Nitronaphtalene	m-AgSAE/DPV	BR buffer (pH 7)—MeOH, 1:9	$3\cdot10^{-7}$ mol/L	(62)
2-Nitronaphtalene	m-AgSAE/DPV	BR buffer (pH 7)—MeOH, 1:9	$5\cdot10^{-7}$ mol/L	(62)
1,3-Dinitronaphtalene	m-AgSAE/DPV	BR buffer (pH 10)—MeOH, 1:1	$2\cdot10^{-6}$ mol/L	(63)
1,5-Dinitronaphtalene	m-AgSAE/DPV	BR buffer (pH 10)—MeOH, 1:1	$1\cdot10^{-6}$ mol/L	(63)
1,8-Dinitronaphtalene	m-AgSAE/DPV	BR buffer (pH 10)—MeOH, 1:1	$5\cdot10^{-7}$ mol/L	(63)
3-Nitrofluoranthen	m-AgSAE/DPV	0.01 M NaOH—MeOH, 1:9	$4\cdot10^{-7}$ mol/L	(64, 65)
3-Nitrofluoranthen	m-AgSAE/AdSV	0.01 M NaOH—MeOH, 1:1	$3\cdot10^{-8}$ mol/L	(64)
2-Nitrofluorene	m-AgSAE/DPV	BR buffer (pH 10)—MeOH, 1:1	$2\cdot10^{-7}$ mol/L	(66)
Nitrobenzene	m-AgSAE/DPV	0.1 M acetate buffer (pH 4.8)	$6\cdot10^{-7}$ mol/L	(47)
1,3-Dinitrobenzene	m-AgSAE/DPV	0.1 M acetate buffer (pH 4.8)	$3\cdot10^{-7}$ mol/L	(47)
2-Nitrophenol	m-AgSAE/DPV	BR buffer (pH 8)	$1\cdot10^{-6}$ mol/L	(67)
2-Nitrophenol	p-AgSAE/DPV	BR buffer (pH 5)	$1\cdot10^{-6}$ mol/L	(67)
2-Nitrophenol	p-AgSAE/HPLC-ED thin-layer detector wall-jet detector	0.05 M phosphate buffer pH 6.0—MeOH (7:3) mobile phase	$10\cdot10^{-6}$ mol/L $25\cdot10^{-6}$ mol/L	(68)
4-Nitrophenol	m-AgSAE/DPV	BR buffer (pH 6)	$1\cdot10^{-6}$ mol/L	(67)
4-Nitrophenol	p-AgSAE/DPV	BR buffer (pH 6)	$3\cdot10^{-6}$ mol/L	(67)
4-Nitrophenol	m-AgSAE/FIA-ED	BR buffer (pH 6)	$3\cdot10^{-6}$ mol/L	(69)
4-Nitrophenol	p-AgSAE/HPLC-ED thin-layer detector wall-jet detector	0.05 M phosphate buffer pH 6.0—MeOH (7:3) mobile phase	$10\cdot10^{-6}$ mol/L $25\cdot10^{-6}$ mol/L	(68)
4-Nitrophenol	AgA-PE/DPV	0.1 M acetate buffer (pH 4.8)	$2\cdot10^{-7}$ mol/L	(35)
4-Nitrophenol	AgSA-CE/DPV	0.1 M acetate buffer (pH 4.8)	$1\cdot10^{-6}$ mol/L	(29)
2,4-Dinitrophenol	m-AgSAE/DPV	BR buffer (pH 4)	$2\cdot10^{-6}$ mol/L	(67)
2,4-Dinitrophenol	p-AgSAE/DPV	BR buffer (pH 5)	$3\cdot10^{-6}$ mol/L	(67)
2,4-Dinitrophenol	p-AgSAE/HPLC-ED thin-layer detector wall-jet detector	0.05 M phosphate buffer pH 6.0—MeOH (7:3) mobile phase	$5\cdot10^{-6}$ mol/L $10\cdot10^{-6}$ mol/L	(68)
5-nitroquinoline	m-AgSAE/DPV	0.05 M borate buffer pH 9.0	$3\cdot10^{-7}$ mol/L	(70)
	m-AgSAE/DCV	0.05 M borate buffer pH 9.0	$5\cdot10^{-7}$ mol/L	
	m-AgSAE/FIA-ED wall-jet detector	0.05 M borate buffer pH 9.0	$4\cdot10^{-6}$ mol/L	
6-nitroquinoline	m-AgSAE/DPV m-AgSAE/DCV	0.01 M NaOH BR buffer (pH 7)	$3\cdot10^{-7}$ mol/L $6\cdot10^{-7}$ mol/L	(70)
2-methoxy-5-nitrophenol (carcinogen)	m-AgSAE/DCV m-AgSAE/DPV	BR buffer (pH 2) BR buffer (pH 6)	$2\cdot10^{-6}$ mol/L $1\cdot10^{-6}$ mol/L	(71)
2-methoxy-5-nitrophenol (carcinogen)	p-AgSAE/HPLC-ED thin-layer detector wall-jet detector	0.05 M phosphate buffer pH 6.0—MeOH (7:3) mobile phase	$10\cdot10^{-6}$ mol/L $25\cdot10^{-6}$ mol/L	(68)
Ostazine orange (carcinogen)	m-AgSAE/AdSV	0.01 M NaOH	$2\cdot10^{-7}$ mol/L	(65)
2-Methyl-4,6-dinitrophenol (herbicide)	m-AgSAE/DPV	BR buffer (pH 4)	$2\cdot10^{-7}$ mol/L	(72)

(*Continued on next page*)

TABLE 2

The use of solid and paste amalgam electrodes for the study and determination of different substances (Continued)

Substance	Electrode/technique	Supporting electrolyte	L_Q	Ref.
Pendimethalin (herbicide)	m-AgSAE/DPV	BR buffer (pH 7)—MeOH, 1:1	$3\cdot10^{-7}$ mol/L	(64)
Oxyfluorfen (herbicide)	m-AgSAE/DPV	BR buffer (pH 10)—MeOH, 1:1	$7\cdot10^{-7}$ mol/L	(73)
Bifenox (herbicide)	m-AgSAE/DPV	BR buffer (pH 7)—MeOH, 1:9	$4\cdot10^{-7}$ mol/L	(74)
Atrazine (herbicide)	p-CuSAE/SWV	0.1 M Na_2SO_4 (pH 2.4)	$5\cdot10^{-8}$ mol/L	(75, 76)
Ametryne (herbicide)	p-CuSAE/SWV	0.1 M Na_2SO_4 (pH 2.4)	$6\cdot10^{-8}$ mol/L	(76, 77)
Doxorubicin (anti-cancer drug)	m-AgSAE/DPV	BR buffer (pH 6)	$3\cdot10^{-7}$ mol/L	(78)
Doxorubicin (anti-cancer drug)	m-AgSAE/AdSV	BR buffer (pH 6)	$9\cdot10^{-9}$ mol/L	(78)
Carmustin (anti-cancer drug)	m-AgSAE/DCV m-AgSAE/DPV	BR buffer (pH 7) BR buffer (pH 7)	$8\cdot10^{-7}$ mol/L $7\cdot10^{-7}$ mol/L	(79)
Flutamid (anti-cancer drug)	m-AgSAE/DCV m-AgSAE/DPV	BR buffer (pH 7)—MeOH, 9:1 BR buffer (pH 7)—MeOH, 9:1	$5\cdot10^{-6}$ mol/L $3\cdot10^{-6}$ mol/L	(80)
Lomustine (anti-cancer drug)	m-AgSAE/DCV m-AgSAE/DPV	0.05 M acetate buffer (pH 4) 0.05 M acetate buffer (pH 4)	$3\cdot10^{-6}$ mol/L $2\cdot10^{-6}$ mol/L	(81)

L_Q—limit of quantitation; R-AgSAE—rotating silver solid amalgam electrode; *MeSAE—thin solid amalgam layer on metal wire; DPV—differential pulse voltammetry; DCV—direct current voltammetry; ACV—alternating current voltammetry; SWV—square-wave voltammetry; ASV—anodic stripping voltammetry; CSV—cathodic stripping voltammetry; AdSV—adsorptive stripping voltammetry; AdTSV—adsorptive transfer stripping voltammetry; FIA-ED and HPLC-ED—flow injection analysis and HPLC with electrochemical detection; catalyt.—catalytic evolution of hydrogen; BR—Britton-Robinson; MeOH—methanol; ODN – oligonucleotide; ssDNA—single-stranded DNA

Composite electrodes containing less then 70% w/w of AgSA have a high resistance and thus AgSA-CE containing 80% w/w of AgSA is recommended (29). If AgSA-CE is dipped into liquid mercury (amalgamation), some amalgam microparticles are covered with liquid mercury. However, typical spherical mercury menisci are not formed. The ratio of ASV peak heights of cadmium for stirred and quiescent solutions was 5.3 for m-AgSAE and 2.2 for AgSA-CE. This suggests that part of the AgSA-CE surface behaves like an array of microelectrodes, the rest being more similar to classical electrodes, the response of which depends on stirring (29).

Paste Electrodes from Silver Solid Amalgam Powder (AgSA-PE)

Powdered solid amalgam can be used for the preparation of paste electrodes (31, 32) similar to classical carbon paste electrodes (CPE) (33) using the same pasting liquids (mineral oil, silicone oil, paraffin oil, or tricresylphospahte). However, the ratio between powdered amalgam and pasting liquid is approximately 20:1 as compared with approximately a 1:1 ratio for CPE. 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 (see Table 1) is comparable with other amalgam electrodes. However, the hydrogen overvoltage in alkaline medium is lower which can be connected with oxygen dissolved in pasting liquid or adsorbed on amalgam particles.

Paste Electrodes from Paste Silver Amalgam (AgA-PE)

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 (34, 35). Amalgams containing 15–18% of Ag relatively quickly solidify and if the content of Ag is below 10% the amalgam is liquid. Therefore, the optimum content of Ag in the paste amalgam is 10–12%. The paste and the electrode can be prepared as follows (35): a mixture of mercury and 10–15% of fine silver powder (particle size 2–3.5 μm, Aldrich) is vigorously mixed for 60 seconds in a compact dental amalgams preparation unit (Dentomat, Degussa, São Paulo, Brazil). A Teflon holder with a movable piston, designed for carbon paste electrodes, is filled with paste amalgam. 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 silver content, a smoothed surface can resemble either mercury film electrode (10–12% Ag) or solid electrode (more than 12% Ag). In the first case, better reproducibility can be achieved. Paste amalgam can also be used for the preparation of disposable paste electrodes (36): a small amount of the amalgam paste prepared as described above was put inside the small pipette tip (hole size 600 ± 25 μm), an electrical connection with the steel wire was made, and then the amalgam surface was 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.

Table 1 contains the potential windows of AgA-PE both in classical (diameter 2 mm) and in disposable pipette tip (diameter 0.6 mm) version in typical supporting electrolytes.

Solid Amalgam Electrodes Covered by Carbon Powder Based Films

It is possible to broaden the available potential window of an amalgam electrode by covering the electrode with a film of a polymer containing conductive particles (37, 38). The used polymer is not conductive and, thus, it completely isolates the analyzed solution from conductive amalgam which acts just as a conductor while microparticles of conductive material (graphite, glassy carbon micro beads, boron-doped diamond particles, nanotubes, etc.), dispersed in the polymer, form the proper electrode material and ensure a contact between the analyzed solution and the conductive part of the electrode (the amalgam in this case). The renewal of this film can be fast and simple. These electrodes can be viewed as a thick film analogue of composite electrodes which, in dependence on polymer : conductive powder ratio, can behave like a microelectrode array or like a classical electrode with homogeneous surface.

The conductive inks were prepared by using graphite powder with 1–2 μm particle size (Fluka, Buchs, Switzerland), graphite powder with 2 μm average particle size existing under trade mark CR2” (Maziva, Tyn nad Vltavou Czech Republic), or glassy carbon spherical micro beads 0.4–12 μm particle size (Alfa Aesar, Karlsruhe, Germany) (37). Conductive carbon ink containing 90% of carbon was prepared by mixing 0.01 g of polystyrene, 0.09 g of corresponding carbon powder, and 0.5 ml of dichloroethane. The mixture is thoroughly homogenized either by sonication or by intensive agitation for 5 minutes. The carbon ink film at a p-AgSAE can then be prepared either by application of a small amount (1–2 μL) of the conductive ink applied on the surface of the electrode or by immersion of the active part of the electrode into the conductive ink (just touch the surface of the ink). After 2 minutes evaporation of dichloroethane, the ink film electrode is ready to use. The old film can be easily removed by wiping it off with a piece of filter paper and a new film can be formed by the above-described procedure. Thus prepared electrodes, can be used up to +1400 mV.

Reference Electrodes Based on Solid Amalgams

In the framework of systematic investigation of amalgam electrodes, a reference calomel (39) and mercurosulphate (40) electrode based on silver solid amalgam were proposed, constructed, and tested. Their main advantages are that liquid mercury is substituted by non-toxic amalgam and that amalgam and liquid mercury types of reference electrodes have practically identical electrode potentials. Long-term potential stability and their resistance toward polarization are comparable to that of classical reference electrodes.

Combined Voltammetric-Potentiometric Sensor (CVPS) with Silver Solid Amalgam Link

This sensor selective for silver and mercury ions combines the selectivity of potentiometry with the sensitivity of voltammetry (41, 42). It consists of a column of silver solid amalgam in a narrow glass tube containing a suitable inert electrolyte in which m-AgSAE is immersed, so that this WE is not in a direct contact with analyzed solution but via the silver solid amalgam link in a three electrode arrangement. Contrary to ion selective electrodes which are not able to detect complexed mercury and silver ions, these sensors can be used for this purpose.

Pre-treatment of Amalgam Electrodes Before Measurements (17–19, 29, 35, 43–46)

In order to assure reliable and reproducible results on amalgam electrodes, it is necessary to perform the following three operations in succession:

1. ***amalgamation*** for m-MeSAE, ***creating of mercury film*** for MF-MeSAE, or ***polishing*** for p-MeSAE and p-AgSA-CE;
2. ***activation*** at the beginning of a series of measurements;
3. ***regeneration*** before each measurement.

With a computer-controlled instrument the last two operations can be realized automatically by means of an appropriate computer program. It is a special advantage of the m-MeSAEs and MF-MeSAEs that the renewal of their surface does not need any mechanical intrusion.

Amalgamation of m-MeSAE and MeSA-CE in the course of continued application of the electrode is done once a week, or any time earlier in case of any trouble (deterioration of sensitivity or reproducibility, absence of liquid meniscus at the electrode surface, etc.). Into a 5 mL bottle, 0.5 mL of metallic mercury and 2 mL of deionized water are introduced; the electrode is dipped into the mercury layer and agitated intensively for about 15 seconds. Then the electrode is rinsed with deionized water and checked by means of a lens to determine whether a meniscus of mercury has been formed. ***Formation of a new mercury film at MF-MeSAE and MF-MeSA-CE*** can be done electrochemically as discussed earlier in this paper and in more detail in papers (22, 23). ***Polishing of p-MeSAE and MeSA-CE*** is done by 0.3–0.05 μm alumina suspension at polyurethane pad for 1–3 minutes. ***Surface renewal of amalgam paste electrodes*** is accomplished by pushing about 1 mm layer of paste out of the electrode by means of a moveable piston, wiping it off with a smooth paper, and smoothing new surface on a glass plate. For the paste electrodes using disposable pipette tips, this tip filed with amalgam paste is simply changed.

Activation of MeSAE, which lasts some 5 minutes, is done at the beginning of the working day, after a pause in measurement longer than 1 hour, and after amalgamation or polishing. The activation is carried out with the electrode dipped into 10 mL of 0.2 M KCl without deaeration; it consists of applying the constant potential of –2200 mV to the electrode for 5 minutes. During that time, at the negative potential any surface layers and adsorbed impurities are removed from the electrode surface whereby the sensitivity and the reproducibility of measurements are restored.

Regeneration of MeSAE lasting about 30 seconds precedes each measurement; it guarantees good reproducibility of results within the usual limits of 2–3%. In many cases it is sufficient to apply to the electrode a constant potential of 50–100 mV more positive than the potential of hydrogen evolution in the given electrolyte. Under those conditions, eventual oxides of mercury or of the metals in the amalgam get reduced, and adsorbed molecules get desorbed. However, in most cases, a more complex activation potential program has to be used (17, 44).

APPLICATIONS OF SOLID AND PASTE AMALGAM ELECTRODES

The ever increasing number of analytical applications of amalgam electrodes is documented in Table 2. Anodic stripping voltammetry (ASV) at m-AgSAE was used for analysis of a mixture of Cu(II), Pb(II), Cd(II), Zn(II), and Tl(I) (44). m-AgSAE enables much longer accumulation times than HMDE (up to 1 hour) (47) so that higher sensitivities can be reached. p-AgSAE is suitable for ASV of Fe(III) (48). A rotating disk electrode of AgSA was used for on-line ASV detection of manganese in a contaminated river water (49). AgSA-CE, which behaves partially as a miroelectrode array, was used for direct reduction of Cu(II), Pb(II), and Cd(II) ions (29). AgA-PE containing 10% of Ag was tested for ASV of Cu(II), Pb(II), and Cd(II) (34, 35). The main advantage of this paste electrode is easy surface renewal, eliminating most problems connected with passivation. Higher probability of intermetallic compounds formation at AgA-PE complicates its application for Zn determination. m-CuSAE is suitable for ASV determination of Cd and Pb (45). However, m-AgSAE is to be preferred for these purposes because of fewer problems connected with the formation of intermetallic compounds. m-AgSAE can be used for the determination of Fe(III) in the presence of triethanolamine in an alkaline medium (47) and CSV at m-CuSAE (45) was applied for the determination of Mn(II) in 0.05 M $Na_2B_4O_7$ at pH 9.2 based on oxidation of Mn(II) to Mn(IV) at +700 mV and accumulation of hydrated MnO_2 which gives a well developed reduction peak at +205 mV during subsequent cathodic scan. m-AgSAE is suitable for AdSV determination of Ni(II) after its complexation with dimehylglyoxime (47). It has been proven that DPASV with m-AgSAE, DPASV with HMDE, and ET-AAS (82) gave the same results for the determination of Cu, Pb, and Cd in four plant reference materials and certified reference materials. Iodates were determined using m-AgSAE (19, 43), p-AgSAE (19, 43), AgSA-CE (29), and AgA-PE (35). m-AgSAE and p-AgSAE were successfully used for the determination of iodates in table salt (43). Because nitrates are not directly reduced at mercury and amalgam electrodes, their catalytic reoxidation in the presence of Ce(III) is used (19, 47). m-AgSAE was thus used for determination of nitrates in drinking water (19). Composition of amalgam electrodes has a strong influence on peak potential of sulphide ions in CSV (61) (HMDE: −732 mV, m-IrSAE: −748 mV, m-AuSAE: −761 mV, m-AgSAE: −776 mV, m-BiAgSAE: −855 mV, m-CuSAE: −1068 mV, m-CdAgSAE: −1506 mV). With other sulphur-containing compounds the situation is similar. Amalgam electrodes were further successfully used for investigation of DNA, various DNA bases, and oligonucleotides (ODNs). The adsorption of DNA on the surface of a working electrode is sufficiently strong to allow preparation of a DNA-modified electrode resisting washing. The electrode with attached DNA can be transferred into a cell with an appropriate supporting electrolyte where the voltammetric measurement takes place. Application of this adsorptive transfer stripping voltammetry (AdTSV) allows analysis of small volumes of the analyte solutions (several microliters), thus making an easy detection of picogram amounts of the modified DNA or ODN possible (56–58, 83, 84). The m-AgSAE can be used for the detection of enzymatic or chemical DNA cleavage in solution or at the electrode surface. AgSAE modified with supercoiled DNA can be utilized as a sensor for DNA nicking substances (58). p-AgSAE and MF-AgSAE were used for the measurements of intrinsic redox and tensammetric voltammetric signals of single- and double-stranded, linear or supercoiled DNAs, synthetic polynucleotides and free adenine base. Similarly as with the HMDE and m-AgSAE, measurements on MF-AgSAE and p-AgSAE were successfully applied for the detection of DNA strand breaks induced by ionizing radiation (57). The catalytic current due to evolution of hydrogen in voltammetry of DNA modified by a complex of osmium tetroxide with 2,2′-bipyridine (DNA-Os,bipy) was studied (56) using m-AgSAE, m-CuSAE, m-AuSAE, and m-BiAgSAE. Besides the HMDE, the catalytic current was observed only on m-AgSAE and m-CuSAE. AuSAE and BiSAE did not give the catalytic current. The m-AgSAE was successfully applied as a detection electrode in double-surface DNA hybridization experiments offering highly specific discrimination between complementary (target) and non-specific DNAs, as well as determination of the length of a repetitive DNA sequence (56). CSDPV of adenine was done with different electrodes (HMDE, m-AgSAE, m-AuSAE, m-IrSAE, m-CuSAE) (17). For all cases (except m-CuSAE) the common electrode reaction was reduction of the Hg-adenine complex at a potential of about +30 mV. p-AgSAE (50), m-AgSAE (17, 47), and m-CuSAE (17, 47) are suitable for CSV of adenine, guanine, and of acid-treated DNA. With these amalgam electrodes using DCV the limits of detection for purine bases, as well as for two types of DNA, are in nanomol level. The m-CuSAE was also used for trace determination of purine bases by CSV which involve accumulation and subsequent stripping of copper(I)-purine complexes (55). Based on these results, the m-CuSAE has been used in a label-free detection technique applicable in double-surface DNA hybridization assays. AgSA-CE is a suitable, reliable, and environmentally friendly substitute for the HMDE in electrochemical analyses of adenine (29). The CSV peak of adenine was obtained also on AgA-PE with 12% of silver (35). The sensitive CSV detection of different ODNs containing the purine units in their chains in the presence of copper was performed on electrodes from the thin layers of Pt, Cu, and Ag solid amalgams (53). The tensammetric responses of different synthetic ODN were investigated by ACV at Pt, Cu, Au, and Ag solid amalgam electrodes (54). From the height and potential of the AC voltammetric peaks it is possible to identify different homopurine ODN lengths and a proportion of purine (adenine and/or adenine + guanine) units to the whole length of different ODNs containing both the purine and pyrimidine units. The kinetics of the phase transitions of adenosine adsorbed at the thin film Cu, Pt, and Ag SAEs was studied by chronoamperometry and by capacitance measurements (51, 52). The effect of adenine and guanine on the second reduction step of oxygen (electroreduction of hydrogen peroxide) on m-AgSAE was studied (85). Furthermore, m-AgSAE and m-CuSAE were successfully applied for monitoring of single-stranded isomeric end-labeled -SH oligodesoxynucleotides (84, 86). The applicability of p-AgSAE covered by graphite film (GF-AgSAE) containing 90% graphite powder was demonstrated by the determination of guanine and adenine based on their electrochemical oxidation at highly positive potentials where mercury and amalgam electrodes dissolve (37). Electrochemical behavior of cysteine at amalgam electrodes was studied in detail (47). Well developed CSV peaks were obtained on m-AgSAE (59), m-CuSAE (45, 59), AgSA-CE(29), and AgA-PE (35). Glutathione and synthetically prepared peptides (phytochelatines) PC2 and PC3 were studied at m-CuSAE (46) in separated extracts of real samples. m-AgSAE was successfully applied for so-called Brdicka reaction with blood plasma samples (87). Specific catalytic signals were observed of the peptide Lys-vasopressin (containing two cysteine residues forming an intramolecular disulfide bridge) as well as of thiol-terminated deoxyribonucleotides with the m-AgSAE (84). Voltammetric signals of cysteine, glutathione, and (γ-Glu-Cys)$_3$-Gly (PC3) were measured in Co(II)-containing solution using AgSAE with different surface modifications (60). The voltammetric responses of all substances with the m-AgSAE and MF-AgSAE are qualitatively similar to those observed with the HMDE. On the other hand, responses of these species measured with the p-AgSAE differed from those measured by electrodes with a mercury surface. Among the electrodes tested with the –SH compounds, the p-AgSAE offered the best sensitivity. The concentration dependence of cystine on m-CuSAE was linear in the concentration range from $5{\cdot}10^{-9}$ to $5{\cdot}10^{-7}$ mol/L (CSV, $t_{\mathrm{ac}} = 300$ s) (18). The optimum accumulation potential, as well as the peak potential, compared with those of the HMDE were shifted by about 200 mV to more negative values. This effect could be utilized for distinguishing between two different species, which on HMDE yield two overlapping voltammetric peaks. Thio compounds form self-assembled monolayers (88) at amalgam electrodes, their stability being dependent on amalgam composition and potential of the amalgam electrode.

Amalgam electrodes (except CuSAE in alkaline solutions) are not very useful for oxidation processes, due to the dissolution of electrode material at relatively low positive potential region (Table 1). In acetate buffer of pH 4.8, ascorbic acid differential pulse voltammetric (DPV) peak is at about +67 mV on m-AgSAE, +76 mV on p-AgSAE, +47 mV on m-AuSAE, +85 mV on m-IrSAE, +55 mV on AgA-PE, and +5 mV on HMDE (35). m-CuSAE can be used for catalytic oxidation of ethanol (61). The applications of AgSAE for determination of various genotoxic nitrated polycyclic aromatic hydrocarbons (NPAH) are summarized in Table 2 which proves the practical applicability of these electrodes. Both the selectivity and the sensitivity of many determinations can be increased by the combination of voltammetry on AEs with preliminary separation and pre-concentration using liquid-liquid extraction (LLE) or solid phase extraction (SPE) which enables determination of nanomolar concentrations of tested substances (67, 89, 90).

The use of p-AgSAE for high performance liquid chromatography with electrochemical detection (HPLC-ED) (68) can greatly improve the selectivity. The thin-layer and wall-jet detectors based on this electrode were constructed and applied for separation and detection of a mixture of 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, and 2-methoxy-5-nitrophenol. Moreover, m-AgSAE in "wall jet" arrangement was used in flow injection analysis with electrochemical detection (FIA-ED) (19, 69, 70, 89, 91). The method was used for the determination of 4-nitrophenol (69) and 5-nitroquinoline (70, 91).

m-AgSAE was used for DPV of a number of pesticides [Pendimethalin (64), 2-Methyl-4,6-dinitrophenol (72), Oxyfluorfen (73), Bifenox (74)]. p-CuSAE was used for square wave voltammetry (SWV) of herbicides Atrazine (75, 76) and Ametryne (76, 77). m-AgSAE was further used for determination of anti-cancer pharmaceuticals Doxorubicin (78), Carmustin (79), Flutamid (80), and Lomustine (81).

CONCLUSIONS

As it has been shown, non-toxic solid amalgam electrodes, especially those covered with mercury meniscus, have found broad analytical applications in both batch and flowing system determinations. They can, in many cases, successfully substitute mercury electrodes, especially in field applications, in measurements in flowing systems, and in AdTSV techniques. Mercury film amalgam electrodes can increase the sensitivity of ASV determination and improve the resolving power because of narrower peaks. They can be useful for investigation of electrochemical properties of various biologically important systems. p-MeSAE can be used when the work with liquid mercury is not desirable or even forbidden. p-AgSAE is useful for ASV of metals with low solubility in mercury (Fe, Mn). Composite amalgam electrodes, which under certain circumstances behave as an array of micro electrodes, can be very useful as well as amalgam paste electrodes with extremely easy renewability of their surface. Liquid mercury in calomel and mercurous sulphate reference electrodes can be substituted by a non-toxic amalgam as well. A combined voltammetric-potentiometric sensor is another interesting example of usefulness of the amalgam electrode concept compatible with so-called green analytical chemistry. Based on the shown examples, it can be stated that amalgam electrodes, in many cases, are not only able to substitute for 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 non-traditional electrode material. At present, very promising results were obtained with solid amalgam microelectrodes based on single silver amalgam crystals (92).

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ABBREVIATIONS

ACV	Alternating current voltammetry
AdSV	Adsorptive stripping voltammetry
AdTSV	Adsorptive transfer stripping voltammetry
AgSA	Silver solid amalgam
AgSAE	Silver solid amalgam electrode
ASV	Anodic stripping voltammetry
AuSAE	Gold solid amalgam electrode
CPE	Carbon paste electrodes
CSV	Cathodic stripping voltammetry
CuSAE	Copper solid amalgam electrode
CVPS	Combined voltammetric-potentiometric sensor
DCV	Direct current voltammetry
DME	Dropping mercury electrode
DPV	Differential pulse voltammetry
ET-AAS	Atomic absorption spectrometry with electrothermal atomization
FIA-ED	Flow injection analysis with electrochemical detection
HMDE	Hanging mercury drop electrode
HPLC-ED	HPLC with electrochemical detection
IrSAE	Iridium solid amalgam electrode
MeA-PE	Paste electrode without pasting liquid based on a paste amalgam
MeSA-CE	Composite electrode based on fine amalgam powder dispersed in a solid polymer
MeSAE	Metal solid amalgam electrode
MeSA-PE	Paste electrode based on a fine amalgam powder dispersed in a suitable pasting liquid
MF-MeSAE	Polished MeSAE covered by mercury film
m-MeSAE	Polished MeSAE covered by mercury meniscus
ODN	Oligonucleotide
PC	Phytochelatin
p-MeSAE	Polished solid amalgam electrode (without liquid mercury)
SCE	Saturated calomel electrode
WE	Working electrode

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