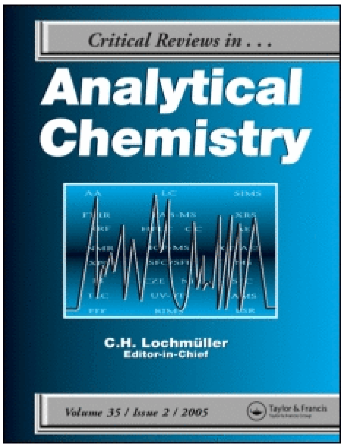

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Nontoxic Electrodes of Solid Amalgams

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ABSTRACT: This is a review of electrodes based on nontoxic solid amalgams (MeSAE) (prepared by amalgamation of soft metal powders) in connection with some other kinds of voltammetric electrodes is given. Information is summarized on various types of MeSAEs (esp. AgSAE, CuSAE, AuSAE), pretreatment of their surfaces, their hydrogen overvoltage in aqueous solutions, conditions for their testing, electroanalytical parameters and use, in compared with the hanging mercury drop electrode (HMDE). Although the solid amalgam electrodes do not reach the quality of the HMDE, in many cases they represent its possible alternative. The broad range of voltammetric applications of the MeSAEs, especially of the AgSAEs, their good mechanical stability, simple handling, and new aspects of their use in electrochemical techniques are documented by numerous examples.

KEY WORDS: voltammetry, silver, copper, gold, solid amalgam electrode, sensor.

I. INTRODUCTION

As is well known, polarizable electrodes used in polarography and voltammetry produce a well-utilizable analytical signal. The most reproducible results have been obtained by the J. Heyrovský's dropping mercury electrode (DME).[1] However, a relatively high detection limit (of an order of 10^{-5} mol·L^{-1}) of classic polarographic measurements prevented them to meet the ever increasing demands on sensitivity of modern electroanalytical procedures. This drawback was overcome by the introduction of the hanging mercury drop electrode (HMDE) allowing, in combination with the pulse polarographic techniques, to put the analytical detection limit down to 10^{-11} or even to 10^{-12} mol·L^{-1}. The use of mercury electrodes in aqueous solution yields the generally known potential range from about +0.4 V to –2.0 V (vs. SCE). Suitable electrodes for the more positive potential region are based on solid materials such as glassy carbon, noble metals, etc.; the drawback of such electrodes are worse reproducibility of their surfaces, a necessity to apply various mechanical as well as electrochemical ways of pretreatment, lower hydrogen overvoltage, etc. Electrodes where the solid surface is covered by mercury, such as Ag/Hg,[2–12] Pt/Hg,[4,12–15] Au/Hg,[16–19] Ir/Hg,[20–22] Cu/Hg,[23–24] represent something like an "intermediate" between the solid surface and pure mercury. These electrodes proved satisfactory especially thanks to their relatively high hydrogen overvoltage and simple regeneration, including an electrochemical pretreatment of their surface. On the other hand, their disadvantages were usually due to the gradual amalgamation of the metallic support, formation of intermetallic products, some technical problems connected, for example, with fixing the solid metal in an insulator body.

A few years ago the nontoxic electrodes of solid amalgams (esp. the silver solid amalgam electrode AgSAE) were designed and introduced,[25–27] based on amalgamation of soft metal powders. Later[28,29] the dental amalgams were suggested as well (one of which was of the same composition like the polished AgSAE). However, they exhibit lower sensitivity and narrower range of working potentials. The present article deals with solid amalgam electrodes, that is, with those comprising solid amalgams of metals or metallic alloys exhibiting high affinity to liquid mercury. The nontoxic metal solid amalgams represent a well-defined, sensitive, and reproducible electrodes. The surface mercury-modified MeSAEs bears on its surface a very small amount of mer-

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cury that cannot be practically removed by accident owing to its strong adhesion to the solid amalgam support.

Some of the MeSAEs exhibit (as mentioned below) only a little narrower range of working potentials when compared with the HMDE, which is the base of similar applicability.

II. GENERAL CHARACTERIZATION

The MeSAE represent a useful group of electrochemical electrodes as outlined by the scheme in Figure 1. One example of preparation of MeSAEs[33] can be described as follows: a fine metal powder (Ag, Cu, Au, etc.) usually together with a platinum wire contact introduced through the upper end of the tube is pressed into the lower part of a narrow tubing usually of about 0.1 to 0.8 mm inner diameter to the height of 5 to 6 mm. The lower tip of the tube is then dipped into about 0.5 to 1 ml of liquid mercury and left out there until the amalgamation process throughout the whole column of the metallic powder is completed. The upper end of the platinum wire is connected to an electric cable and the electrode is allowed to a rest for 10 to 12 h for the solidification process of the amalgam phase to be completed. Finally, the resulting electrode surface could be polished (*p*-MeSAE) with a fine emery paper and with 0.3 μm alumina powder using a wet polishing cloth.

The main advantages of such types of electrodes are

- broad range of working potentials;
- simple electrochemical regeneration of the electrode surface;
- rapid (only 5 to 10 min) pretreatment procedure, even after several months out of use;
- long-lasting activity without significant changes during several years of use;
- complete nontoxicity of the solid amalgam phase;
- applicability even in mobile laboratories and in countries prohibiting the use of liquid mercury;
- use of diverse metals (Ag, Au, Cu, …) without need of any adhesives, sealing operations, and without penetration of mercury and solution into the electrode interior;
- simple preparation of electrodes of different size and shape;
- simple design without any moving mechanical parts.

The sketches of the electrode designs were published in Refs. 26,33. The range of working potentials of the *p*-AgSAE (which is one of the representatives of nontoxic *p*-MeSAEs free of liquid mercury) for a few electrolytes is summarized in Table 1. The *p*-AgSAE thus is suitable for the study of processes at very negative potentials, the determination of ions such as Zn^{2+}, Mn^{2+}, IO_3^-,[30] etc., of catalytic hydrogen evolution, of potential-controlled electrodesorption of organic surfactants, etc. Further surface or other modifications of *p*-MeSAEs, well known in the field of other solid or mercury electrodes, are of course applicable as well. Moreover, the composition of MeSAEs can be designed for special selective applications (e.g., CuSAE or AgSAE for determination of adenine[31] or cysteine[32]).

From the viewpoint of electroanalytical parameters, the best results were obtained by the mercury meniscus (*m*-MeSAE) or mercury film (MF-MeSAE)-modified electrodes. In contradistinction to common solid electrodes, their ideally smooth liquid surface eliminates the necessity of their mechanical surface regeneration. As is well known, the most important factor concerning all solid electrodes is their reaching a reasonably reproducible signal. In the case of the *m*-MeSAEs and the PC-controlled systems, the situation was simplified by the inclusion of the selected optimum experimental parameters into the software, thereby ensuring the automatic application of the proper electrochemical regeneration of the electrode surface at the beginning of each measuring cycle; in that way all measuring parameters could be selected, changed, fixed, and stored in advance to enable performing automated measurements. The found experimental parameters, specific for the given type of MeSAE, purpose and experimental conditions, proved satisfactory especially from the point of view of reproducibility, selectivity, and the detection limit of measurements. It allowed to reach RSD better than 2 to 3%.[30–32]

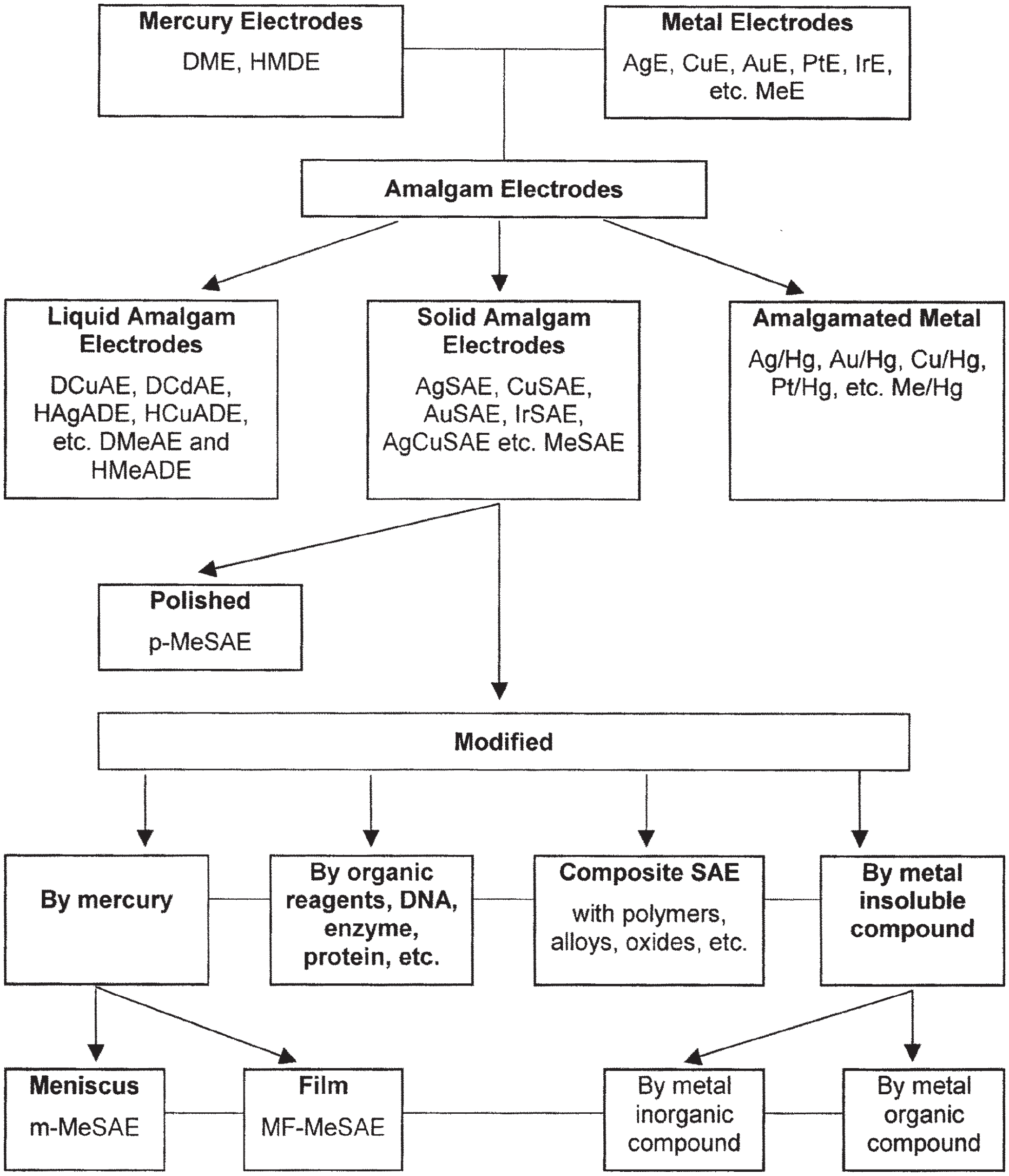

FIGURE 1. Interconnection between different types of electrodes.

TABLE 1
Range of Working Potentials of Different Wlectrodes

Experimental results obtained by DC voltammetry; reference electrode SCE; scan rate 0.02 V/s; the potential limits correspond to 1 μA current level; air oxygen was removed by nitrogen.

Electrode (disc's diameter)	Potential range, V											
	0.1 M $HClO_4$		0.1 M HCl		0.2 M acetate buf. pH 4.8		0.05 M Na_2EDTA, 0.2 M acetate buf. pH 4.8		0.05 M $Na_2B_4O_7$ pH 9.2		0.1 M NaOH	
HMDE	-1.19	+0.44	-1.27	+0.11	-1.70	+0.31	-1.55	+0.09	-1.98	+0.15	-1.97	-0.07
AgE (0.40 mm)	-0.64	+0.39	-0.81	+0.08	-0.99	+0.36	-0.99	+0.35	-1.20	+0.38	-1.41	+0.19
p-AgSAE (0.70 mm)	-1.12	+0.45	-1.12	+0.11	-1.51	+0.31	-1.45	+0.11	-1.88	+0.16	-1.96	-0.06
m-AgSAE (0.70 mm)	-1.08	+0.43	-1.09	+0.11	-1.44	+0.21	-1.33	+0.09	-1.92	+0.16	-1.95	-0.07
(0.54 mm)	-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-CuSAE (0.48 mm)	-1.17	+0.06	-1.18	-0.07	-1.44	-0.03	-1.43	-0.13	-1.75	+0.95	-1.86	-0.24
AuE (0.40 mm)	-0.54	+1.69	-0.55	+0.93	-0.91	+1.49	-0.84	+0.75	-1.39	+1.15	-1.62	+0.81
m-AuSAE (0.40 mm)	-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 mm)	-1.01	+0.43	-1.01	+0.12	-1.32	+0.29	-1.34	+0.10	-1.63	+0.15	-1.72	-0.06

MeSAEs thus can be included in amperometric detectors of flow-thorough systems, of HPLC, or they can be combined with autosampling devices as well. As described earlier,[5] of all mercury electrodes the analytically most sensitive proved to be the film ones, and it was found with the mercury fil*m*-modified electrodes that the thinner the film, the higher was the sensitivity of measurements. However, as a rule, covering the metal plates by too thin films (less than about 1 to 2 μm) caused[5,6,10] a nonreproducible signal, at most after only a few hours work. The preparation and use of metal plate electrodes modified by mercury film represents in fact a nonequilibrium electrode arrangement exhibiting a gradual disappearance of the liquid film with time, due to slow amalgamation of the metal plate. For this reason some authors[10] (in agreement with their previous paper[7]) suggested to first perform a chemical surface amalgamation of the silver plate and then to deposit on it the mercury film in an electrochemical way. In this case the solid amalgam layer between the silver plate and liquid mercury prevents the direct interaction between silver and mercury and thus prolongs the working period of the prepared mercury film of, for example, 1 μm thickness, up to about 6 h. A substitution of the metal plate by the solid amalgam brought favorable changes in electrode properties. Our experiments confirmed that a mercury fil*m*-modified AgSAE of 1 μm thickness provided well-reproducible results for a period of 1 day, and of 3 μm thickness for several days, respectively, without any mechanical modifications.

For a common analytical use the meniscus modified MeSAE seemed to be the most appropriate version of metal solid amalgam electrodes. The mercury meniscus prepared by a 10 to 15 s contact with mercury has not exhibited visual changes for several months; however, certainly, its simple renewal at the beginning of every experimental week proved to be favorable and generally could be recommended. After several minutes' electrochemical activation (after a rest period longer than 1 h) the *m*-MeSAE, in fact, represents a saturated liquid amalgam of the given metal. This is why, for example, *m*-CuSAE behaves partly as a solid copper electrode and partly as a hanging copper amalgam drop electrode.[31]

III. SILVER SOLID AMALGAM ELECTRODE

Silver is one of the most frequently utilized material for mercury film or meniscus modified solid electrodes. In contradistinction to Pt, Au, or Cu it does not almost produce silver intermetallic compounds with other metals.[10,12] Mercury film prepared at Ag looks more homogenous than that at Pt or Ir, although its stability is worse then that at the latter metals.[10] Table 1 gives examples of the range of working potentials of AgSAE, which is close to that of HMDE; in fact, *p*-AgSAE is the only nonliquid mercury electrode with such broad range of working potentials. However, the sensitivity and repeatability of measurements with *p*-AgSAE are considerably worse than that of *m*-AgSAE.[30] *p*-AgSAE as a solid state electrode needs to be repolished from time to time. AgSAE can be an effective and simpler alternative to HMDE for many analytical applications; it seems to be suitable for incorporation into flow-through detectors, for analysis in the field, and for analysis in glass corroding media (HF) as well. In the absence of specific interactions between the analyte and silver the DPV-peak potentials on *m*-AgSAE and HMDE are nearly the same.[33]

A. Determination of Cations

Up to now, AgSAE (esp. *m*-AgSAE and MF-AgSAE) has proved best for the determination of electroactive metals such as As(III), Cd(II), Cr(III), Cu(II), Fe(III), In(III), Mn(II), Ni(II), Pb(II), Sn(II), Tl(I), Zn(II), etc. The voltammetric analysis on mercury-modified AgSAE proceeds under analogous conditions as that on HMDE; it only takes by about 30 s more owing to the regeneration period. Thanks to the practically same peak potentials and background currents on both types of electrodes the parameters of voltammetric analyses found for HMDE can be taken for *m*-AgSAE as well.

The use of *m*-AgSAE for determination of Cu(II), Pb(II), Cd(II), and Zn(II) is demonstrated in Figure 2. At the accumulation time t_{ac} = 300 s *m*-AgSAE provided the detection limit of 1-ppb level. Testing the *m*-AgSAE has shown its conve-

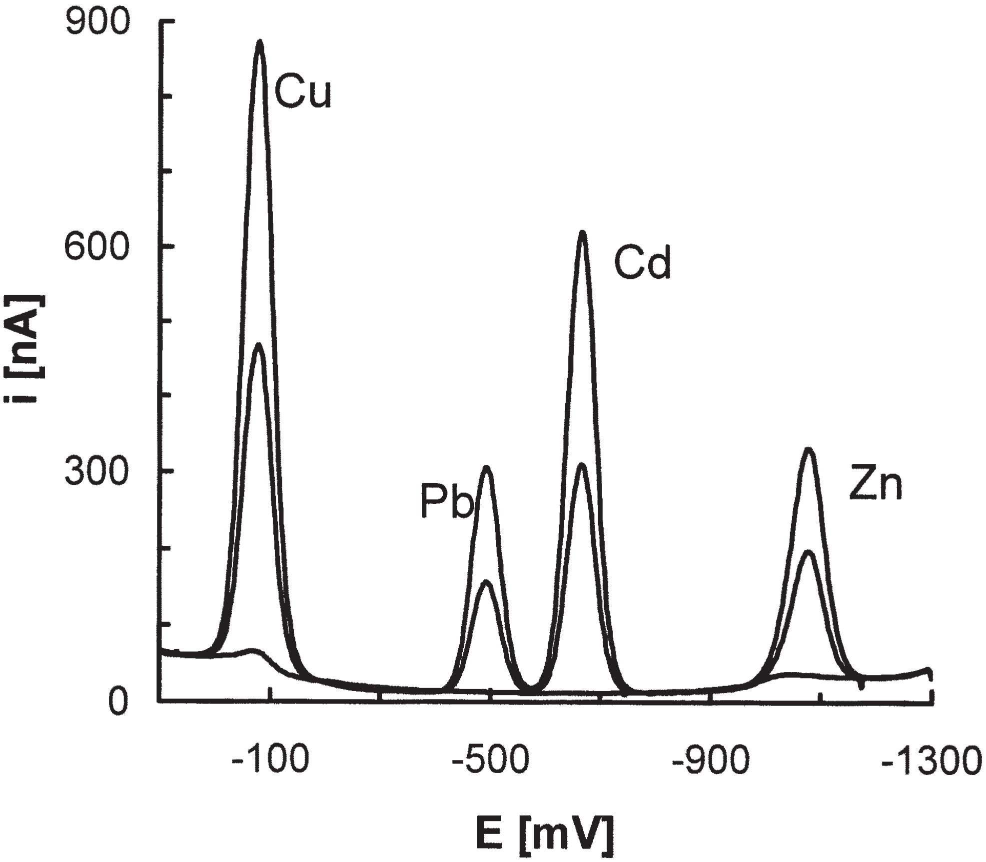

FIGURE 2. Anodic stripping DPV curves of 0, 0.05 and 0.1 ppm Cu(II), Pb(II), Cd(II) and Zn(II) in 0.1 *M* acetate buffer (pH 4.8); m-AgSAE; E_{ac} = -1.3 V; t_{ac} = 60 s; E_{in} = -1.3 V; E_{fin} = 0.1 V; v = 0.02 V·s^{-1}.

nience for anodic stripping voltammetry of amalgamable metals at long accumulation times. For instance, the DPV-peak current i_p of 10 ppb Pb(II) in 0.2 *M* acetate buffer of pH 4.8 was proportional to t_{ac} in the range of 0.5 to 60 min (R^2 = 0.9996). Under the same conditions, the HMDE provided linear i*p*-t_{ac} dependence in the range of 0.5 to 10 min. These differences are caused by a slow diffusion flux of amalgamed lead into the capillary electrode producing the HMDE. Further increase in sensitivity of analysis on *m*-AgSAE can be reached by longer accumulation time t_{ac}.

B. Determination of Anions

Determination of anions (or elements involved in anions) by using AgSAE can be based on cathodic (chemisorption) stripping (like Cl^-, Br^-, I^-, CNS^-), electroreduction (Nb(V), IO_3^-),[30] catalytic effects (NO_3^-),[26,33] adsorptive stripping (Cr(VI)), etc. For instance, use of silver solid amalgam electrodes for determination of iodates, which have been used extensively in iodination of commercial table salts as an effective thyroid blocker, can serve a good example of one contemporary voltammetric applicability of AgSAE. The electroreduction of iodates occurs at negative electrode potentials and therefore up until now voltammetry of IO_3^- had been performed at mercury electrodes only. *p*-AgSAE or even better *m*-AgSAE proved very good for this purpose.[30] The corresponding linear calibration dependence in the concentration range pertaining to IO_3^- in table salt is shown in Figure 3. The published statistical data[30] outline a rapid, simple, and broad practical application of the mentioned procedure that takes 8 to 9 min as a whole, including the 5 min for removal of oxygen. Although the *m*-AgSAE exhibited better sensitivity and reproducibility, the use of *p*-AgSAE provided completely satisfactory results as well, and therefore at con-

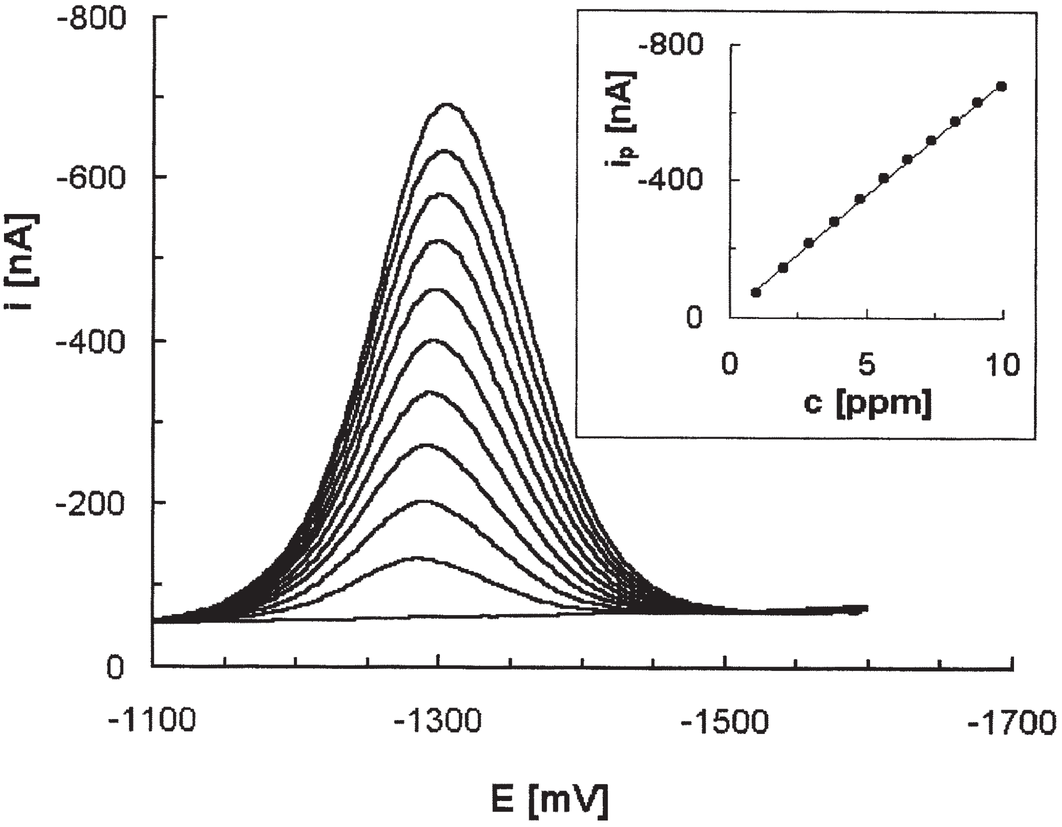

FIGURE 3. The set of DPV curves and the corresponding calibration dependence in 0.1 M NaOH in presence of 0 to 9.91 ppm IO_3^- obtained using m-AgSAE; E_{in} = -0.9 V; E_{fin} = 1.6 V; v = 0.02 V·s^{-1}; the peak height i_p = -68.433 c – 11.372, R^2 = 0.9995.

ditions under which the presence of liquid mercury (even in microvolumes) is undesirable the application of *p*-AgSAE is preferred.

C. Determination of Organic Species

Voltammetric determination of bio- or ecoactive species and other organic compounds represents an important sphere of electroanalytical applications. For example, the detection limit of adenine and other nucleotides,[36–38] cysteine,[32] or cystine was of the order 10^{-9} mol·L^{-1}. *m*-AgSAE has been used successfully for analysis of nitrobenzenes,[26,33] nitrated polycyclic aromatic hydrocarbons NPAH (1-nitronaphtalene, 2-nitronaphtalene, 2-nitrobiphenyl, 3-nitrobiphenyl and 4-nitrobiphenyl),[34] cysteine,[32] two single-stranded isomeric deoxyoligonucleotides,[35] chloridazon (herbicide), cystine, adenine, guanine, DNA, SH species of blood plasma, etc. One example is given in Figure 4 showing the linear concentration dependences of the heights of two peaks of *m*-dinitrobenzene obtained on AgSAE.

AgSAE (or other types of MeSAE in general) could also be utilized in combination with a separation (HPLC) step in amperometric detectors or for measurements in small amounts of samples. For instance, such small three-electrode cell with AgSAE containing 5 to 20 μl of analyzed DNA aqueous solutions proved satisfactory and, moreover, a further increase in sensitivity of the analysis could be reached by evaporation via preconcentration.

IV. COPPER SOLID AMALGAM ELECTRODE

As mentioned previously, the working electrodes based on solid amalgams showed many advantages, because their behavior is similar to that of both mercury and solid electrodes. A further good ex-

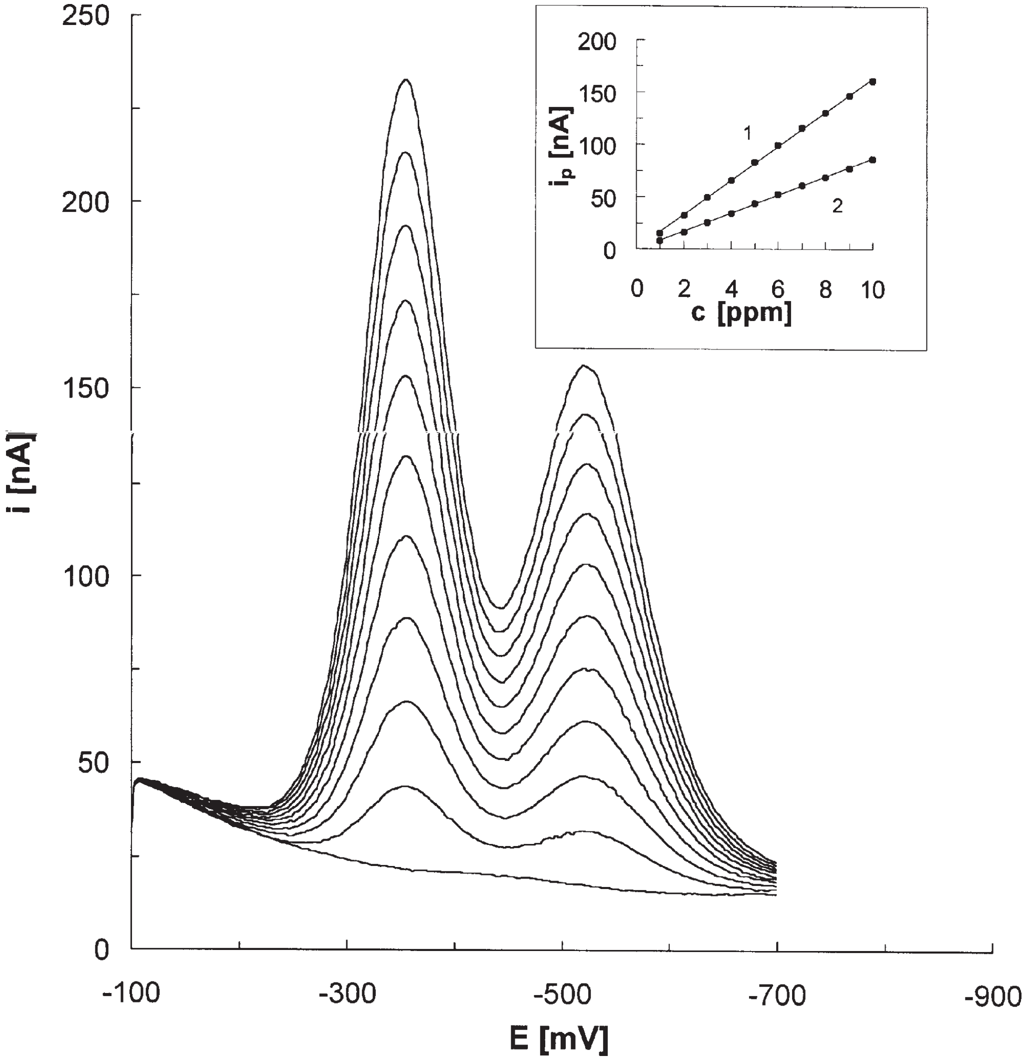

FIGURE 4. The set of DPV curves in 0.1 *M* acetate buffer (pH 4.8) in presence of 0 to 10 ppm m-dinitrobenzene; *m*-AgSAE; E_{in} = –0.1 V; E_{fin} = –0.7 V; v = 0.02 V·s^{-1}; the peak 1 height i_p = 16.293 c + 0.7667, R^2 = 0.9995; the peak 2 height i_p = 8.7394 c – 0.3667, R^2 = 0.9996.

ample is the CuSAE prepared in the *m*-CuSAE version. As seen from Table 1 both *m*-CuSAE and HMDE exhibit nearly the same hydrogen overvoltage. The positive potential limit is due to electrooxidation of copper. An extraordinarily broad polarization potential range was observed in sodium tetraborate buffer where at positive potentials the copper surface is covered by the deposited oxides preventing its further electrooxidation. This remarkable effect was used and tested in the presence and in the absence of Mn(II). The determination of manganese is based on the oxidation of Mn(II) at 0.7 V vs. SCE into an insoluble hydrated dioxide accumulated at the electrode.[31] Figure 5 illustrates a set of concentration dependent voltammograms. Peaks at 0.25 V correspond to the reduction of Mn(IV) to Mn(II), and linear calibration dependences of very good reproducibility suggest that the described conditions could be utilized for the determination of Mn^{2+} in aqueous solutions. In the range of –0.2 V to –0.5 V the voltammograms provided two peaks that could be described by the reduction scheme $Cu^{2+} \rightarrow Cu^{+} \rightarrow Cu$. At -1.5V the peak connected with the electroreduction of Mn^{2+} to Mn occurred.

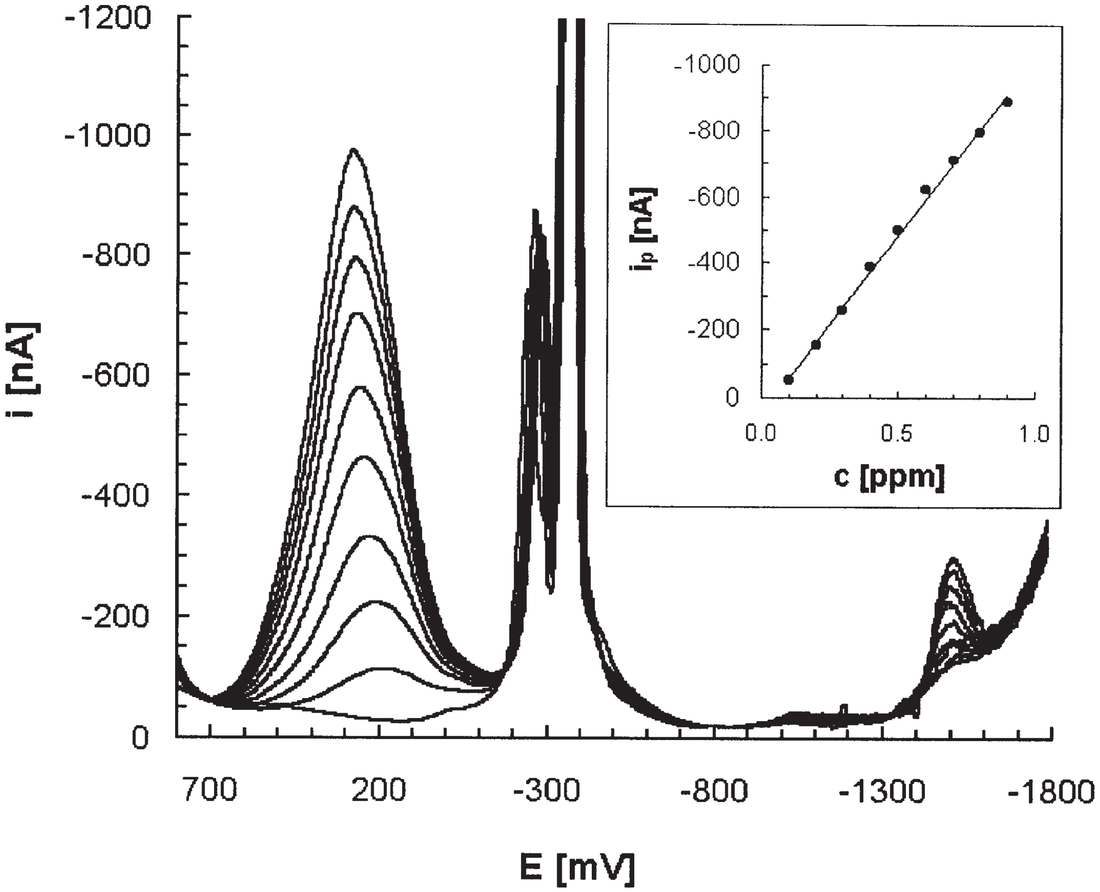

FIGURE 5. Concentration-dependent DPV curves using *m*-CuSAE record in 0.05 *M* $Na_2B_4O_7$ in the presence of 0 to 0.9 ppm Mn(II); conc. step 0.1 ppm; E_{ac} = 0.7 V; t_{ac} = 60 s; E_{in} = 0.8 V; E_{fin} = –1.8 V; v = 0.02 V·s^{-1}; the peak height i_p = –1069.8c + 49.586, R^2 = 0.9968.

m-CuSAE is, to our knowledge, the only electrode allowing to realize in one measuring cycle the scheme Mn(II) → Mn(IV) → accumulation Mn(IV) → Mn(II) → Mn. Up until now, there has been no information available on the electroanalytical use of amalgam or liquid mercury electrodes at the extremely positive potentials of around 0.9 V in the literature.

Although the CuSAE could in principle be used for an anodic stripping voltammetry of the more electronegative metals, than copper, better electroanalytical behavior in this respect was exhibited by AgSAE.

On the other hand, *m*-CuSAE proved special advantages as to the cathodic stripping voltammetry of cysteine, cystine, adenine, and guanine. The catalytic effect of its surface was examined in case of the catalytic reduction of hydrogen peroxide in 0.1 *M* $NaClO_4$.[31]

Preliminary results indicated[31] that *m*-CuSAE could well substitute electrodes based on solid copper, on solid copper covered by mercury films, on liquid copper amalgams, as well as on the need of adding Cu^{2+}-ions into the measured solutions.

V. GOLD SOLID AMALGAM ELECTRODE

The above-mentioned general principles connected with preparation and use of MeSAEs concern *m*-AuSAE as well. A partly wider potential window (see Table 1) observed in some base electrolytes on AuSAE was rather due to its smaller size. Owing to a well-known tendency of gold to form intermetallic products with Cd, Zn, In, and numerous other metals,[39] the analytical sensitivity of AuSAE with respect to these metals is low, if not negligible. Figure 6 brings a comparison of *m*-AuSAE with *m*-AgSAE in anodic stripping determination of Zn(II), Cd(II), Pb(II), and Cu(II).

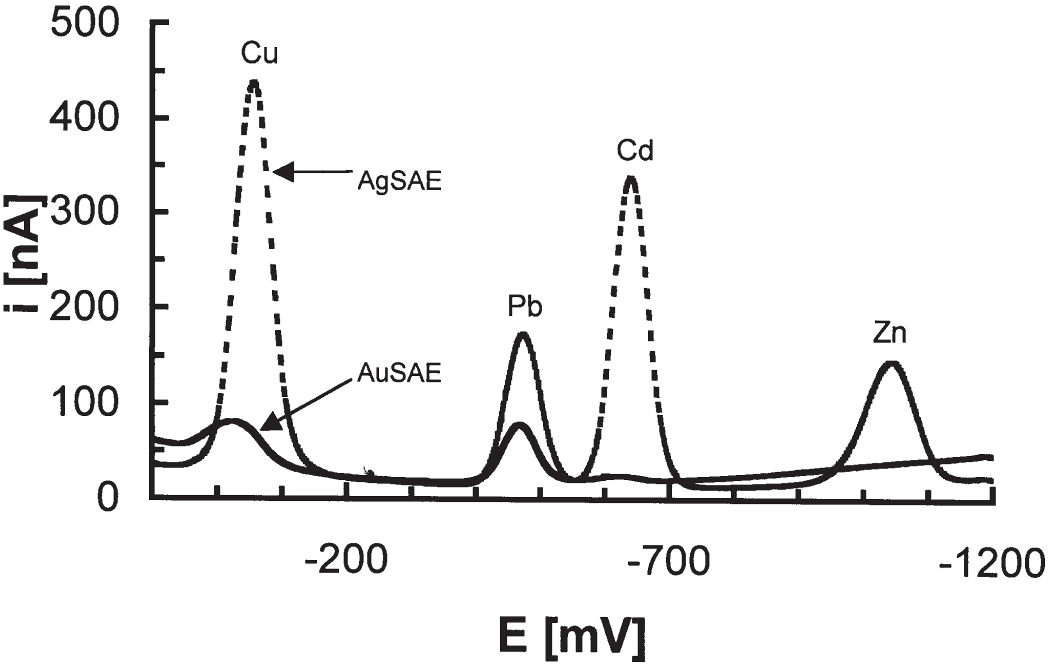

FIGURE 6. Anodic stripping DPV curves of 0.02 ppm Cu(II), Pb(II), Cd(II) and Zn(II) in 0.2 *M* acetate buffer (pH 4.8); *m*-AuSAE and *m*-AgSAE; E_{ac} = -1.3 V; t_{ac} = 180 s; E_{in} = -1.2 V; E_{fin} = 0.1 V; v = 0.02 V·s^{-1}.

m-AuSAE exhibited here lower sensitivity for Zn and Cd which produced only very small voltammetric signals. Thus, these results indicate only a limited applicability of *m*-AuSAE for analysis of series of metals. On the other hand, this electrode could be used for voltammetric determinations of selected analytes under appropriate analytical conditions and with high selectivity; it could be illustrated, for example, by the determination of lead in presence of practically nonactive cadmium, determination of nitrocompounds,[33] of some SH species in blood.

VI. CONCLUSIONS

The above MeSAEs exhibited considerably high hydrogen overvoltage, in some cases comparable with that of the HMDE. These electrodes are utilizable in broad range of application; their actual behavior is dependent on their given composition, on surface or other modification of the amalgam matrix, on the regime of work, etc. A prerequisite for their good functioning is proper mechanical preparation (in the case of *p*-MeSAE), electrochemical activation, and regeneration.

The composition of *p*-AgSAE is more or less close to that of the electrodes based on dental amalgams, which, however, exhibited a considerably narrower range of working potentials and higher background currents (of the level of μA) than the *p*-AgSAE.

Although the solid amalgam electrodes do not reach the quality of the HMDE, in many cases they (especially the AgSAE) represent a possible alternative to the HMDE; among other aspects, they bring good mechanical stability of the electrode, simple handling, and new fields of application in electrochemical techniques. The pen type MeSAEs represent a sturdy, reliable, and simple electrode design, practically nontoxic in both cases of *p*-MeSAE and *m*-MeSAE.

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