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SOLID ELECTRODES PLATED WITH METALLIC FILMS

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This review article surveys basic characteristics and typical electrochemical properties of solid electrodes employed as the supports for the preparation of metallic film electrodes, predominantly of mercury- and gold film electrodes. Individual types of metallic film electrodes are critically compared, including their confrontation with classical voltammetric sensors such as hanging mercury drop electrode or solid gold electrode. Discussed are scope and limitations of metallic film electrodes in anodic stripping voltammetry. Practical applications of these electrodes are demonstrated using some typical examples based on authors' experience with mercury- and gold film plated carbon paste electrodes.

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Introduction

Electrochemistry belongs among those instrumental techniques that can be successfully confronted with continuously growing demands on present day's qualitative and quantitative analysis [1]. A typical example confirming this statement is a combination of electrochemical stripping techniques with metallic film electrodes [2-4]. This set-up offers a flexibility in use, very low detection limits, and mostly even a sufficiently high selectivity of methods based on the use of stripping techniques at film electrodes [2,4]. The main reason due to which metallic film electrodes had been introduced into the analytical practice was the fact that this type of electrode was shown to be a new and promising alternative to commonly used electrodes (e.g. mercury drop electrode, solid gold electrode, platinum, etc.) [1-5].

Metallic film electrodes (MeFEs) represent a very thin layer of a metal deposited onto a suitable inert support (substrate). The thickness of this layer, usually called "film", is quoted to have micrometric dimensions, but some sources have reported on few examples of ultrathin films whose thickness can be measured in tens of nanometers [2,6]. The resultant electrochemical characteristics of MeFEs depend on the material forming the proper film as well as upon the type and quality of the support used [7,8]. Also the preparation and regeneration of metallic films or, eventually, of the support itself may play an unnegligible role in the behaviour of MeFEs [4,7].

A classification of metallic film electrodes can be made as shown in Fig. 1.

Metallic film electrodes surveyed in this contribution consist of a film of noble metal and are used preferably for measurements in the regime of anodic stripping voltammetry (ASV) [2,4]. The deposition potential of noble metals ensures that all the elements (predominantly metals) exhibiting more negative deposition potentials and being accumulated at the film electrode give rise to their stripping signals before a decomposition (electrochemical re-oxidation) of the film itself. With respect to the material used for the preparation of films, MeFEs are fall into two main groups [2,3]:

- mercury film electrodes (MFEs),
- gold film electrodes (AuFEs).

Other metallic materials are rarely used; however, even such cases can be traced up in the literature (e.g. silver film electrode [9]). Both main groups of common film electrodes, i.e. MFEs and AuFEs, comprise a wide scale of various construction types, which is illustrated in the scheme. Mostly, in routine analysis, various plain film electrodes are preferred. This can be explained by the fact that numerous commercially available plain electrodes can be employed as the supports with well-defined properties [4]. MFEs and AuFEs are usually used in a stirred solution where the preconcentration process in ASV is the most effective [2]. One can choose either the rotation of the electrode itself (rotating

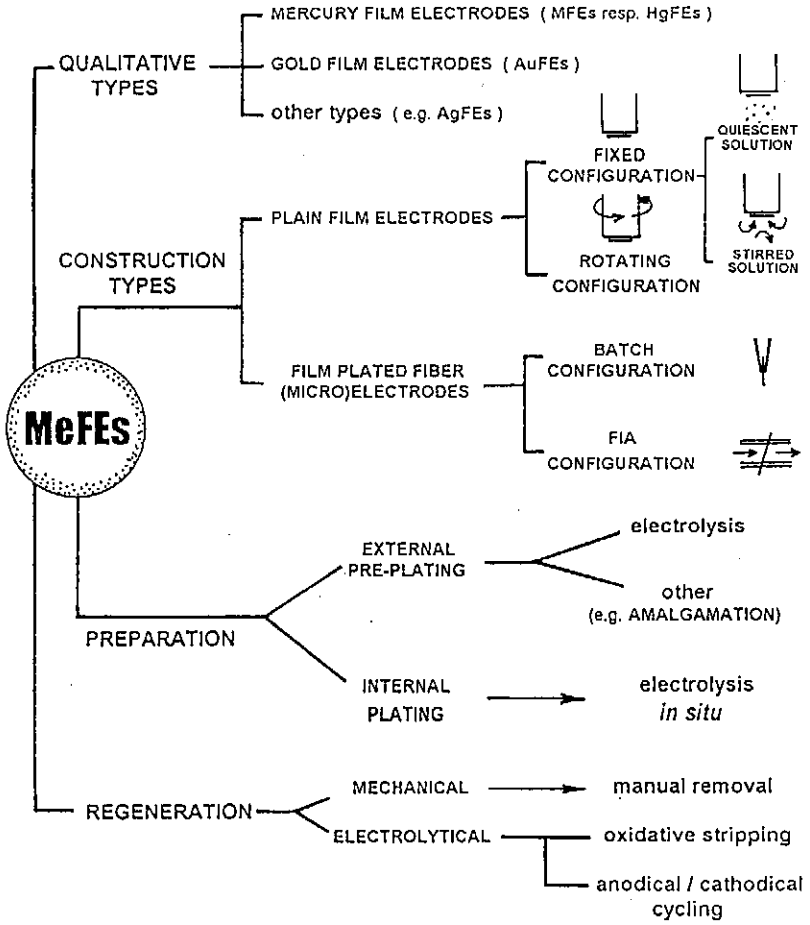

Fig. 1 Classification scheme

configuration) or a stirring with the solution. In this case, it is recommended to use rather the stirring with a magnetic bar than with a propeller (here, undesirable turbulences can be observed or the material of propeller may cause contamination of the solution).

The scheme in Fig. 1 introduces some types of MFEs and AuFEs which have been designed as fiber microelectrodes. These construction variants can find their special use in flow injection analysis (FIA) [10].

In fact, mercury film deposited onto a support is formed by a compact layer of tiny mercury droplets [6,8,11]. This is given by the nature of mercury as such which, under normal conditions, represents the only liquid metal. Figure 2 shows that mercury droplets at plain electrode support exhibit nearly the same diameter. As it has been proved in microscopic studies [8,11], their size and distribution strongly depends upon the potential applied during the deposition step (electrolysis). This is illustrated (Hg-film at a support) in Fig. 3 which documents the relation between deposition potentials and the character of mercury droplets. Undoubtedly, the choice of the deposition potential plays a very important role on the overall properties of each MFE [8,11]. An analogous statement is valid even for the deposition time. The time period chosen is reflected mainly in the thickness of the film; the longer is the electrolysis, the thicker is the resultant film [8].

In order to prepare MFEs, numerous materials have hitherto been proposed as the supports for mercury films. The most frequently used is glassy carbon, which is a specially produced synthetic graphite. Electrodes made of this material, so-called glassy carbon electrodes (GCEs), are commercially available

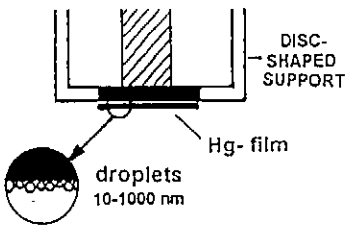

Fig. 2 Mercury film at plain electrode support

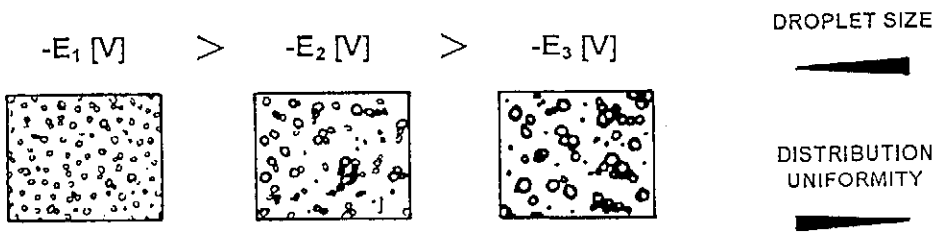

Fig. 3 Microstructure of mercury film in dependence upon deposition potential and time (according to Refs [8,11])

from various manufacturers [7]. Occasionally, other substrates for mercury films have also been employed; for example, carbon fibers [12], pyrolytic or epoxy-impregnated graphite [13], and Pt- or Ag-disks [14,15]. The latter noble metal-based electrodes seem to be unsuitable for being plated with mercury films due to their possible interactions with metallic mercury [7]. In recent years, carbon paste electrodes (CPEs) as another type of carbon electrodes have also been recommended to be another possible alternative to common electrode supports for mercury films [5]. With respect to the fact that film plated CPEs represent a dominant part of the authors' research interest in the field of metallic film electrodes, the problematics of carbon paste-based electrode is discussed in special sections. Some of the above-mentioned carbon supports are depicted in Fig. 4 which reveals their microscopic structure. The pictures in Fig. 4 show that glassy carbon provides a very uniform surface which resembles a crystalline structure. This can explain why GCEs are often adopted as optimal supports for mercury films [7]. It has been confirmed that GCEs exhibit complete inertness towards the film (no interactions with mercury) and offer compact, homogenous and fairly adhesive surface [4,7].

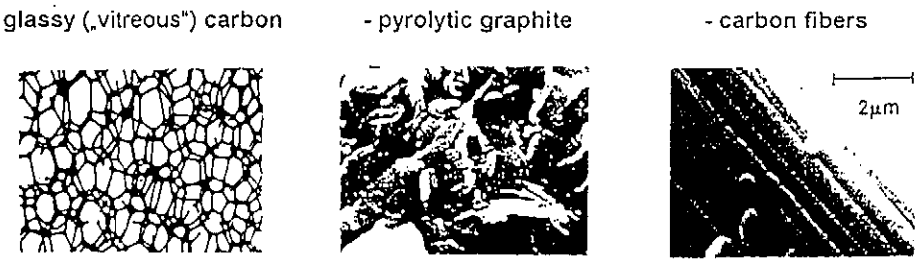

Fig. 4 Microstructure of three carbon supports (according to Refs [1,8])

The proper preparation of MFEs is quite simple - mercury film is deposited onto a support by parameter-controlled electrolysis [7]. Sometimes, it is suitable to pretreat the bare support prior to its plating with a film; for example, using a short-term electrochemical activation at extremely high potentials [16]. Basically, electrolytical deposition of the film is usually carried out in two ways (see scheme in Fig. 1):

External pre-plating means that a mercury film is deposited in a separate plating solution containing Hg^{II} species. For instance, suitable plating solution for the preparation of MFEs can be obtained by dissolving 1g $HgCl_2$ in 1000 ml 1.3 M HCl [17]. When using external pre-plating, it is advisable to utilize a plating program [18] enabling a controlled gradient electrolysis. Such a program can simply be formulated as follows

$$E_{PLAT}(t_{TOTAL}) = E_{ACT}(t_0) + [E_1(t_1) + E_2(t_2) + ... + E_n(t_n)]$$

where E_i means individual partial deposition potentials including the above-mentioned electrochemical activation expressed as E_{ACT} (activation, if included in the program, is not performed in plating solution); t_i represent the corresponding time periods during which individual potentials E_i are to be applied. The overall time course of the E_{PLAT} potential is then a sum of individual potential vs time segments. Plating program is usually assembled empirically and is exploited mainly in such situations when a MFE with strictly defined properties have to be prepared, i.e. in routine analysis [4,18]. Only a well-proposed program makes it possible to utilize, in the optimum way, the dependence of the quality of mercury film on the deposition potential and time (see Fig. 3).

The second approach of how to prepare MFEs is the so-called *in situ* deposition, i.e. the manner when a support is plated with a film during the accumulation, directly in the solution to be analyzed [8]. Such a solution may contain either Hg^{2+} ions or Hg^{II} species spiked in. This approach—experimentally very welcome—has been propagated by Florence [6], who is generally recognized to be an inventor and pioneer of MFEs [2,3]. Florence's extensive investigations on *in situ* plated MFEs can be summarized in the following paragraphs:

(i) Concentration of bivalent mercury added into the solution prior to ASV measurements should be at least 100–1000-fold higher than those of ions to be analyzed. If one considers conventional concentration levels for trace analysis, which is the case of typical applications of MFEs, an optimal concentration of spiked species is about $1 - 5\times10^{-5}$ mol l^{-1} Hg^{2+} or Hg^{II} [6].

(ii) In principle, *in situ* deposition gives rise to mercury films that are markedly thinner than those obtained by external electrolysis. Florence and his continuators admit that mercury films formed *in situ* may be composed solely from several molecular layers of elemental mercury [3,6]. Such a unique layer arrangement can explain some specific properties of MFEs plated *in situ,* which should be taken into account when observing and interpreting incidental differences between the behaviour of MFEs prepared by the two deposition procedures [6,7].

In the case of MeFEs, the term "regeneration" (otherwise frequently used in electrochemical nomenclature) means rather the total renewal of the film than its regeneration for further use. The proper character of the preparation of MFEs offers a simple way of their renewal - the replacement of the used film by a new one. Mostly, the renewal of a MFE is done after a certain time of its use when it is expected—on basis of experience—that further measurements with "an old" MFE may result in deteriorating its properties. Procedures in which the used film is renewed after each ASV measuring cycle have also been described [16]. The renewal of the film can be performed using the so-called oxidative stripping, which is an approach where the used film is electrolytically oxidized (dissolved, i.e., "stripped off" from the support surface) during the proper

voltammetric scan. Under ordinary conditions, such an oxidation of the film takes place at potentials of about 0.0 V vs SCE and can be completed at approx. +0.2 V vs SCE (normally, however, the stripping of the film is finished at still higher potentials, e.g. +0.4 – +0.6 V, in order to ensure the total re-oxidation of mercury [16]). Another possibility on how to renew mercury film is its mechanical removal from the support by wipping the used film off, e.g. with a paper tissue or using a wet filter paper [8]. Naturally, this approach is not very practical and represents a discontinuous operation which is undesirable for fully-automated procedures in routine analysis. In addition, there also exists a danger that after the mechanical removal, the support surface may be damaged (e.g. easy scratching of the polished GCE [16]).

Finally, it is useful to comment on typical electrochemical characteristics of MFEs with emphasis upon their comparison with those of classical hanging mercury drop electrode (HMDE). Apparently, the most significant contrast in behaviour of both MFE and HMDE is due to their geometry; there is completely different ratio between the volume of mercury and its active surface for both alternative mercury electrodes. At the MFE, highly concentrated amalgams are formed, thus providing favourable conditions for the rise of various intermetallic compounds [6]. Otherwise expressed, MFEs suffer much more from the presence of intermetallites than the HMDE, and in some cases—for certain combinations of metal ions in the sample—film electrodes are almost inapplicable to simultaneous analyses. In this context, a typical example is a mixture of Zn^{2+} + Cu^{2+} at comparable concentration level. Owing to the formation of the Cu_aZn_b intermetallites, the parallel determination of these metals at a MFE is practically unperformable whereas their analysis using the HMDE is not very problematic [19]. However, it is quite interesting that a method based on a MFE has been proposed even for such a type of sample containing both the above cations [20]; undesirable interferences from intermetallites were suppressed by means of exchanging the supporting electrolyte between the accumulation and the stripping step. Such a medium exchange approach has been enabled *via* a special electrode construction in FIA mode.

Another disadvantage of MFEs is their relatively low hydrogen overpotential in comparison with that at the HMDE. Regarding MFEs, the effect on the overpotential lowering is usually attributed to the influence of the support used [7]. Based on previous observations, it can be stated that the lower is the overpotential of the bare support the smaller is the overpotential of a film deposited onto such a support [8]. For comparison, commonly used carbon-based supports (for which a low overpotential is a characteristic parameter [2,3]) plated with a mercury film exhibit the cathodic potential limit (i.e. overpotential) at a potential of about -1.0 V vs SCE in common media. In contrast to this, a voltage of ca -1.5 V vs SCE can easily be achieved when using the HMDE under the same conditions. Thus, compared to the HMDE, mercury film electrodes have a more limited use in ASV because of their unsuitability for

such metal ions that are cathodically reducible at highly negative potentials [2,3].

If MFEs have become wide-spread and very attractive in practical electrochemical analysis, it is evident that their valuable characteristics must prevail over their drawbacks. In confrontation with the HMDE, mercury film electrodes are capable to achieve substantially lower detection limits [6]. This is mainly thanks to a high mechanical stability of the film at rotated supporting electrodes or in stirred solutions [6,7]. There does not exist any danger that the film might be torn off from the surface, including measurements at very high revolutions when the most effective accumulation is usually reached. The mechanical stability of MFEs is also advantageous with respect to their employment under atypical conditions; for example, in field analysis and terrain monitoring or in special ship-board laboratories [2]. Finally, problematic usage of metallic elemental mercury, i.e. also HMDE, is another important aspect which makes MFEs more suitable for practical use. In some countries, the use of elemental mercury is strictly forbidden (including chemical laboratories) and thus various types of MFEs represent practically the only alternative of mercury electrodes available for experimental work [21].

Applications of Mercury Film Electrodes in Stripping Analysis

A more detailed discussion on a wide spectrum of possible employments of MFEs is beyond the scope of this article and can be found elsewhere [2-4]. Typical applications of various types of MFEs taken from these reviews and monothematic chapters are summarized in Table I. As shown in the table, MFEs are applicable to various samples. Predominantly, they are employed in trace analysis of heavy metals, toxic metals and metalloids. The lowest detection limits of methods are achievable for those metals that spontaneously form amalgams with mercury, but even other elements mentioned in the table can be determined at surprisingly low concentration levels. Numerous methods are suitable for simultaneous analyses, for instance those employing MFEs in combination with potentiometric stripping analysis (PSA) or flow injection analysis (FIA).

Gold Film Electrodes

Principles, Preparation and Basic Characterization

Whereas the main motivation for introducing MFEs into electrochemical practice was an effort to eliminate problems with a mechanical lability of mercury drop-based electrodes, gold film electrodes (AuFEs) as a special type of gold electrodes attracted attention for another reason. It is known that metallic gold—

Table I Application of Mercury Film Electrodes in Electrochemical Stripping Analysis

Type of analyte	Examples	Type of MFE		Accumulation mechanism	Detection limit	Type of sample
		Configuration	Support	(method)	(deposition time)	
Heavy metals	Zn, Cd, Pb, Tl, Cu	fixed, RDE, FIA	GCE, C-fiber, Pt-disk	electrolysis, amalgamation (ASV, PSA)	0.001 - 1.0 $\mu g\ l^{-1}$ (30 min)	water samples, river sediments, fly ash, milk, wine, beer, urine, blood
Other metals	Ni, Co, Fe, Mn, Sb, Bi, Sn	fixed, RDE, FIA	GCE C-fiber, Pt-fiber	adsorption, amalgamation (ASV, AdSV, PSA, CCSA)	0.1 - 1.0 $\mu g\ l^{-1}$ (30 min)	water samples, river sediments, fly ash, soils
Metalloids	As, Se	fixed, RDE, FIA	GCE, C-fiber	various (CSV, CCSA)	< 1 $\mu g\ l^{-1}$ (30 min)	water samples, milk, blood, fish tissues

Abbreviation used:
RDE - rotating disk electrode, GCE - glassy carbon electrode, PyCE - pyrolytic graphite electrode, FIA - flow injection analysis, ASV - anodic stripping voltammetry, CSV - catodic stripping voltammetry, AdSV - adsorptive stripping voltammetry, PSA - potentiometric stripping analysis, CCSA - constant current stripping potentiometry

although highly resistant material—undergoes electrochemical oxidation [22]. Since solid gold electrodes are employed mainly for measurements at highly positive potentials, i.e. under rather extreme conditions, their surface layer may be rapidly oxidized and has to be regenerated. This operation is not very simple and requires certain experience. If the regeneration is needed more often (sometimes, such a step is included directly in analytical procedure), methods based on the use of solid gold electrodes may become more complicated, time consuming, and hence inattractive for routine analysis [23].

On the contrary, AuFEs have been shown to be an especially useful alternative to their solid gold counterparts. Still keeping all valuable properties of gold electrodes, the active surface of AuFEs can easily be renewed by means of plating with a new film. Similarly to MFEs, glassy carbon electrodes appear to be the most convenient for gold films [4]. Occasionally, Pt-disk and gold- or carbon fibers have also been employed as AuFEs, mostly in a form of

electrochemical detectors for FIA [10].

Regarding the preparation of AuFEs and renewal of their surface, recommended procedures are practically identical to those known for MFEs. External deposition of a gold film or *in situ* plating is usually performed in solutions containing the Au^{III} species (e.g. $[AuCl_4]^-$ or $[AuBr_4]^-$ in acidified medium [24]). The oxidative stripping necessary for reproducible film renewal may be somewhat problematic if the support exhibits a lower oxygen overvoltage (i.e. limited anodic potential range). Hence, even some methods employing AuFEs may include in their procedures an additional step permitting to perform a regeneration of the bare support (e.g. using electrochemical activation or cycling [24]) before the gold film is deposited.

Electrochemical characteristics of AuFEs and their solid analogues are very similar, however, the effect of incidental interferences (e.g. from intermetallic compounds) may result in evident differences in behaviour of both types of gold electrodes [23].

Applications of Gold Film Electrodes in Stripping Analysis

Typical applications of AuFEs taken from several reviews [2-4] are given in Table II. Also the use of AuFEs in practical analysis is quite extensive, but the main attention has been focused on the determination of mercury. When using systems based on gold detectors (including all electrochemical sensors) a high affinity of gold towards mercury [24] can be advantageously utilized. Methods combining this specific ability of gold with the effectiveness of stripping techniques are then capable of determining extremely low concentrations of Hg (see data in Table II).

Carbon Paste Electrode as Support for Metallic Film

Carbon paste electrodes (CPEs) representing a special type of solid electrodes belong among typical heterogenous electrodes [5]. Carbon paste, i.e. a mixture of carbon (graphite) powder and a suitable binder (pasting liquid) is packed—as a relatively soft and uncompact material—into a specially designed electrode holder, forming thus the proper electrode. More details on the preparation, properties and some specific characteristics of CPEs can be found in specialized literature [5,25-28]. In context with this overview, it can briefly be stated that mainly the type and quality of individual paste constituents (i.e. carbon, binder, and eventually another component) as well as their mutual ratio determine the overall electrochemical behaviour of carbon paste electrodes. These rather complicated relations are reflected in the overall structural character of carbon pastes. Figure 5 represents a cross section of typical structure of a carbon paste. As seen in this schematic view, the surface of each carbon paste can be

Table II Application of Gold Film Electrodes in Electrochemical Stripping Analysis

Type of analyte	Examples	Type of AuFE		Accumulation mechanism	Detection limit	Type of sample
		Configuration	Support	(method)	(deposition time)	
Noble metals	Hg, Ag	fixed, RDE, FIA	GCE, PyCE, Au-fiber	electrolysis, Me/Au - affinity (ASV, PSA)	0.001 - 1.0 $\mu g\ l^{-1}$ (10 min)	water samples, river sediments, sewage sludge, food samples
Heavy metals	Pb, Cu	FIA	Au-fiber	electrolysis (ASV, PSA)	1.0 $\mu g\ l^{-1}$ (10 min)	water samples, urine
Other metals	Sb, Bi, Sn	fixed	GCE, Au-fiber	electrolysis (ASV, PSA)	< 1 $\mu g\ l^{-1}$ (10 min)	water samples, fruits
Metalloids	As, Se	fixed, FIA	GCE, Au-fiber	various (CSV, CCSA)	< 1 $\mu g\ l^{-1}$ (30 min)	water samples, milk, urine, fish

For the abbreviation used see footnote under Table I.

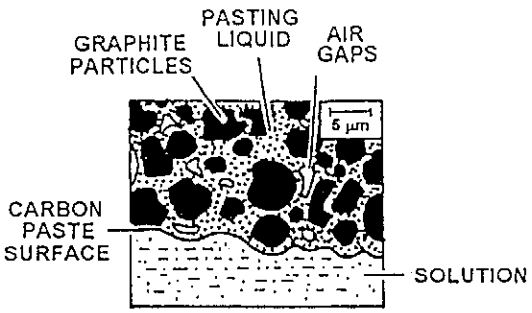

Fig. 5 Structure of carbon paste (schematic view - according to Ref. [29])

characterized by the presence of a pasting liquid as well as by badly defined geometry, both markedly contributing to specific conditions at this surface [5]. According to previous chapter, both the properties of a film and the surface structure of a support represent very important factors for behaviour of mercury- and gold film plated carbon paste-based electrodes [MF(CPEs) and

AuF(CPEs)].

In 1982, Kauffmann et al. [30] were probably the first who published a paper summarizing possibilities and limitations of mercury film plated carbon paste electrodes in anodic stripping voltammetry. In their report, CPEs were described as unsuitable for the preparation of mercury film electrodes due to unappropriate surface conditions at the carbon paste surface (e.g. its heterogeneity and roughness). The authors therefore proposed the special surface pretreatment of CPEs based on spraying the carbon paste with a solution containing dissolved colloidal graphite in poly(methyl metacrylate). After evaporation of the solvent, the carbon paste surface was coated with a compact layer of graphite particles [30]. Owing to this procedure, however, the carbon paste at the surface was transformed into the solid phase, and therefore, such a pretreated CPE was not of an actual carbon paste character. Some years later, applications of MF(CPEs) in ASV of selected heavy metals (e.g. Cd, Pb, Bi, and Cu) were studied by Říha [31], but also in his work, CPEs (made of silicone oil) plated with mercury films did not operate satisfactorily. Thus, in both references [30,31], pure carbon paste was not recommended as a convenient support for mercury films.

Investigations into various carbon pastes of different composition performed recently [32,33] revealed that despite doubts there exists a way of how to prepare MF(CPEs) with good electrochemical characteristics. Had a close attention been paid to the choice of carbon paste constituents, formerly criticized poor reproducibility and limited polarizability of MF(CPEs) could be significantly bettered [32]. This improvement was achieved by using atypical pasting liquids in the paste mixture as well as by optimal choice of graphite powder. Pursuing the same strategy, AuF(CPEs) have also been prepared as shown more recently [34,35]. Experiments and observations [32-35] have revealed close relations between the carbon paste composition, typical characteristics of CPEs, and the resultant behaviour of both MF(CPEs) and AuF(CPEs), which is in accordance with some arguments offered in previous paragraphs. Individual dependences and relations can be generalized and shown in Fig. 6. It can be stated that, in comparison with mercury- and gold-film electrodes prepared from common supports, film plated carbon paste substrates may exhibit markedly different electrochemical behaviour due to already mentioned specifics of carbon pastes, including their unique surface structure. Some of such properties of both MF(CPEs) and AuF(CPEs) are illustrated in the following two examples.

Mercury Film Plated Carbon Paste Electrodes in Stripping Analysis

Carbon pastes containing liquid organic esters exhibit some specific properties that can advantageously be utilized for the preparation of MF(CPEs). Namely, a CPE containing tricresyl phosphate as a pasting liquid has been shown to be

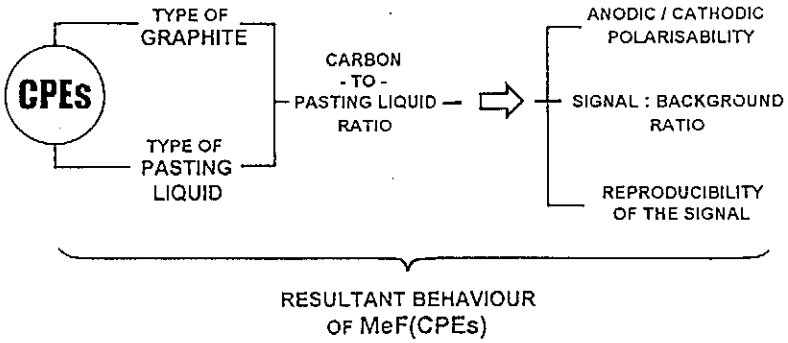

Fig. 6 Effect of the carbon paste composition upon resultant behaviour of MeF(CPEs) [schematically]

able to operate within a very wide potential range [36]. In particular, the tricresyl phosphate-based CPE exhibited a higher cathodic potential limit than that being typical for other carbon electrodes, including common CPEs.

Figure 7 makes a comparison of anodic stripping voltammograms obtained at common carbon paste prepared from silicone oil (C/SO) and at tricresyl phosphate-based carbon paste electrode (C/TCP). In order to demonstrate an unusual polarizability of the C/TCP, a model mixture of four metals was analyzed using ASV. Whereas both Mn and Zn are elements reducible at high negative potentials, and hence, hardly depositable onto ordinary solid electrodes, mercury is a typical noble metal stripped off at a potential near 0 V vs SCE. Mercury added into the mixture gave rise to a mercury film deposited *in situ*. An extreme polarizability of the C/TCP support was observed in an ammonia buffer: Mn had been preconcentrated in its elemental form and reoxidized in a potential range from −2.0 to +2.0 V vs Ag/AgCl. This experiment hardly performable with any other electrode then resulted in four signals, revealing subsequent reoxidation of manganese in individual steps (for details, see original article [32]).

Till now, the reason why the MF(C/TCP) electrode can be polarized in such a way has not yet been fully explained. Perhaps, it can be due to the fact that tricresyl phosphate is not chemically inert and its molecules can be protonated in acidic solutions [32]. The alteration of surface characteristics of the MF(C/TCP) in consequence of the formation of various proton-bearing functional groups may play a significant role in the process of deposition of a mercury film. However, this does not explain satisfactorily the behaviour of the C/TCP electrode in alkaline ammonia solution where a protonation can hardly be assumed. Apart from explanation, experiments have confirmed that the type of pasting liquids in the paste mixture strongly influences the polarizability of individual CPEs [32,33]. Namely, CPEs containing binders of related character (e.g. parafin or silicone oil) exhibited quite similar polarization limits whereas

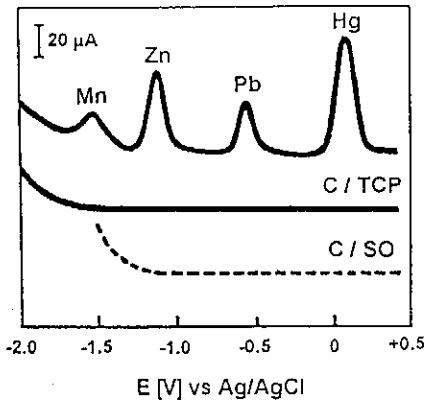

Fig. 7 Anodic stripping voltammograms of Mn, Zn, Pb, and Hg at the C/TCP electrode (according to Refs [32,33]). C/TCP (C/SO): tricresyl phosphate (silicone oil, respectively) containing carbon paste electrode; supporting electrolyte, 0.1 M $NH_3 + NH_4Cl$; $c\,(Me^{2+})$ = 10^{-6} mol l^{-1}; deposition time, 40 s; deposition potential, -2.0 V vs Ag/AgCl; scan rate, 20 mV s^{-1}

CPEs prepared from organic esters representing a different kind of pasting liquid (e.g tricresyl phosphate) could be polarized at markedly higher cathodic potentials. This phenomenon is well documented in Fig. 7 which reveals the differences in cathodic polarizability of both C/SO and C/TCP. Higher cathodic polarizability of the C/TCP indicates a higher value of hydrogen overvoltage at this electrode. It means that if the C/TCP is so fairly polarizable, the deposition of a mercury film onto this electrode can be performed even at highly negative potentials without evident hydrogen evolution. According to previous text, this aspect is very important for an optimal generation of metallic films: the more negative potential is applicable during the deposition of the film, the more effective is its generation and the better quality of the film can be obtained. It is also clear that the mercury film deposition at highly negative potentials onto supports with insufficient hydrogen overvoltage will lead to the rise of bubbles of gaseous hydrogen at the surface. Obviously, these bubbles are generated simultaneously with the film and have, in principle, a very negative effect on the resultant properties of such a film. It should also be mentioned that the hydrogen evolution is connected with unnegligible current signals which limit the cathodic potential range of each MFE. These undesirable currents may also interfere—as a background—with the analyte current signal or cause its complete overlapping.

The unique cathodic polarizability of the C/TCP electrode was utilized for the development of a method for ASV determination of zinc in drinking water. The optimization of the carbon paste composition resulted in a mixture of 0.5 g "RW-B" graphite + 0.2 ml tricresyl phosphate [32]. Figure 8 shows the response of Zn at three different CPEs and documents that MF(C/TCP) electrode gave the best signal. Responses of the remaining two electrodes (prepared from

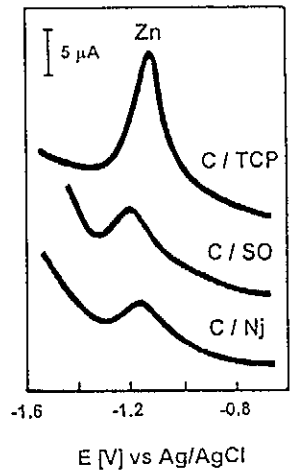

Fig. 8 Response of Zn at three different MF(CPEs) (according to Refs [34,35]). C/TCP (C/SO, C/Nj): tricresyl phosphate (silicone or Nujol oil, respectively) containing carbon paste; supporting electrolyte, 0.1 M $NH_3 + NH_4Cl$; $c\,(Hg^{2+}) = 2.5\times10^{-6}$ mol l^{-1}; deposition time, 60 s; deposition potential, -1.6 V vs Ag/AgCl; scan rate, 20 mV s^{-1}

the same graphite powder) suffer from high background currents due to starting proton reduction. Figure 8 therefore illustrates that the background caused by the hydrogen evolution at electrodes with low hydrogen overvoltage may negatively affect the signal of interest. In the case of Zn, its peaks obtained at both MF(C/SO) and MF(C/Nj) are markedly deformed as being superposed on the parabolic base-line of background currents.

The method for the determination of Zn has been successfully applied to samples of drinking water collected from several sources. The procedure employing the MF(C/TCP) electrode is simple, quick, not time-consuming, and provides acceptably precise results as well as a sufficiently low detection limit in order to be used for practical analysis of Zn in drinking water and related samples. Here, however, it should be pointed out that the method is based on the use of a MFE, and it is therefore sensitive towards interferences from elements forming intermetallic compounds with zinc, especially from copper. Numerous experiments have confirmed that this method is inapplicable to such samples in which the concentration of Cu^{2+} ions is equal to or higher than that of Zn^{2+}.

Compared to the determination of Zn at otherwise frequently used MF(GCE), the MF(C/TCP) electrode is superior in its background-to-signal characteristics; evidently, owing to an excellent cathodic polarizability of the tricresyl phosphate-based CPE [32]. In addition, the carbon paste support does not need any regeneration, its surface can be simply renewed. This is in contrast with GCEs which, from time to time, require a manual surface polishing [7]. Regarding the comparison with mercury drop electrodes (e.g. HMDE), the

method employing the MF(C/TCP) can be more convenient in situations when manipulations with elemental mercury may cause troubles [21,32].

CPEs plated with mercury films can also be recommended for ASV determination of other amalgam forming metals such as Cd, Pb, Tl, Bi, and Cu. However, for this purpose, their use does not bring any evident improvement of already existing methods which employ the GCE or other solid supports. To analyse metals reported above, substrates from carbon pastes are applicable as an occasional alternative to common supports, possessing comparable electrochemical characteristics.

Gold Film Plated Carbon Paste Electrodes in Stripping Analysis

The results of studies on MF(CPEs) soon initiated a new series of investigations dealing with the development of carbon paste electrodes suitable as the support for gold films. These investigations of AuF(CPEs) [34,35] represented a completely new subject because, up until that time, no report on gold film plated CPEs had been published. It was, however, advantageous that some findings and observations obtained during investigations with MF(CPEs) as well as with accumulation of tetrachloroaurate(III) at various CPEs [36,37] could also be exploited for studying AuF(CPEs).

One of the main reasons for testing CPEs as the supports for gold films was the fact that carbon pastes were able to offer very favourable properties for measurements at high positive potentials [5,26]. As already mentioned, such potentials are often attained when using ASV in combination with gold electrodes and, especially, with their film modifications. In classical ASV arrangement which obviously comprises the oxidative stripping approach, gold films have to be stripped off at potentials higher than +1.0 V vs SCE [22]. Naturally, this requirement pre-determines the choice of an appropriate supporting electrode which should operate at potentials even higher than that corresponding to the oxidation of gold itself. This is necessary for the total electrochemical oxidation of the film and its stripping off (i.e. dissolving) from the support surface. Only then can the removal of the film lead to its reproducible renewal, which is the main advantage of the oxidative stripping procedure [24]. There are few electrode materials resistant to highly positive potentials without a risk of being oxidized or otherwise damaged. The carbon paste is a typical example of an electrode which can be exposed to such extreme conditions. In acidic supporting electrolytes (which are normally used for measurements with gold electrodes [22,36]), CPEs are polarizable up to ca +1.5 V vs SCE, and some types even beyond this value [36]. It is also important that the background currents level of CPEs is very low and remains stable over the whole anodic potential range [22].

Investigations of AuF(CPEs) included detailed studies on several types of carbon pastes [34,35]. The paste mixtures were prepared from Nujol parafin oil,

silicone oil and tricresyl phosphate, respectively, and from the same graphite powder; always at identical ratio. Properties of these three CPEs were very similar and the corresponding AuF(CPEs) exhibited familiar characteristics (this was in contrast to MF(CPEs) whose behaviour differed from case to case, according to which pasting liquid had been used). All carbon pastes tested as supports for gold films were shown to be convenient, providing AuF(CPEs) with optimal properties. A silicone oil-containing carbon paste electrode (C/SO) was, nevertheless, taken as the support of choice, mainly owing to its excellent stability and for ease in which its surface could be renewed [38-40]. The C/SO carbon paste plated with a gold film was then tested for ASV of some heavy metals (e.g. Pb and Cu), and in particular, for the determination of Hg. The usefulness of AuF(C/SO) electrode for practical analysis has been demonstrated on the determination of Hg in heavily contaminated drinking water (containing about $1\,\mu g\,l^{-1}$ Hg^{II}). For this analysis, the method developed is quick, simple and employing inexpensive, easy-to-prepare working electrode. The proper procedure has been optimized especially for water samples which, after acidifying with HNO_3 to pH 1, irradiating with UV-light and spiking with Au^{III}, can be immediately analyzed. The method is suitable mainly for the determination of Hg at the microgram (ppb) level as the results of analyses are reproducible with a relative standard deviation about ± 5 %. Figure 9 also documents good reproducibility of the signal for Hg at the AuF(C/SO) electrode. Using this method, the sub-ppb level of Hg is achievable as well (the detection

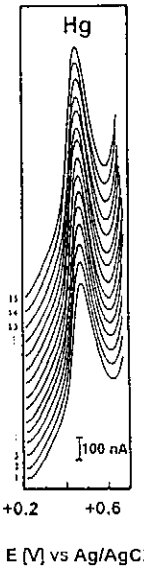

Fig. 9 Signal reproducibility in anodic stripping voltammetry of mercury at the AuF(C/SO) electrode; (according to Ref. [34]). supporting electrolyte, 0.1 M HNO_3 + 0.02 M KCl; $c\,(Hg^{2+}) = 5\times10^{-9}$ mol l^{-1} ($\mu g\,l^{-1}$); deposition time, 3 min; deposition potential, +0.2 V; scan rate, 20 mV s^{-1}

limit is about 0.05 $\mu g\, l^{-1}$ Hg^{II}), but with adequately higher error (± 10–50 %) [34]. The determination of Hg did not suffer from the presence of interfering species, only higher concentrations of Ag^{+} and Se^{IV} may cause difficulties [34,35].

The employment of AuF(CPEs) in anodic stripping voltammetry is still in development because especially the method for the determination of mercury requires further improvements. Indeed, its detection limit although achieving below the ppb level is not yet sufficiently low in order to be acceptable for the determination of Hg in natural water samples [4,34].

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