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NON-TRADITIONAL FILM ELECTRODES IN VOLTAMMETRIC AND AMPEROMETRIC ANALYSIS OF ORGANIC COMPOUNDS

*New perspectives on analytical chemistry**

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A huge diversity of problems currently solved by modern analytical chemistry requires a great variety of approaches, methods, and materials used for finding optimal solutions. Although the advantages and possibilities of current spectrometric and separation methods are fascinating, it can certainly be declared that modern electrochemical and electroanalytical methods may represent a competitive alternative, especially if they use new electrode materials and progressive approaches. In this review, our contribution in the field of non-traditional film electrodes based on mercury, bismuth, antimony, and carbon conductive layers applied in voltammetric and amperometric analysis of organic compounds is documented. The possibilities and limitations of these novel electrochemical sensors, their advantages and drawbacks, their practical applications, as well as their contribution in the field of modern analytical chemistry are presented.

Keywords: electrochemistry, non-traditional film electrodes, polarography, voltammetry, amperometry, organic analysis

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1. Introduction

Electrochemical methods certainly have their place among the most used analytical techniques today. Modern voltammetric methods in a batch arrangement and amperometric methods for flow analysis can be valuable tools for monitoring biologically active organic substances that adversely affect human health or the environment. The main advantages of electroanalytical methods include: low acquisition and operating costs, high sensitivity, accepta-

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ble selectivity, easy miniaturization and, due to the low weight and size of the apparatus itself, the possibility to perform analyses directly *in situ*. One of the most important factors influencing successful voltammetric analysis is the selection of a suitable working electrode. The choice of working electrode influences many parameters of a given electroanalytical method, including the choice of appropriate analytes, sensitivity and selectivity, limits of detection and quantification.

Perhaps the greatest limitation of the use of solid working electrodes in routine analyses is the passivation of their surface by electrode reaction products or components of the solution being analyzed. This contributes to the growing popularity of contactless electroanalytical measurements. The problem of electrode passivation can be eliminated by surface polishing, or by chemical or electrochemical cleaning. In addition, ultrasound, heat, laser, or electrical discharge can also be applied. In our opinion, one of the great challenges for modern electroanalytical chemistry is the creation of an electrode material that is resistant to passivation, allows modification of its surface, and can be used for the design of new sensors and biosensors as well as for analysis in flow-through arrangements. The non-traditional film electrodes meet the above requirements while being compatible with the idea of "green" and "white" analytical chemistry.

2. Types of film electrodes

2.1. Mercury film electrodes

Despite the great success of the hanging mercury drop electrode (HMDE), which consists of a renewable drop of mercury at the end of a narrow capillary, the HMDE has its shortcomings[1]. It is quite bulky, requires a mercury reservoir to be present and also regular maintenance of the capillary. It also contains complicated electronic and mechanical components responsible for the precise formation and release of the mercury drop. Another problem is the use of metallic mercury. The potential risk from mercury poisoning, contamination, or release has led some states to ban its use altogether[2,3]. Unlike solid electrodes, the HMDE is not mechanically robust (*i.e.*, a drop of mercury will easily fall off on impact), which makes them unsuitable for analysis outside the laboratory and also for measurements in a flow-through arrangement. Modification of the HMDE with permselective membranes to improve analytical properties (*e.g.*, sensitivity and selectivity) is quite complicated. Nevertheless, it can be done, but these procedures have rarely been used, mainly due to the mechanical lability of the electrode and its primary principle of use (one drop for each individual measurement)[4,5].

Some of the above shortcomings can be overcome by using mercury film electrodes (HgFEs, also referred to as a MFE from the English term "mercury film electrode"), prepared by coating a suitable substrate with a thin film of metallic mercury[5]. HgFEs have come into use mainly because of the following advantages: their size is very small, they do not require any additional accessories, they provide a better ratio of electrode surface area to solution volume, they are mechanically more stable than the HMDE, and they allow use in multiple arrangements (*e.g.*, rotating electrode or flow measurement). Furthermore, they can be chemically modified and the preparation of the HgFE itself requires only minimal amounts of mercury. The limitations of use lie in the lower accuracy and reproducibility of the measurements, the limited potential range, and the difficulties in preparing, cleaning, and reactivating the mercury film[4,5].

Silver amalgam appears to be one of the suitable substrate materials. The polished surface of solid amalgam is free of liquid mercury, exhibits a high hydrogen overvoltage[6,7], and is suitable for both direct electrochemical measurements and chemical modification with various modifiers[8,9], which may broaden its range of applications. One possible approach to the chemical modification of amalgam electrodes is to coat their surface with a film of liquid mercury. Mercury films can be formed on different types of conductors. However, ideally, a smooth film can only be prepared on the surface of a conductor that can be wetted with mercury (*e.g.*, only a collection of mercury microdroplets is formed on carbon materials[5]). Silver[6,10–13], gold[14,15], platinum[5,16], iridium[17,18], or copper[19] are among suitable substrate materials for mercury films. Solid amalgams of various metals are easily homogeneously coated with mercury and are, therefore, among the most commonly used materials for the preparation of HgFEs (ref.[20]).

According to the ref.[21], the mercury film electrode on the surface of silver solid amalgam (HgF-AgSAE) was prepared using a special apparatus for the preparation of mercury films of a precisely defined thickness on a solid electrode[20], which consists of a plastic tube filled with 0.2 mL of 0.01M $HgCl_2$ and 1M KI containing liquid mercury and with a carbon electrical contact on the bottom. The HgF-AgSAE must be prepared daily as the 1–2 mm thick mercury film can only be used for 2 hours. A suitable potential for mercury film deposition was found at –200 mV (ref.[20]). A suitable time required for mercury film deposition was also found, and the repeatability of the determination of selected compounds (4-nitrophenol and 5-nitrobenzimidazole) on the HgF-AgSAE was very good on film prepared for 300–3600 s. Shorter deposition times were not tested because the film did not cover the entire layer of electrode material[20]. The relative standard deviation for the determination of 4-nitrophenol ($c = 1\times10^{-5}$ mol L^{-1}) by differential pulse voltammetry (DPV) in Britton-Robinson (BR) buffer at pH 6.0 on the HgF-AgSAE was 0.3, 2.5, 1.4, and 2.0% for deposition times of 300, 900, 1800, and 3600 s, respectively.

The results obtained after different deposition times are comparable[21]. Films prepared over a shorter time interval are not as stable as those prepared with longer deposition times. The thickness of the freshly formed film prepared for 3600 s was 11.4 ± 4.2 mm. After two hours of measurements with such prepared electrode, the film thickness decreased to 1.6 ± 0.6 mm. The film thickness was calculated from the charge passed during its decomposition[20]. The decomposition of the mercury film was observed from the shift of the peak potential of the test compound closer to the peak potential on the p-AgSAE ("p" from the English term "polished", *i.e.*, polished AgSAE without being covered by a mercury meniscus or film). A mercury film deposition time of 3600 s was selected as optimal.

It can therefore be concluded that the HgF-AgSAE represents a suitable alternative to traditional mercury electrodes[21]. This electrode, when combined with linear sweep voltammetry (DCV) and DPV, can be used to determine submicromolar concentrations of 4-nitrophenol and 5-nitrobenzimidazole (see Table I). This electrode shows stable and reproducible results in long-term measurements and is also applicable for DPV determination of these substances in model samples of drinking water.

Table I
Survey of analytes determined by voltammetry or amperometry on different types of film electrodes

Analyte	Working electrode	Technique	Medium	Concentration [μmol L^{-1}]	*LOQ* [μmol L^{-1}]	Ref.
Chemical Carcinogens						
2-Amino-6-nitrobenzothiazole	BiF-AgSAE	DCV	BR buffer pH 10.0–methanol (9:1)	0.2–100	0.16	47
			DW–BR buffer pH 10.0 (9:1)	0.2–10	0.35	47
			MW–BR buffer pH 10.0 (9:1)	0.2–10	0.40	47
		DPV	BR buffer pH 10.0–methanol (9:1)	0.2–100	0.22	47
			DW–BR buffer pH 10.0 (9:1)	0.2–10	0.31	47
			MW–BR buffer pH 10.0 (9:1)	0.2–10	0.44	47
	GF-AgSAE	DCV (reduction)	BR buffer pH 4.0	0.2–10	0.89	61
			DW–BR buffer pH 4.0 (9:1)	0.2–10	0.51	61
			RW–BR buffer pH 4.0 (9:1)	0.2–10	0.20	61
		DCV (oxidation)	BR buffer pH 4.0	2–10	5.1	61
			DW–BR buffer pH 4.0 (9:1)	2–10	3.4	61
			RW–BR buffer pH 4.0 (9:1)	2–10	3.4	61
		DPV (reduction)	BR buffer pH 4.0	0.2–10	0.77	61
			DW–BR buffer pH 4.0 (9:1)	0.2–10	0.17	61
			RW–BR buffer pH 4.0 (9:1)	0.2–10	0.50	61
		DPV (oxidation)	BR buffer pH 4.0	2–10	4.0	61
			DW–BR buffer pH 4.0 (9:1)	2–10	1.7	61
			RW–BR buffer pH 4.0 (9:1)	2–10	2.4	61
5-Aminoquinoline	GF-AgSAE	DCV	BR buffer pH 3.0	2–100	4	62
		DPV	BR buffer pH 6.0	0.2–100	0.2	62
		FIA-AD	BR buffer pH 3.0	2–100	1	62
5-Nitrobenzimidazole	HgF-AgSAE	DCV	BR buffer pH 8.0	0.2–100	0.97	21
			DW–BR buffer pH 8.0 (9:1)	0.2–100	0.93	21
		DPV	BR buffer pH 8.0	0.2–100	0.70	21
			DW–BR buffer pH 8.0 (9:1)	0.2–100	0.76	21
	LSBiF-AgSAE	DCV	BR buffer pH 7.0	0.2–100	0.37	52
			DW–BR buffer pH 7.0 (1:1)	0.2–100	0.68	52
			DW–BR buffer pH 7.0 (9:1)	0.2–100	0.23	52
			MW–BR buffer pH 7.0 (1:1)	0.2–100	0.78	52
			MW–BR buffer pH 7.0 (9:1)	0.2–100	0.55	52

Table I
Continued

Analyte	Working electrode	Technique	Medium	Concentration [μmol L^{-1}]	*LOQ* [μmol L^{-1}]	Ref.
5-Nitrobenzimidazole	LSBiF-AgSAE	DPV	BR buffer pH 7.0	0.2–100	0.068	52
			DW–BR buffer pH 7.0 (1:1)	0.2–100	0.98	52
			DW–BR buffer pH 7.0 (9:1)	0.2–100	0.66	52
			MW–BR buffer pH 7.0 (1:1)	0.2–100	0.42	52
			MW–BR buffer pH 7.0 (9:1)	0.2–100	0.36	52
	GF-AgSAE	DCV	BR buffer pH 7.0	0.2–100	0.62	61
			DW–BR buffer pH 7.0 (9:1)	0.2–100	0.25	61
			RW–BR buffer pH 7.0 (9:1)	0.2–100	0.19	61
		DPV	BR buffer pH 7.0	0.2–100	0.31	61
			DW–BR buffer pH 7.0 (9:1)	0.2–100	0.13	61
			RW–BR buffer pH 7.0 (9:1)	0.2–100	0.13	61
	BiF-AuE	DCV	BR buffer pH 9.0	2–100	0.54	53
			DW–BR buffer pH 9.0 (9:1)	20–100	0.77	53
			RW–BR buffer pH 9.0 (9:1)	20–100	0.75	53
		DPV	BR buffer pH 9.0	2–100	2.1	53
			DW–BR buffer pH 9.0 (9:1)	20–100	1.0	53
			RW–BR buffer pH 9.0 (9:1)	20–100	2.5	53
5-Nitroquinoline	GF-AgSAE	DCV	BR buffer pH 11.0	0.4–100	1.0	63
		DPV	BR buffer pH 11.0	0.2–100	0.4	63
			DW–BR buffer pH 11.1 (9:1)	0.2–10	0.2	63
			RW–BR buffer pH 11.1 (9:1)	0.2–10	0.6	63
		SPE-DPV	BR buffer pH 11.0–methanol (9:1) (SPE from DeW)	0.2–1	0.17	64
			BR buffer pH 11.0–methanol (9:1) (SPE from DW)	0.2–1	0.055	64
			BR buffer pH 11.0–methanol (9:1) (SPE from RW)	0.2–1	0.027	64
		FIA-AD	BR buffer pH 11.0	2–100	1.0	64
6-Aminoquinoline	GF-AgSAE	DCV	BR buffer pH 5.0	4–10	4	65
		DPV	BR buffer pH 5.0	2–10	3	65
Agricultural Chemicals						
2-Nitrophenol	GF-AgSAE	DCV (reduction)	BR buffer pH 5.0	2–100	1.2	72
			DW–BR buffer pH 5.0 (9:1)	2–100	0.37	72
		DPV (reduction)	BR buffer pH 6.0	2–100	2.0	72
			DW–BR buffer pH 6.0 (9:1)	2–100	1.0	72
		DPV (oxidation)	BR buffer pH 6.0	0.2–10	0.2	73
			DW–BR buffer pH 6.0 (9:1)	0.2–10	0.1	73
4-Nitrophenol	HgF-AgSAE	DCV	BR buffer pH 6.0	0.2–100	0.87	21
			DW–BR buffer pH 6.0 (9:1)	2–100	4.7	21
		DPV	BR buffer pH 6.0	0.2–100	0.37	21
			DW–BR buffer pH 6.0 (9:1)	2–100	1.4	21
	BiF-AuE	DCV	BR buffer pH 7.0	1–100	0.69	66
			DW–BR buffer pH 7.0 (9:1)	1–100	0.95	66

Table I
Continued

Analyte	Working electrode	Technique	Medium	Concentration [μmol L^{-1}]	*LOQ* [μmol L^{-1}]	Ref.
4-Nitrophenol	BiF-AuE	DPV	BR buffer pH 7.0	1–100	0.48	66
			DW–BR buffer pH 7.0 (9:1)	1–100	0.75	66
	LSGF-PtE	DCV (reduction)	BR buffer pH 6.0	2–100	2.3	67
			DW–BR buffer pH 6.0 (9:1)	1–100	1.0	67
			RW–BR buffer pH 6.0 (9:1)	2–100	1.9	67
		DCV (oxidation)	BR buffer pH 3.0	6–100	1.5	68
			DW–BR buffer pH 3.0 (9:1)	4–100	1.6	68
			RW–BR buffer pH 3.0 (9:1)	6–100	1.7	68
	LSGF-PtE	DPV (reduction)	BR buffer pH 7.0	2–100	1.8	67
			DW–BR buffer pH 7.0 (9:1)	1–100	1.3	67
			RW–BR buffer pH 7.0 (9:1)	1–100	1.0	67
		DPV (oxidation)	BR buffer pH 7.0	1–100	0.46	68
			DW–BR buffer pH 7.0 (9:1)	1–100	0.46	68
			RW–BR buffer pH 7.0 (9:1)	1–100	0.60	68
		SPE-DPV (oxidation)	BR buffer pH 7.0 (SPE from DeW)	0.01–1	0.014	68
			BR buffer pH 7.0 (SPE from DW)	0.01–1	0.011	68
			BR buffer pH 7.0 (SPE from RW)	0.01–1	0.010	68
Drugs						
4-Nitro-3-(trifluoromethyl)aniline	GF-AgSAE	DCV	BR buffer pH 5.0–methanol (9:1)	40–100	27	69
		DPV	BR buffer pH 5.0–methanol (9:1)	2–100	24	69
Dimenhydrinate	GF-AgSAE	DCV	BR buffer pH 3.0	2–100	0.08	70
		DPV	BR buffer pH 3.0	0.2–100	0.02	70
Doxycycline	GF-AgSAE	DCV	BR buffer pH 12.0	20–100	15	70
		DPV	BR buffer pH 12.0	20–100	15	70
Flutamide	GF-AgSAE	DCV	BR buffer pH 5.0–methanol (9:1)	2–100	28	69
		DPV	BR buffer pH 5.0–methanol (9:1)	2–100	7.7	69
Paracetamol	GF-AgSAE	DPV	BR buffer pH 4.0	0.02–100	0.034	71
			Human urine–BR buffer pH 4.0 (1:1)	2–100	0.48	71
Tumour Biomarkers						
Homovanillic acid	GFE	DPV	BR buffer pH 2.0	0.8–100	0.3	74
Vanillylmandelic acid	GFE	DPV	BR buffer pH 2.0	1–100	0.8	74
Compounds Used in Cosmetic Industry						
Triclosan	GFE	DPV	BR buffer pH 7.0–methanol (9:1)	1–100	1.6	75

Abbreviations not previously defined in the text: DeW – deionized water, DW – drinking water, FIA-AD – flow injection analysis with amperometric detection, *LOQ* – limit of quantification, MW – mineral water, RW – river water, SPE-DPV – differential pulse voltammetry after preconcentration of the analyte by solid phase extraction

2.2. Bismuth film electrodes

Bismuth is also a suitable inorganic material for the preparation of film electrodes. Bismuth electrodes, whose potential use in electroanalytical chemistry was described in 2000, have gained considerable popularity in recent years[22]. Due to the low toxicity of bismuth, this "green" metal can replace mercury electrodes. In most respects, bismuth electrodes exhibit similar properties to mercury electrodes (except for a more limited potential window in the anodic region), while being solid at room temperature, expanding the possibilities in the preparation of bismuth-based sensors. The use of bismuth electrodes has been described in a number of reviews that report their dominant use in heavy metal trace analysis using electrochemical stripping methods[23–29]. Although bismuth appears to be an attractive electrode material for the determination of reducible organic compounds because of its wide potential range in the cathodic region, only a few applications have been described so far[30].

The simplest bismuth electrode for organic electroanalysis is the bismuth solid (bulk) electrode. It is made either from commercially available bismuth wire coated with an insulator[31], or by sucking molten bismuth into a hollow glass tube to form a bismuth wire inside[32,33]. The advantages of these sensors are ease of preparation, simple and rapid surface recovery (by simple mechanical polishing, or trimming or chipping the end of the tube), and the relative homogeneity of the electrode surface.

Bismuth film electrodes (BiFEs) are commonly prepared *in situ* or *ex situ* by electrochemical deposition of a thin bismuth film on the surface of a suitable conductor. *In situ* plating is only suitable for trace metal analysis by anodic stripping voltammetry, which involves cathodic electrolysis. All possibilities of using BiFEs for organic analysis include pretreatment of the substrate surface from a separate plating solution containing bismuth ions in an acidic environment to prevent their hydrolysis. The plating conditions vary: the concentration of bismuth ions in the plating solution ranges from units of mg L^{-1} (ref.[34]) to thousands of mg L^{-1} (ref.[35]) with the most common concentration between 50 and 500 mg L^{-1} (ref.[36,37]). Acid[38,39] or low pH buffer[36,40,41] is commonly used as an auxiliary electrolyte. The presence of potassium bromide improves the adhesion of the bismuth film to the electrode surface[42,43]. The plating potential is usually less than −0.6 V, however, cases of applied potentials between 0.1 and –0.3 V have been described (ref.[44–46]). The plating time varies between 60 s to several minutes[47,48].

Different substrate materials have been used for the preparation of BiFEs: copper[46,49,50], glassy carbon[37–40,42,43], mesoporous platinum[44,45], carbon paste[41], lead[36], or screen-printed carbon ink[51]. Flow cells for the use of BiFEs have also been described (ref.[34,35]).

New types of BiFEs prepared by electrodeposition of a bismuth film on a silver solid amalgam substrate – a bismuth film-modified silver solid amalgam electrode (BiF-AgSAE)[47] and a large surface bismuth film-modified silver solid amalgam electrode (LSBiF-AgSAE, "LS" from the English term "large surface")[52] – have been described in ref.[47,52]. These were used for the voltammetric determination of the electrochemically reducible organic compounds 2-amino-6-nitrobenzothiazole[47] and 5-nitrobenzimidazole[52] as model compounds. Silver solid amalgam electrodes with diameters of 0.5 and 2.64 mm were used as a substrate for film preparation. For *ex situ* deposition of the bismuth film on the AgSAE, a constant potential of –1.2 V for 300 and 1800 s was used with constant stirring in 10 mL of deposition solution which was purged of dissolved oxygen by bubbling with nitrogen gas for 5 min and which contained 0.5 mL of bismuth ion solution at a concentration of 1000 mg L^{-1} and 9.5 mL of 1M

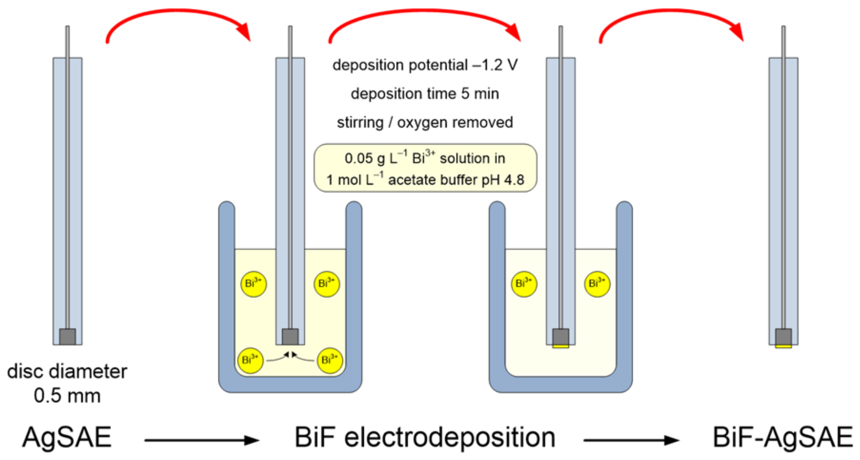

Fig. 1. **Schematic representation of the bismuth film electrode (BiF-AgSAE) preparation on a silver solid amalgam substrate (AgSAE) by electrodeposition of a bismuth layer (BiF)**

acetate buffer at pH 4.8 (Fig. 1). The LSBiF-AgSAE, in contrast to the smaller surface area of the BiF-AgSAE, provided higher voltammetric signals[52].

Bismuth film for the BiF-AgSAE has to be prepared every day because its shelf life is relatively short, on the order of a few hours. The prepared film electrode was not cleaned mechanically, electrochemically, or chemically as these steps lead to damage of the bismuth film, resulting in less reproducible results. The surface of the electrochemically prepared bismuth film on the LSBiF-AgSAE was characterized by atomic force microscopy (AFM)[52]. This showed that the bismuth film was not uniform over the entire surface of the substrate electrode, but formed on the nanocrystalline film three-dimensional formations covering only a portion of the surface. These grains are between 30 and 130 nm in size and very likely originated due to the inhomogeneous surface of the substrate electrode. Vertical surface non-uniformities up to a size of 20 nm were evident on AFM scans of the substrate electrode surface prior to deposition. It was not possible to decide whether the appearance of the three-dimensional grains was due to the amalgam electrode or due to the effect of formed bismuth oxide[52].

Bismuth film electrodes on the silver solid amalgam substrate reported in ref.[47,52] represent a valuable alternative to the previously mentioned BiFEs, with one of the lowest limits of quantification achieved in organic electroanalysis (this is probably due to the ability of bismuth to form "alloys" with heavy metals, analogous to amalgams formed from mercury[23]). The substrate material, AgSAE, also plays an important role in the overall properties of the BiF-AgSAE. In comparative studies[52,53], the LSBiF-AgSAE was compared with the BiFE formed on different substrate materials, such as glassy carbon (BiF-GCE) and gold (BiF-AuE), for the voltammetric determination of 5-nitrobenzimidazole. The limit of quantification of 5-nitrobenzimidazole on the LSBiF-AgSAE (ref.[52]) was of the order of 10^{-8} mol L^{-1}, whereas on the BiF-GCE and the BiF-AuE, this limit was two orders of magnitude higher[53]. The repeatability for 20 consecutive DPV determinations of 5-nitrobenzimidazole ($c = 1\times10^{-4}$ mol L^{-1}) was 3, >5, and 1% for the LSBiF-AgSAE, the BiF-GCE, and the BiF-AuE, respectively.

The simple mechanical recovery of the BiF-AgSAE surface, the good reproducibility of the measurements, and the elimination of the problem associated with the "electrode history" confirm the practical applicability of these electrodes. Disadvantages of all BiFEs include the limited potential window in the anodic region, which prevents the determination and accumulation of analytes at more positive potentials[23].

2.3. Antimony film electrodes

Another non-traditional material for the preparation of film electrodes is antimony. Gajdár[54] prepared an antimony film electrode (SbFE) on different substrate materials (copper, gold, silver, polished silver solid amalgam, or glassy carbon). The best results were obtained on glassy carbon. With this electrode, he determined the pesticide trifuralin, where after preconcentration on solid phase (SPE), he reached a limit of quantification of 1.3×10^{-8} mol L^{-1}.

2.4. Carbon film electrodes

The main disadvantage of mercury electrodes is their limited potential window in the anodic region due to the dissolution of mercury at about +0.4 V (compared to a saturated calomel electrode). In the presence of substances that form complexes or insoluble salts with mercury ions, the decomposition potential is shifted to even more negative potentials. Therefore, mercury electrodes are not suitable for the determination of analytes oxidizable in the anodic region[1]. This also applies to silver solid amalgam electrodes, which exhibit similar properties to mercury electrodes[7,55,56]. In contrast, gold, platinum, and other noble metal electrodes are suitable for anodic oxidation. On the other hand, their applicability for working at cathodic potentials is limited mainly due to the low overvoltage of hydrogen[4]. The potential range of many carbon materials is wider. The biggest problem of all solid electrodes is the reproducibility of their surface and its passivation, which fundamentally affects their analytical properties. Therefore, attention has been given to pretreatment of solid electrodes prior to analysis to improve the reproducibility of voltammetric measurements performed on them.

The reproducibility and potential range of many solid electrodes can be improved by coating their surface with a film prepared from a polymer containing conductive particles. The polymer itself should not be conductive and should perfectly isolate the solution to be analyzed from the conductive part of the electrode (the concept of a so-called composite electrode). Under these assumptions, the traditional solid electrode is only a conductor, while microparticles of conductive material (graphite, glassy carbon microparticles, carbon nanotubes, graphene, *etc.*) are dispersed in the polymer to form a suitable electrode material that ensures contact between the solution to be analyzed and the conductive part of the electrode[9]. Renewal of this film is simple and fast. These electrodes can be seen as analogous to composite electrodes[4,57,58] in the form of a thin film which, depending on the ratio between the polymer and the conducting particles, can behave either as an array of microelectrodes or as a classical electrode with a homogeneous surface.

A newly developed composite film electrode based on microcrystalline natural graphite in polystyrene (GFE), formed by coating a conventional solid working electrode with a film containing suitable conductive micro- or nanoparticles, represents a promising alternative for electrode surfaces modified with various carbon nanoparticles with advantageous electrocatalytic properties (nanotubes, graphene, *etc.*). The smallest particles of micronized natural graphite (type CR 2 995, Graphite Týn, Týn nad Vltavou, Czech Republic) reach a size of about 1000 nm (ref.[59]), which is very close to the size of carbon nanoparticles commonly used in modern electroanalytical applications. The price of this electrode material is incomparably lower (units of Czech crowns per 10 g) than that of commercially available carbon nanoparticles. This fact enables wider use of the GFE in practice.

GFEs are also a suitable alternative to commercially available disposable carbon screen-printed electrodes[9]. Their preparation is simple, fast, and inexpensive (the surface of a conventional solid working electrode is coated with carbon ink and then waits for the solvent to evaporate), and the mechanical renewal of the electrode surface is also simple (removing the old film by wiping it on filter paper and then creating a new one). Electrodes prepared in this way provide good reproducibility of measurements, eliminate the problem of "electrode history", and also allow simple chemical modification of their surface.

Cathodic voltammetry of electrochemically reducible compounds on carbon paste electrodes (CPEs) does not provide suitable limits of quantification and good reproducibility, as the oxygen present in the carbon paste provides a strong signal[60]. In ref.[61], the authors focused on the use of silver amalgam covered with a film of a composite of micronized natural graphite and polystyrene (GF-AgSAE) as a working electrode material, which eliminates the aforementioned problem of oxygen present in the carbon paste. This working electrode represents the possibility of using a non-toxic alternative to traditional mercury electrodes for monitoring both reduction and oxidation processes[9]. In this work[61], the behavior of two genotoxic nitro compounds (namely 2-amino-6-nitrobenzothiazole and 5-nitrobenzimidazole) was investigated by DCV and DPV on the GF-AgSAE. Suitable conditions for their determination in a BR buffer medium were found (see Table I), and the practical application of the newly developed voltammetric methods was verified on model samples of drinking and river water. The GF-AgSAE is very stable and can be used within days. If there are problems associated with electrode passivation, it takes only a few minutes to prepare a new film.

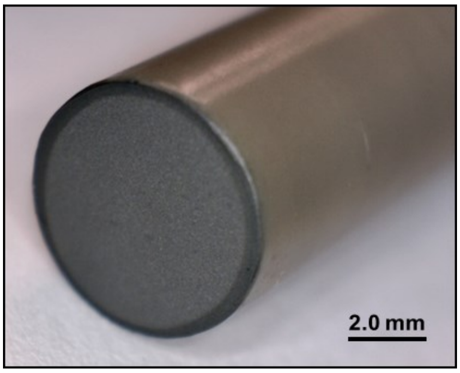

Fig. 2. **Detailed photograph of the film electrode made of a composite of micronized natural graphite and polystyrene (LSGF-PtE)[76]**

An overview of the organic compounds determined by voltammetry or amperometry on different types of GFEs (not only based on silver solid amalgam, but also on the large surface platinum substrate (PtE) used for the comparison[67,68], where the resulting working electrode is a large surface graphite film electrode LSGF-PtE (Fig. 2)) is given in Table I, where examples of the use of the aforementioned HgFEs and BiFEs are also mentioned.

3. Conclusion

Film electrodes have found their application in both batch arrangement and flow methods. In many cases, they can replace mercury electrodes, especially in flow-through arrangements. They can also be used to monitor the electrochemical properties of various biologically important compounds. Their simplicity of preparation and suitable analytical properties allow them to be more widely used in practice. Problems of electrode surface passivation can be reduced by a simple renewal of the film on the substrate electrode. The possibility of modifying the electrode surface leading to many other applications is also worth mentioning.

With the above examples, it can be concluded that film electrodes are not only a suitable replacement for the HMDE, but offer new possibilities that cannot be realized on mercury electrodes. Further research on these electrode materials will undoubtedly show new possibilities for the use of non-traditional film electrode materials and their modifications.

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