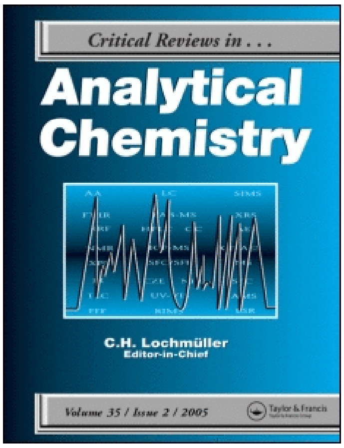

Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Analytical Applications of Composite Solid Electrodes

Tomas Navratil[a]; Jiří Barek[b]
[a] J. Heyrovský Institute of Physical Chemistry of AS CR, Prague, Czech Republic [b] Faculty of Science, Department of Analytical Chemistry, UNESCO Laboratory of Environmental Electrochemistry, Charles University in Prague, Prague, Czech Republic

To cite this Article Navratil, Tomas and Barek, Jiří(2009) 'Analytical Applications of Composite Solid Electrodes', Critical Reviews in Analytical Chemistry, 39: 3, 131 — 147

To link to this Article: DOI: 10.1080/10408340903011796

URL: http://dx.doi.org/10.1080/10408340903011796

Critical Reviews in Analytical Chemistry, 39:131–147, 2009
Copyright © Taylor and Francis Group, LLC
ISSN: 1040-8347 print / 1547-6510 online
DOI: 10.1080/10408340903011796

Analytical Applications of Composite Solid Electrodes

Tomas Navratil[1] **and Jiří Barek**[2]
[1]*J. Heyrovský Institute of Physical Chemistry of AS CR, v.v.i., Prague, Czech Republic*
[2]*Faculty of Science, Charles University in Prague, Department of Analytical Chemistry, UNESCO Laboratory of Environmental Electrochemistry, Prague, Czech Republic*

Recent trends and advances in electrochemistry with composite solid electrodes (CSEs) are reviewed. Their properties, methods of preparation, pre-treatment, and analytical applications are summarized and their advantages and disadvantages are discussed. Special attention is paid to the determination of inorganic and organic compounds important from the point of view of the protection of environment and human health. The review is focused on easily prepared electrodes frequently used in the authors' laboratory and their practical applications. However, some other electrodes and their fields of applications are mentioned as well.

Keywords Composite solid electrodes, voltammetry, amperometry, environmental analysis, review

INTRODUCTION

Voltammetry and amperometry are among the most frequently used electroanalytical methods. They are especially suitable for large scale environmental monitoring of electrochemically active pollutants in various types of matrices, because they are inexpensive, extremely sensitive, suitable for speciation, and they present an independent alternative to so far prevalent spectrometric and separation techniques (1). The crucial and fundamental problem in their practical application is the choice of a suitable working electrode. In the field of cathodic reductions, as well as anodic oxidations, the so-called composite solid electrodes (CSE) can be successfully utilized and can be a useful alternative to mercury, solid metal, or carbonaceous electrodes. CSEs are composed from at least one conducting and one insulating phase, which are mixed keeping their final solid state. They have been intensively developed and used for the last twenty years and, in some cases, they can successfully compete with traditional electrodes consisting of only one conducting phase. They offer certain advantages, e.g., low cost, low weight, high signal-to-noise ratio, broad potential window, resistance toward passivation and/or easy mechanical and electrochemical cleaning, compatibility with the concept of so-called "green analytical chemistry" (2, 3), and the possibility of chemical modification of the conductor or of the insulator phase or of their surface. Their mechanical robustness enables their application in flowing systems and/or in field measurements. The resistance towards passivation and the possibility of electrochemical cleaning is especially important because electrode fouling is probably the biggest obstacle to more frequent applications of electroanalytical methods in environmental analysis. According to the Web of Science, about 2200 papers dealing with analytical applications of composite electrodes (excluding paste electrodes) have been published up to now (more than 350 per year in the last two years). Approximately 15% of them have been devoted to the SCEs (Fig. 1). Nevertheless, these numbers can be underestimated due to non-uniform terminology and classification in electrode description. The CSEs have found their applications in practically all branches of electrochemistry. The construction and composition of used CSEs depends on the intended purpose of application. They can be used as amperometric sensors for the determination of both inorganic (3–5) and organic analytes (6, 7), in voltammetry (8–11), chronopotentiometry [potentiometric stripping analysis (PSA) (12, 13)], and as amperometric sensors in HPLC (14), in flow-injection analysis (15, 16), in capillary electrophoresis (17), and in electrochemiluminescence (ECL) devices (17). The measurements can be realized both in aqueous and in non-aqueous solutions (18, 19); some CSEs are even used for analysis of air and gases (20, 21). CSEs can be used for routine determinations (22) as well as for research purposes, e.g., investigation and construction of array of microelectrodes (23, 24). The occurrence of underpotential deposition effect (UPD) effect on CSEs (8–10) extends their analytical applicability in comparison with hanging mercury drop electrode (HMDE). Previous reviews on these topics [e.g., (2, 3, 25–32)] were limited as far as matrix or analytes are concerned.

Dedicated to the Memory of Professor Jaroslav Heyrovský on the occasion of the 50th Anniversary of the Nobel Prize for polarography.

Address correspondence to Tomas Navratil, J. Heyrovský Institute of Physical Chemistry of AS CR, v.v.i., Dolejškova 3, CZ-182 23 Prague 8, Czech Republic, E-mail: Tomas.Navratil@jh-inst.cas.cz

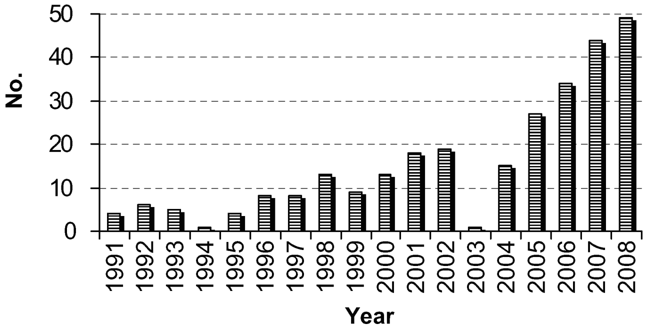

FIG. 1. The number of publications on the subject "composite solid electrodes" identified by Web of Science (33).

Therefore, this review is an attempt to critically evaluate the present situation in the field of analytical applications of CSEs. It is mostly focused on our own recent results in the context of the general development in the field. Nevertheless, some other interesting applications of this type of electrode materials are mentioned as well.

PROPERTIES OF COMPOSITE SOLID ELECTRODES

CSEs can be classified in several ways. The "classical" scheme proposed about 20 years ago (25, 32) has been most frequently used. We updated this scheme taking into account new types of composite electrodes (Fig. 2). The CSEs described in the following paragraphs belong to the group of composite electrodes with randomly dispersed minimally two components, which exhibit after their mixing solid consistency. These electrodes are, excepting consistency, in a way analogous to carbon paste electrodes (CPE) (34, 35), which are discussed in another paper in this special issue (35). We focused in this manuscript on the application of CSEs, in which the insulator phase is represented by a polymeric material [e.g., acrylic polymer (9, 31), epoxy resin (11, 31), polyvinyl chloride (PVC) (15), Teflon® (31, 36), vinyl acetate (31), polyester (31), polyethylene (31), etc.] (Fig. 2). The conductor phase can be a metal [silver, gold, etc. (9, 37)], a non-metallic conducting material [e.g., graphite powder (11, 38)] or their mixture (9, 10, 37). Some other components can be added to bulk electrode material to achieve requested properties for the determination of some analytes, e.g., cobalt phthalocyanine (39), Cu_2O (15, 40), Ni/Cu (14), hexacyanoferrate (6, 41, 42), manganese (41, 42), methylene blue (40), Ru[(tpy)(bpy)Cl]PF_6 (43, 44), or their mixtures (41, 42). CSEs are mostly applied in a polished form. Nevertheless, their surface can be also modified, e.g., by mercury film (23, 24, 45), mercury meniscus (23), by Nafion (40, 46), silica gel (31, 47, 48), by a catalyzer [e.g., tyrosinase (49), glucose oxidase

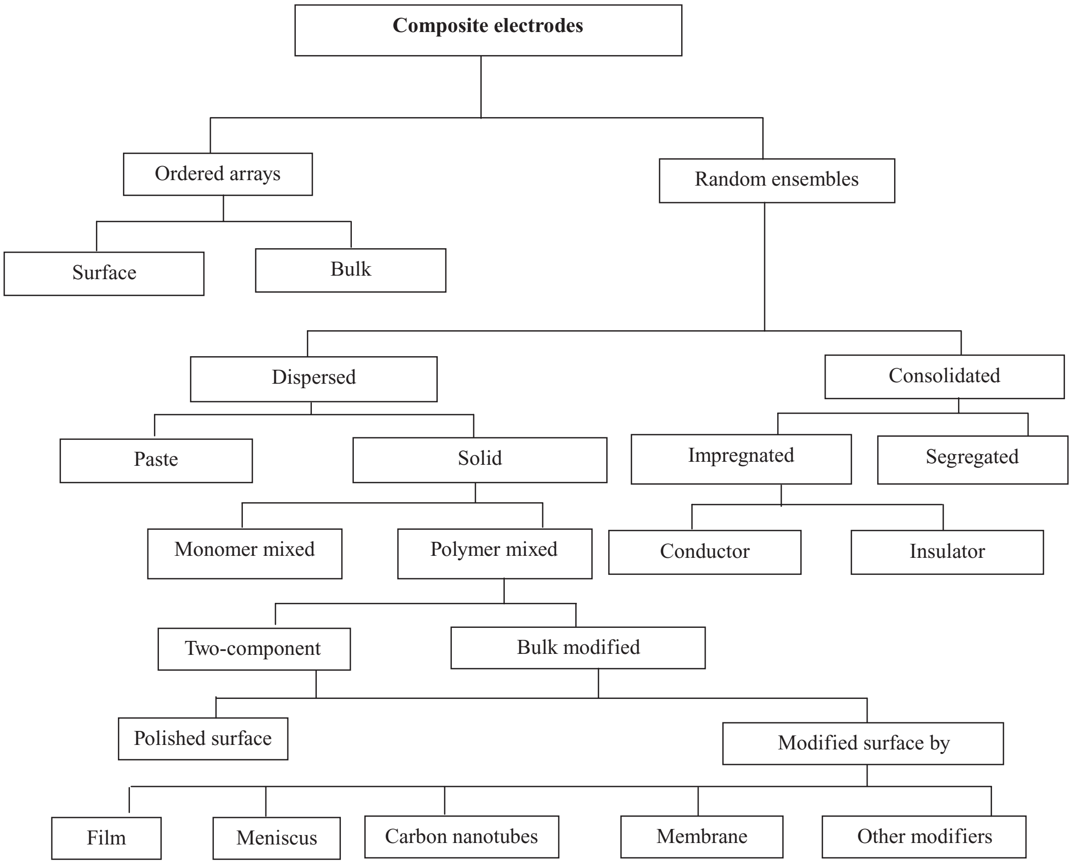

FIG. 2. A classification scheme for composite electrodes employed in analytical chemistry.

(50, 51), Nafion/protein (52), Au-Pd (31), RuO_2 (31)], by multiwalled carbon nanotubes (MWNT) (53–55), or gold nanowires (56). Such coating layers play the "passive" role [sorting of the molecules electrolyzed on the surface] or "active" catalytic role [enzymes (57)] (Fig. 2). Despite the high content of insulator phase (90–40%), the conductivity of CSEs is comparable with the conductivity of the pure conductive phase. This effect is explained by so-called percolation theory (25, 32, 58, 59). Some CSEs with random distribution of conducting particles exhibit properties of an array of microelectrodes (8–10, 23, 24, 32, 45), i.e., the measurements (in ideal cases) are not affected by oxygen, the signal is wave-shaped (sigmoidal) (3, 24, 25), partly independent of solution stirring (3, 23, 24). Structures and surfaces of CSEs have been studied by many various techniques, such as cyclic voltammetry and related techniques, coulometry (2, 3, 31, 60), optical microscopy, scanning electron microscopy (SEM) [in investigation of polished (3, 25, 38, 61, 62) or meniscus or film modified electrodes (3, 23)], electrochemical impedance spectroscopy (63), capacitance measurements (32), X-ray diffraction (XRD) (62, 64), atomic force microscopy (AFM) (62, 63, 65), energy dispersive X-ray analysis (EDX) (62, 66), X-ray photoelectron spectroscopy (XPS) (32, 64), and electrogenerated chemiluminiscence (ECL) imaging (32). A relatively new mathematical method—elimination voltammetry with linear scan (EVLS) (67–71)—can be used for revealing and the description of processes realized on the surface of CSEs (11, 38, 48). The usable potential window of CSEs is relatively broad and it can be tuned by their composition or by the way of their preparation. Working potentials of three composite electrodes (2, 3, 23) (silver solid amalgam composite electrode [p-AgSA-CE], silver composite solid electrode [CAgE], and graphite solid composite electrode [CCE]) most frequently used in our laboratory are compared in Table 1. For comparison, potential windows for p-AgSAE and HMDE are given as well.

FABRICATION OF COMPOSITE SOLID ELECTRODES

The composition of the CSEs can be adjusted according to the purposes of the use and they can be very easily prepared in any lab. Nevertheless, it is necessary to be very particular about the reproducibility of the surface area and shape in small-scale production. The electrode materials can be pressed into a cylindrical electrode body (Teflon, polyethylene, perspex, etc.) or it can be fixed on some substrate in practically any form (Fig. 3). Because the insulator material (e.g., epoxy resin) usually exhibits very good affinity to the electrode body or substrate material, the electrode constructions are relatively stable. It enables simple renewal of their surface or preparation of disposable sensors. In some cases it is necessary to choose a proper electrode body and material which is not damaged by the solvent used [e.g., methanol damages epoxy resin (72)]. There are many procedures for fabrication of CSEs and practically each author prepares them according to its own procedure. We can mention some of the relatively easiest and most reliable ways of their preparation (9, 11, 37, 72, 73), which were successfully realized in our lab: Firstly, the appropriate amount of conductor phase [e.g., silver (9, 10) or gold (37)] is homogenized with modifier [e.g., graphite (8–10)] in a pan. The particle size of metallic parts is usually 1–100 μm, mostly 5–10 μm, and of graphite usually below 50 μm (5, 38, 74, 75). Gold, prepared by reduction of Au(III) chloride solution with sulfur dioxide, has particle size of 50 μm (37). Silver solid amalgam (AgSA) (76–79) is to be freshly prepared by mixing of the silver particles (size 5–10 μm) with liquid mercury and a crystalline form of amalgam must be formed [final composition of such AgSA: Ag 40% and Hg 60%, crystalline form Ag_2Hg_3 (69, 80)]. The insulator phase is usually prepared separately, because in many cases polymers are prepared from two or more components [e.g., metacrylate resin Superacryl Plus® (Spofa, Prague, Czech Republic) (3, 9, 10), the resin consists of two basic parts: polymethylmetacrylate and methylmetacrylate monomer], and the hardening process can be faster than conducting phase preparation (from minutes up to a few days). It is necessary to mix these parts according to the rules given by the producer or according to the intended purposes (9, 11, 37, 72, 73).

The appropriate amount of homogenous insulator phase is added to the homogeneous phase of conductor and bulk modifier. The optimum ratio of these two parts varies, graphite—epoxy resin electrode contains 10–30% of graphite (11, 74), metallic (e.g., silver or gold) composite electrode contains 10–40% of metal and about 15% of graphite (9, 10). The bulk modifier content usually ranges from tenths to tens per cents, e.g., the amount of added graphite to silver-methacrylate electrode is about 15% (9, 10, 72). The content of the conducting phase can be expressed directly in the name (abbreviation) of the electrode, e.g., "CCENo" was prepared from No % of graphite powder and from (100–No) % of epoxy resin (72, 74, 75). After a short time of polymerization (a few minutes) (2) the thus-created paste is pressed into the electrode body or is placed on the electrode substrate, where the complete polymerization process is carried out. The course of this process can, in some cases, be very simple (under room temperature and pressure); in other cases it is necessary or advisable to put the formed electrode material into the oven, where the temperature is regulated in dependence on time (9, 10, 24). Such a controlled process can be very complicated in dependence on polymerization material, conducting phase, intended surface, etc. The electric contact can be realized by filling the inner part of the electrode body with graphite powder (8) into which a wire is inserted, by insertion of the contact wire directly into the composite material before polymerization (23), or by a drop of mercury placed on the internal surface of the composite material (24). The surface of the composite electrodes must be adjusted into a suitable form, e.g., by polishing by emery papers of various granulity and finally with alumina paste of various granulity (1–0.1–0.03 μm) (23). Similar polishing must be performed in case of any mechanical

TABLE 1
Ranges of working potentials in V of 3 composite electrodes and 2 metalic electrodes obtained with DCV at scan rate 20 mV/s

Electrode	Composition	Electrode area [mm^2]/current range [μA]/current range density [μA/mm^2]	0.1 M $HClO_4$		0.1 M HCl		0.1 M acetate buffer pH 4.55		0.05 M borax buffer pH 9.2		0.1 M NaOH	
p-AgSA-CE	(Ag_2Hg_3) : epoxy 80:20	6.61/1/0.15	−1.09	+0.45	−1.07	+0.15	−1.31	+0.40	−1.63	+0.52	−1.85	+0.17
CAgE20	Silver : graphite: polyacrylate 20:30:50	0.78/20/25.5	−0.85	+0.37	−0.80	+0.12	−1.15	+0.52	−1.65	+0.60	−1.74	+0.35
CCE30	Graphite : epoxy 30:70	0.78/1/1.27	−1.90	+1.70	−1.65	+1.40	−1.80	+1.60	−2.15	+1.90	−2.19	+1.60
HMDE	100 % Hg	1.01/1/0.99	−1.19	+0.44	−1.27	+0.11	−1.70	+0.31	−1.98	+0.15	−1.85	+0.07
p-AgSAE	Ag:Hg : 2:3	0.38/1/2.6	−1.12	+0.45	−1.12	+0.11	−1.51	+0.31	−1.88	+0.16	−1.96	−0.06

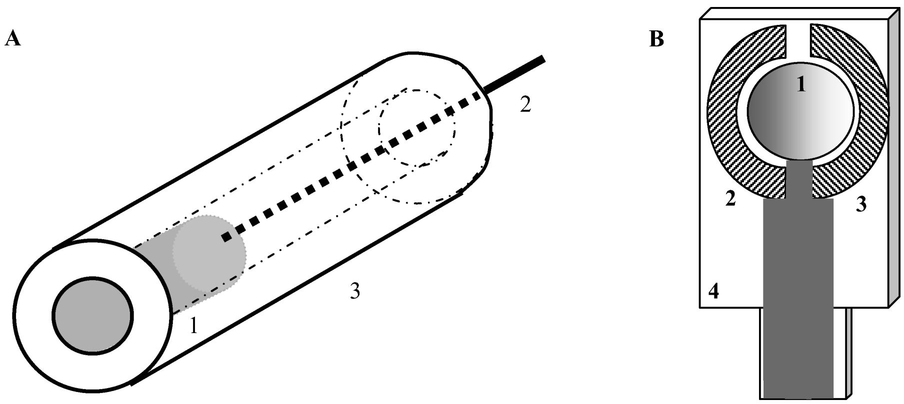

FIG. 3. Schemes of two different arrangements of composite electrodes. **A**—Disk electrode: (1) composite electrode material, (2) electrical contact, (3) electrode body. **B**—Screen printed disposable sensor: (1) working electrode made of solid composite material, (2) reference electrode, (3) auxiliary electrode, (4) sensor substrate.

surface damage or if it is not possible to remove some adsorbed compound electrochemically (74).

There are many other ways to fabricate CSEs. For example, so-called sol-gel electrodes are prepared in liquid form and then they are solidified. The active parts are added to the electrode matrix before or during gelatation (81). Surfaces of CSEs [e.g., SA-CE (23) or silica gel modified CCE (SiGCCE) (45)] can be modified in various ways [e.g., by electrolytic deposition of the mercury film (in situ [45] or before the start of the measurement on the solid surface [23]) or by formation of mercury meniscus (by short dipping of the electrode into liquid mercury) [e.g., m-AgSA-CE (23)]. The surface can be modified by an electrochemically active film as well [e.g., chemical derivatization of lead atoms at the surface of the sol-gel electrode matrix by immersing of the electrode into a solution of sodium pentacyanonitrosylferrate (82) or preparation of MF-AgSA-CE (23)]. A one-step method of the deposition of hybrid mesoporus thin films on various electrode surfaces was described in (83).

PRE-TREATMENT OF COMPOSITE SOLID ELECTRODES

As in the case of other solid electrodes, activation and regeneration processes are frequently applied to eliminate problems with passivation and to renew electrode surface. The details of this procedure depend on the particular electrode, matrix, analyte, and application. For measurements in flowing systems, the danger of passivation is lower because possibly passivating compounds are frequently removed by the flowing medium (14). In the case of batch analysis it is necessary to perform either mechanical (usually after a few weeks of the utilization) or electrochemical pre-treatment of the surface (3).

Electrochemical activation is to be carried out after fabrication, polishing, certain time of inactivity, or after surface modification (8–10). It can last several minutes, but it can be automated by proper controlling software of the computer-controlled instrument used (84). This activation is achieved by periodical polarization (tens to hundreds of cycles with the scan rate of hundreds or thousands mV/s (3) or by potential jumps between two cleaning potentials (E^1_{Cl}, E^2_{Cl}) (38) [e.g., by 50–100 mV more positive than the potential of hydrogen evolution and by 50–100 mV more negative than the potential of electrode material dissolution or supporting electrolyte decomposition (3)]. Another possibility is to apply a selected potential for a given time-interval, usually in the supporting electrolyte used for the further voltammetric measurement (23, 37). The parameters of activation (regeneration) processes for different electrodes are listed in Table 2.

Electrochemical regeneration usually takes from 5 seconds to 2 minutes before each new scan or set of records to guarantee good repeatability (9–11, 72). Only in special cases mechanical removal of formed reaction products by wet filtration paper is necessary [e.g., determination of aminonaphthalene at graphite solid composite electrode (CCE) (38)]. The electrochemical regeneration is usually based on switching between positive and negative potentials or on application of a constant potential for defined time. In comparison with activation, the time intervals are shorter, number of cycles lower, and the potential limits are narrower in dependence on type and quantity of undesired compounds on the electrode surface (Table 2). Nevertheless, despite of very careful surface preparation, it is advisable to repeat each measurement minimally three times, the first two records usually being omitted.

DETERMINATION OF INORGANIC SUBSTANCES

CSEs are applicable for both metals (Pb, Tl, Cd, Ag, Bi, etc.) and some anions (Cl^-, Br^-, etc.) determination (see Table 3). For determination of metals, it is possible to utilize the so-called UPD effect (85, 86), i.e., the existence of a very sensitive monolayer peak of the analyte in area of very low concentrations (8–10). The careful preparation of the electrode surface plays a very important role. CCE was used for differential pulse adsorptive stripping voltammetry (DPASV) determination of lead (monolayer peak at about −430 mV and bulk peak at about −540 mV) (5). In the case of a simultaneous deposition of two metals on the

TABLE 2

Conditions for activations and regenerations of composite electrodes based on several scans between E_{Cl}^{1} and E_{Cl}^{2} at given scan rate with t_{Cl}^{1} and t_{Cl}^{2} time delays at E_{Cl}^{1} and E_{Cl}^{2}, respectively. The potentiostatic conditioning can follow at E_{cond} for t_{cond} (S.E.— the procedure is realized in supporting electrolyte applied for the determination; E_{acc}—the applied potential is to be equal to the accumulation potential)

Substance (electrode)	Type	Medium	No. of scans	Scan rate [mV/s]	E_{Cl}^{1} [mV]	t_{Cl}^{1} [s]	E_{Cl}^{2} [mV]	t_{Cl}^{2} [s]	E_{cond} [mV]	t_{cond} [s]	Ref.
Graphite-Epoxy electrode (CCE)											
All analytes	Activation	S.E.	100	500	−950	0	+1200	0			(38)
Manganese, amino naphthalene, adenine, guanine	Regeneration	S.E.	50	500	−950	0.1	+1200	0.1			(38)
Alizarine chrome black PT	Regeneration	S.E.	200	500	−950	0.1	+1200	0.1	−950	5	(74)
Graphite-Metallic electrode (CMeE)											
Nitrites, nitrates (CAgE)	Activation	S.E.	50	250	−100	0	−1500	0			(3, 9, 10)
Nitrites, nitrates (CAgE)	Regeneration	S.E.	50	250	+100	0.2	−1500	0.2			(3, 9, 10)
Pb,Cd, Cu, Tl, Bi (CAgE)	Regeneration	S.E.	50	500	−150	0.2	−900	0.2	+250	25	(8–10)
Halides (CAgE)	Regeneration	S.E.	50	500	+350	0.1	−900	0.1		5	(96)
Arsenic (CAuE)	Regeneration	H_2SO_4	50	500	+1900	0	+200				(37)
Arsenic (CAuE)	Regeneration	S.E.							2500	5	(37)
Alizarine chrome black PT (CAgE)	Regeneration	S.E.	200	500	−950	0.1	+350	0.1	−950	5	(74)
Graphite—Silica gel (SiGCCE)											
Silver	Activation	S.E.							500	30	(24)
Silver	Regeneration	S.E.							500	30	(24)
Solid amalgam—epoxide (AgSA-CE)											
All analytes	Activation	0.1 M KCl							−2200	30	(23)
All analytes	Regeneration	S.E.	50	0	−1500	0.3	−200	0.2			(23)

TABLE 3

Examples of determinations of inorganic analytes at solid composite electrodes (S.E.—supporting electrolyte, BR—Britton-Robinson buffer, AB—Acetate buffer, PB—Phosphate buffer, BB—Borate buffer, LOD—limit of detection)

Analyte	Electrode/technique	S. E.	LDR [g/L]	LOD [g/L]	Ref.
		Graphite-Epoxy electrode (CCE)			
Mn	CCE (30:70)/DPV	0.05M $Na_2B_4O_7$	$0.3 \cdot 10^{-3}$–$3.3 \cdot 10^{-3}$	$0.15 \cdot 10^{-3}$	(38)
Pb	CCE (30:70)/DPV	0.1 M KCl + 0.01 M HCl	$5 \cdot 10^{-6}$–$350 \cdot 10^{-6}$	$3 \cdot 10^{-6}$	(5)
Cd	CCE (30:70)/DPV	0.1 M KCl + 0.01 M HCl	$0.1 \cdot 10^{-3}$–$10 \cdot 10^{-3}$	$0.1 \cdot 10^{-3}$	(5)
Tl	CCE (30:70)/DPV	0.1 M KCl + 0.01 M HCl	$50 \cdot 10^{-6}$–$10 \cdot 10^{-6}$	$10 \cdot 10^{-3}$	(5)
Pb	CCE/DPV	0.1 M HCl	$10 \cdot 10^{-6}$–$150 \cdot 10^{-6}$	$10 \cdot 10^{-6}$	(87)
Cd	CCE/DPV	0.1 M HCl	$100 \cdot 10^{-6}$–$150 \cdot 10^{-6}$	$100 \cdot 10^{-6}$	(87)
Cu	CCE/DPV	0.1 M HCl	$50 \cdot 10^{-6}$–$150 \cdot 10^{-6}$	$50 \cdot 10^{-6}$	(87)
		Graphite-Metallic electrode (CMeE)			
As	CAuE20/DPV	0.7 M KCl + 0.1 M H_2SO_4	$0.4 \cdot 10^{-6}$–$250 \cdot 10^{-6}$	$0.32 \cdot 10^{-6}$	(37, 88)
Nitrates	CAuE20/DPV	0.1 M NaOH	$5 \cdot 10^{-6}$–$400 \cdot 10^{-6}$	$4.5 \cdot 10^{-6}$	(9)
Pb	CAgE20/DPV	0.1 M $HClO_4$+ 0.01 M KCl	$0.1 \cdot 10^{-6}$–$100 \cdot 10^{-6}$	$3.0 \cdot 10^{-6}$	(8)
Cu	CAgE20/DPV	0.1 M $HClO_4$+ 0.01 M KCl	$0.1 \cdot 10^{-3}$–$10 \cdot 10^{-3}$	$0.1 \cdot 10^{-6}$	(8)
Cd	CAgE20/DPV	0.05 M NaF	$1 \cdot 10^{-6}$–$750 \cdot 10^{-6}$	$1 \cdot 10^{-6}$	(8)
Tl	CAgE20/DPV	0.1 M $HClO_4$+ 0.005 M KCl	$10 \cdot 10^{-6}$–$1000 \cdot 10^{-6}$	$10 \cdot 10^{-6}$	(8)
Cl^-	CAgE20/DPV	0.1 M HNO_3	$1 \cdot 10^{-3}$–$60 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	(9, 73, 96)
Br^-	CAgE20/DPV	0.1 M HNO_3	$1 \cdot 10^{-3}$–$50 \cdot 10^{-3}$	$0.1 \cdot 10^{-3}$	(96)
I^-	CAgE20/DPV	0.1 M HNO_3	$1 \cdot 10^{-3}$–$15 \cdot 10^{-3}$	$0.3 \cdot 10^{-3}$	(96)
		Carbon ceramic electrode modified by copper complex			
Bromates	Cu-CCeE/CV	0.1 M PB, pH 2.3	$64 \cdot 10^{-6}$–$25 \cdot 10^{-3}$	$13 \cdot 10^{-6}$	(97)
		Graphite-polymer electrode			
Mn	Graphite-styrene-acrylonitrile copolymer/SWV	Acetate-ammonium buffer (pH 9)	$0.2 \cdot 10^{-6}$–$10 \cdot 10^{-6}$	$0.2 \cdot 10^{-6}$	(89)
		Graphite-Silica gel (SiGCCE)			
Ag	SiGCCE/DPV	0.1 M KNO_3	$1 \cdot 10^{-3}$–$50 \cdot 10^{-3}$	$1 \cdot 10^{-6}$	(24)
Pb	SiGCCE/DPV	0.1 M KNO_3	$2 \cdot 10^{-6}$–$5 \cdot 10^{-2}$	$2 \cdot 10^{-6}$	(45)
		Solid amalgam—epoxide (AgSA-CE)			
Pb	p-AgSA-CE/DPV	AB 0.1 M, pH 4.8	$5 \cdot 10^{-6}$–$1500 \cdot 10^{-6}$	$15 \cdot 10^{-6}$	(23)
Cd	p-AgSA-CE/DPV	AB 0.1 M, pH 4.8	$5 \cdot 10^{-6}$–$5000 \cdot 10^{-6}$	$15 \cdot 10^{-6}$	(23)
Cu	p-AgSA-CE/DPV	AB 0.1 M, pH 4.8	$50 \cdot 10^{-6}$–$5000 \cdot 10^{-6}$	$120 \cdot 10^{-6}$	(23)
Iodates	p-AgSA-CE/DPV	NaOH, 0.1 M	$0.5 \cdot 10^{-3}$–$10 \cdot 10^{-3}$	$0.12 \cdot 10^{-3}$	(23)
Tl	m-AgSA-CE/DPV	AB 0.1 M, pH 4.8	$5 \cdot 10^{-6}$–$100 \cdot 10^{-6}$	$15 \cdot 10^{-6}$	(23)

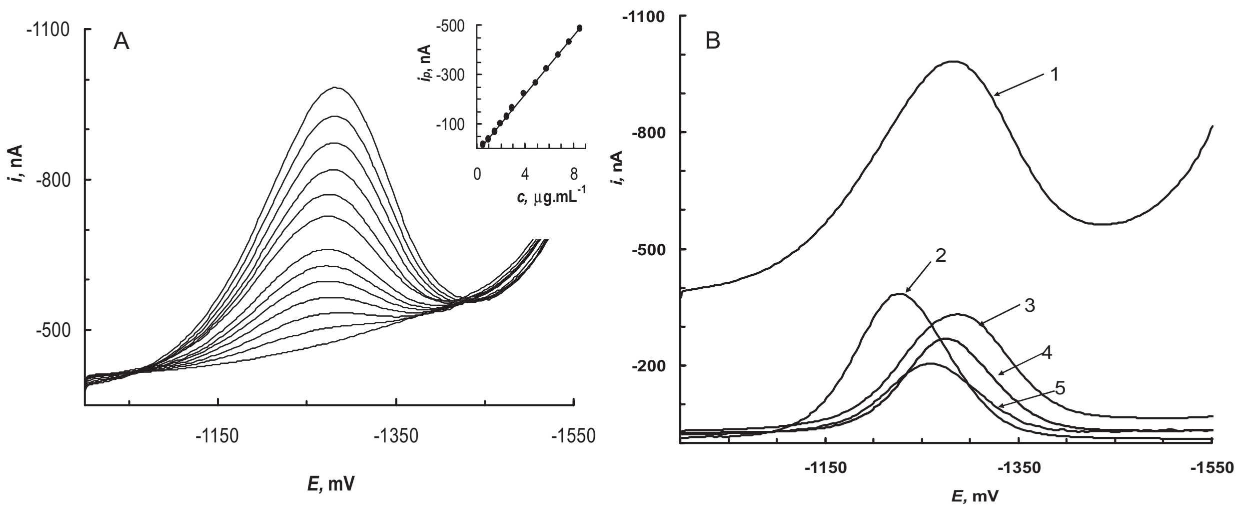

FIG. 4. A—DP voltammograms of iodates on m-AgSA-CE; **A—**concentration dependence from 0.5 to 8.58 μmol/L. **B—**comparison of DP voltammograms of iodates (8.58 μmol/L) on various electrodes: 1—m-AgSA-CE, 2—HMDE, 3—m-AgSAE, 4—m-CuSAE, 5—p-AgSAE; DPV; supporting electrolyte–0.1 M NaOH; $v = 20$ mV/s.

surface of the composite electrode, the anodic dissolution of the metal, which is anodically dissolved at more negative potential, is substantially affected by the presence of the other deposited metal (5, 8–10). CCE 30 can be utilized for determination of Tl(I) using monolayer as well as bulk peak. At the DPASV determination of Pb in the presence of Tl, the anodic dissolution process of deposited Pb is not affected by the dissolution process of Tl, which occurs at more negative potential. The determinations are only little affected by the presence of surface active substances (SAS) (5).This electrode was further used for determination of lead in tap water—reached LODs on CCEs are higher in comparison with mercury ones; nevertheless, they are sufficient according to the valid standards for drinking water (3, 5, 87). This type of electrode can be applied in batch as well as flow-through measurements (87). Carbon composite solid electrode modified with 10% silica gel (SiGCCE) was used for the preparation of mercury film electrodes (MFE) applicable for ASV determination of Cu, Pb, Zn, and Cd. This electrode partly behaves as a set of microelectrodes (24) and was used for the determination of metals in used motor oil (45). Solid composite silver electrodes (CAgE), in which a certain part of graphite is replaced by metallic silver, were used for ASV of Pb(II). Higher graphite content (i.e., higher conductivity) improved the quality of the recorded curves.The UPD effect was observed on both electrodes, with and without graphite. The electrochemical reaction occurs preferably on the metallic particles in the electrode mixture [in a good agreement with literature (85) p. 145]. Nevertheless, in contrast with (85), it was confirmed that the UPD effect exists on a graphite surface as well. The sensitivity to Cu is much lower than to Pb probably due to its complicated deposition on the CAgE surface (8). Differential pulse anodic stripping subtractive voltammetry (DPASSV) (mathematical subtraction of the curves recorded with and without application of analyte accumulation) (3) was successfully tested for easier evaluation of results at low concentrations of Pb(II). Unfortunately, both the monolayer and the bulk of Pb peaks at CAgE are affected by the presence of other metals (8). However, CAgE is suitable for determination of mentioned metals in natural water samples even without sample pre-treatment and gives results comparable with HMDE (8). Solid amalgam composite electrodes (SA-CE) give the best reproducible results due to a high content of conducting, mercury-containing particles in the electrode material. The UPD effect is not observable on SA-CE (23), similarly as on other amalgam and generally mercury-containing electrodes. The accumulation step was applied in Tl(I) determination at m-AgSA-CE (23). As can be determined using CAuE (37, 88), which can be applied for the determination of Cu, too. Because only As(III) is electrochemically active, it is necessary to prevent the oxidation of As(III) immediately after sampling (37). CCE30 can be used for oxidation of Mn(II) to an insoluble hydrated dioxide, which is accumulated on the electrode and offers a well defined peak during its electrochemical reduction (38, 89). Square wave voltammetric (SWV) determination at a graphite-styrene-acrylonitrile copolymer electrode (89) is much more sensitive. SiGCCE proved to be a useful sensor for the determination of Ag(I) ions in waters (24). The FIA-determination of silver and of other noble metals can be successfully realized using graphite-PVC electrode (90). We can also mention determination of hexacynaoferate using SiGCCE (24) or of Se(IV) using ceramic composite (sol-gel and screen-printed) electrodes in mineral and natural waters (91). Bismuth film-modified electrode with incorporated highly conductive ionic liquids 1-butyl-3-methyl-imidazolium hexafluorophosphate in a solid matrix [poly(sodium 4-styrenesulfonate), silica, and Nafion] at glassy carbon was used for Cd(II) and Pb(II) (92). Solid graphite-epoxy composite electrode was used for PSA determination of Pb(II),

TABLE 4
Examples of determinations of organic substances at solid composite electrodes (S.E.—supporting electrolyte, BR—Britton-Robinson buffer, AB—Acetate buffer, PB—Phosphate buffer, BB—Borate buffer, LOD—limit of detection)

Substance	Electrode/technique	S. E.	LDR [mol/L]	LOD [mol/L]	Ref.
		Graphite-epoxy electrode (CCE)			
Alizarine chrome black PT	CCE (30:70)/DPV	BR, pH 8	$2\cdot 10^{-6}$–$16\cdot 10^{-6}$	$0.4\cdot 10^{-6}$	(74)
2-Amino naphtalene	CCE (30:70)/DPV	BR, pH 8	$5\cdot 10^{-6}$–$90\cdot 10^{-6}$	$0.9\cdot 10^{-6}$	(38)
Phenylglyoxylic acid in urine	CCE (30:70)/DPV	BR, pH 2	$4\cdot 10^{-5}$–$7\cdot 10^{-4}$	$4\cdot 10^{-5}$	(11)
Adenine	CCE (30:70)/DPV	BR, pH 8	$1\cdot 10^{-4}$–$2.5\cdot 10^{-4}$	$0.9\cdot 10^{-6}$	(38)
Guanine	CCE (30:70)/DPV	PB, pH 7	$1\cdot 10^{-4}$–$2.5\cdot 10^{-4}$	$1\cdot 10^{-4}$	(38)
2-Nitronaphtalene	CCE (30:70)/DPV	BR, pH 10	0–$30\cdot 10^{-6}$	$2\cdot 10^{-6}$ (LOQ)	(75)
6-Nitroquinoline	CCE (30:70)/DPV	BR, pH 11	$20\cdot 10^{-6}$–$100\cdot 10^{-6}$	$21\cdot 10^{-6}$ (LOQ)	(75)
5-Nitrobenzimidazole	CCE (30:70)/DPV	BR, pH 9	10–$100\cdot 10^{-6}$	$10\cdot 10^{-6}$(LOQ)	(75)
Ascorbic acid in cosmetic products	CCE/DPV	0.1M PB, CH_3OH 70%, pH 4	$5\cdot 10^{-5}$–$1.7\cdot 10^{-3}$	$9\cdot 10^{-7}$	(104)
Magnesium ascorbyl phosphate in cosmetic products	CCE/DPV	0.1M PB, CH_3OH 70%, pH 4	$3\cdot 10^{-5}$–$1\cdot 10^{-3}$	$2\cdot 10^{-6}$	(104)
Ascorbyl palmitate in cosmetic products	CCE/DPV	0.1M PB, CH_3OH 70%, pH 4	$2\cdot 10^{-5}$–$7\cdot 10^{-4}$	$2\cdot 10^{-7}$	(104)
Ascorbic acid in fruit juices and vitamin tablets	CCE modified with cobalt phthalocyanine/FIA, DPV	0.05 M PB, pH 5	$2.5\cdot 10^{-5}$–$1\cdot 10^{-3}$	$1.3\cdot 10^{-5}$	(105)
Octyl salicylate in sunscreens	CCE /DPV	0.1 M tetrabutyl ammonium perchlorate in DMSO	$4\cdot 10^{-5}$–$2\cdot 10^{-3}$	2.10^{-5}	(18)
		Graphite-metacrylate electrode (CME)			
Tryptophan in feed	CME/CV	0.1 M KCl + 0.1 M phosphate, pH 7.5	$6\cdot 10^{-6}$–$2\cdot 10^{-5}$	6.10^{-6}	(106)
Cysteine	CME/CV	0.1 M KCl + 0.1 M phosphate	$2\cdot 10^{-5}$–$6\cdot 10^{-5}$		(107)
Tryptophan	CME /CV	0.1 M KCl + 0.1 M phosphate	$1.6\cdot 10^{-6}$–$5\cdot 10^{-5}$		(107)
Tyrosine	CME /CV	0.1 M KCl + 0.1 M phosphate	$2\cdot 10^{-5}$–$6\cdot 10^{-5}$		(107)
		Graphite-metallic electrode (CMeE)			
Nitrates	CAgE20/DPV	0.01M KCl	1.10^{-4}–$5\cdot 10^{-3}$	1.10^{-4}	(9)
Alizarine chrome black PT	CAgE20/DPV	BR, pH 7	$2\cdot 10^{-6}$–$10\cdot 10^{-5}$	$1.8\cdot 10^{-6}$	(74)
Dopamine	CAgE-Nafion	0.1 M KNO_3, pH 7	$6.6\cdot 10^{-6}$–$1.2\cdot 10^{-3}$	$1.4\cdot 10^{-6}$	(46)
1-Nitronaphtalene	CAgE20/DPV	BR, pH 9, CH_3OH (4%)	$0.2\cdot 10^{-6}$–$100\cdot 10^{-6}$	$0.3\cdot 10^{-6}$ (LOQ)	(98)
2-Nitronaphtalene	CAgE20/DPV	BR, pH 9	0–$100\cdot 10^{-6}$	$9\cdot 10^{-6}$ (LOQ)	(75)
6-Nitroquinoline	CAgE20/DPV	BR, pH 10	$10\cdot 10^{-6}$–$100\cdot 10^{-6}$	$12\cdot 10^{-6}$ (LOQ)	(75)
5-Nitrobenzimidazole	CAgE20/DPV	BR, pH 9	0–$100\cdot 10^{-6}$	$37\cdot 10^{-6}$ (LOQ)	(75)

(*Continued on next page*)

TABLE 4
Examples of determinations of organic substances at solid composite electrodes (S.E.—supporting electrolyte, BR—Britton-Robinson buffer, AB—Acetate buffer, PB—Phosphate buffer, BB—Borate buffer, LOD—limit of detection) (Continued)

Substance	Electrode/technique	S. E.	LDR [mol/L]	LOD [mol/L]	Ref.
Graphite-PVC (GPVCE)					
Quercetin in ginkgo biloba	GPVCE/RP-HPLC	methanol–acetonitrile–NaClO4 (0.1 M) (30:30:40, v/v/v)	$1.9\cdot 10^{-3}$–$8.9\cdot 10^{-3}$	$1.6\cdot 10^{-5}$	(108)
Quercetin in ginkgo biloba	GPVCE/NP-HPLC	hexane–dioxane–methanol with LiCl (0.1%, w/v) (50:25:25, v/v/v)	$3.6\cdot 10^{-4}$–$3.9\cdot 10^{-3}$	$3.5\cdot 10^{-6}$	(108)
Kaempferol in ginkgo biloba	GPVCE/ RP-HPLC	methanol–acetonitrile–NaClO4 (0.1 M) (30:30:40, v/v/v)	$2.0\cdot 10^{-3}$–$9.4\cdot 10^{-3}$	$1.6\cdot 1.^{-5}$	(108)
Kaempferol in ginkgo biloba	GPVCE/ NP-HPLC	hexane–dioxane–CH3OH+LiCl (0.1%, w/v) (50:25:25, v/v/v)	$3.56\cdot 10^{-6}$–$3.8\cdot 10^{-3}$	$3.5\cdot 10^{-6}$	(108)
Dopamine	GPVCE/DPV	0.1M PB, pH 7.4	$4\cdot 10^{-7}$–$1.6\cdot 10^{-4}$	$2\cdot 10^{-7}$	(109, 110)
Uric acid	GPVCE/DPV	0.1M PB, pH 7.4	$2\cdot 10^{-7}$–$1.6\cdot 10^{-4}$	$1\cdot 10^{-7}$	(109, 110)
Glucose	GPVCE-Cu_2O/FIA	25 mM PB, pH 6.9	$1.1\cdot 10^{-3}$–10^{-2}	$1.1\cdot 10^{-3}$	(15)
Amalgam composite electrode					
p-Nitrophenol	m-AgSA-CE, DPV	AB, pH 4.8	$5\cdot 10^{-6}$–$85\cdot 10^{-6}$	$0.7\cdot 10^{-6}$ (LOQ)	(23)
Other solid composite electrodes					
Metallothionein (Cd, Zn)	Graphite+ paraffin oil+ silica gel	BB, pH 8.5	$1\cdot 10^{-6}$- $1\cdot 10^{-4}$	$1\cdot 10^{-6}$	(47, 48)
Dopamine	Sol-gel CCE/CE	25 mM PB, pH 6.5	$2\cdot 10^{-6}$–$8\cdot 10^{-4}$	$3\cdot 10^{-8}$	(111)
Epinephrine	Sol-gel CCE/CE	25 mM PB, pH 6.5	$5\cdot 10^{-6}$–$8\cdot 10^{-4}$	$6\cdot 10^{-8}$	(111)
Glucose	carbon/PVC-COOH/ferrocene + enzyme		$1\cdot 10^{-4}$–$2\cdot 10^{-2}$	$5\cdot 10^{-5}$	(51)
Ethanol	Cu-PVC, Ni/Cu-PVC	0.1M KOH			(14)
Butylated hydroxyanisole	Graphite-wax – Mn(II) hexacyanoferrate /DPV	0.1M NaCl	$5\cdot 10^{-7}$–$1.5\cdot 10^{-3}$	$5\cdot 10^{-8}$	(42)
Ascorbic acid	Graphite-wax – Mn(II) hexacyanoferrate/DPV	0.1M NaCl	$5.5\cdot 10^{-5}$–$1.4\cdot 10^{-3}$	$2.2\cdot 10^{-5}$	(41)
Ascorbic acid	Glassy carbon-Cu/DPV	pH 7	$1\cdot 10^{-6}$–$40\cdot 10^{-6}$	$1\cdot 10^{-9}$	(112)
Ascorbic acid in human urine	Glassy carbon-tetraphenylborate/DPV	pH 7	0.06-$25\cdot 10^{-6}$	$0.02\cdot 10^{-6}$	(113)
Dopamine in human urine	Co(II)-Tetrakisphenylporphyrin (CoTPP)- glassy carbon	pH 7	$0.06\cdot 10^{-8}$–$25\cdot 10^{-6}$	$2\cdot 10^{-8}$	(113)
Uric acid in human urine	Co(II)-Tetrakisphenylporphyrin (CoTPP)- glassy carbon	pH 7	$0.1\cdot 10^{-7}$–$35\cdot 10^{-6}$	$7\cdot 10^{-8}$	(113)

Butylated hydroxyanisole	Graphite-wax hexacyanoferrate /DPV	0.1M KNO_3, pH 6	$7.5\cdot 10^{-6}$–$8\cdot 10^{-4}$	$3.7\cdot 10^{-6}$	(114)
Butylated hydroxyanisole	Cobalt hexacyanoferrate-Graphite–paraffin/CV	0.1M NaCl, pH 7	$8\cdot 10^{-7}$–$2\cdot 10^{-4}$	$2\cdot 10^{-7}$	(6)
Hydroquinone in photographic developers	Graphite-castor oil polyurethane (60% of graphite, w/w)/DPV	0.1 M AB, pH 4	$1\cdot 10^{-6}$–$1\cdot 10^{-4}$	$9\cdot 10^{-7}$	(115)
Tricyclic antidepressant imipramine	Rigid graphite-polyurethane/SWV	0.1M BR, pH 7		$4.6\cdot 10^{-9}$	(116)
Dopamine	Glassy carbon-nano-Cu_2O-methylene blue		$1\cdot 10^{-7}$–$3\cdot 10^{-4}$	$4.6\cdot 10^{-8}$	(40)
Insulin	Carbon ceramic electrode –Ni-potassium octacyano-molybdate(IV)/FIA	pH 7.4	$5\cdot 10^{-10}$–$5\cdot 10^{-7}$	$4\cdot 10^{-10}$	(7)
Alkaline phosphatase in milk	Graphite-Teflon-tyrosinase/FIA	pH 8.5	$2\cdot 10^{-13}$–$2\cdot 10^{-11}$	$7\cdot 10^{-14}$	(49)
Cysteine	Carbon ceramic –Ru[(tpy)(bpy)Cl]PF_6/FIA	0.1M PB, pH 2	$5\cdot 10^{-6}$–$7\cdot 10^{-4}$	$1\cdot 10^{-14}$	(43)
Glutathione	Carbon ceramic –Ru[(tpy)(bpy)Cl]PF_6/FIA	0.1M PB, pH 2	$5\cdot 10^{-6}$–$7\cdot 10^{-4}$	$1\cdot 10^{-14}$	(43)
Insulin	Carbon ceramic –Ru[(tpy)(bpy)Cl]PF_6/FIA	0.1 M PB, pH 7	$5\cdot 10^{-10}$–$8\cdot 10^{-7}$	$4\cdot 10^{-10}$	(44)
Glucose	Ceramic-carbon- glucose oxidase –silicate/ electrochemiluminescence	0.1 M PB (pH 8.5)	$5\cdot 10^{-5}$–$1\cdot 10^{-2}$	$8\cdot 10^{-6}$	(50)

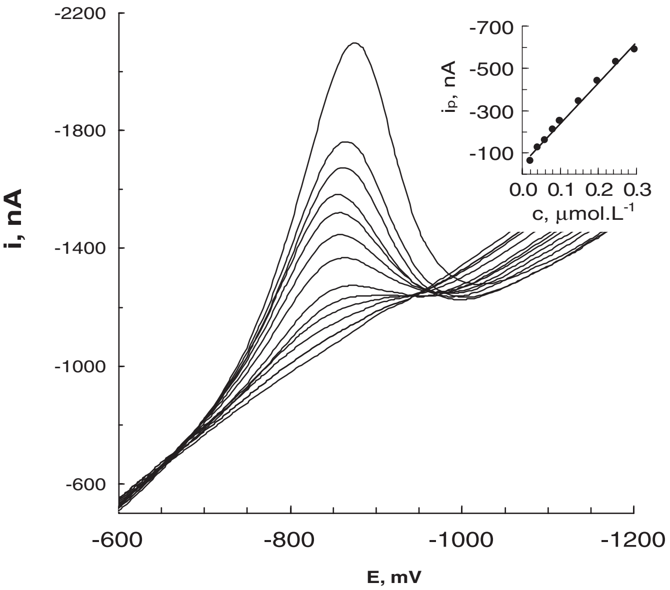

FIG. 5. DP voltammograms of adenine on m-AgSA-CE; concentration dependence from 0.02 to 0.03 μmol/L; supporting electrolyte 0.005 M NaOH and 5 μM Cu(II); $v = 20$ mV/s, $E_{\text{cond}} = -1800$ mV, $t_{\text{cond}} = 30$ s.

Cu(II), and Cd(II) (12). The UPD effect was used for very sensitive determination of Pb(II) at titanium-graphite electrodes (61). Iron(III) can be determined at a reactive electrode ("reactrode") made of silver(I), hexacyano-ferrate(III), graphite, and paraffin oil (93). NO_2 was determined in the air using Au/PVC composite electrode (20). Graphite-polystyrene composite electrode, containing an AgO-CuO catalyst, was used to measure electrochemical oxygen demand (94). Two different types of composite electrodes [CAgE20 (9) and clay-polypyrrole composite electrode covered by nitrate reductase (95)] were used for the determination of nitrates and nitrites. Parameters of electrochemical activation and regeneration are summarized in Table 2. The reproducibility can be improved by electrochemical regeneration applied before each new sample. CAgE was used for cathodic DC and DPSV determination of Cl^-, Br^-, and I^- (3, 96), CAgE20 and CAg15 being the most suitable for these purposes (Table 3). The presence of oxygen and low levels of SASs does not interfere (2, 3, 73, 96). Different accumulation potentials can be applied to improve the low selectivity (96). The achieved LODs are below standards for tap, mineral, and natural water and results are comparable with HMDE and Ag electrode (96). AgSA-CE can be used for the determination of iodates (23) in 0.1 M NaOH (see Fig. 4). It can be seen from Fig. 4B that the peaks of iodates at m-AgSA-CE are fully comparable with non-composite amalgam electrodes. Carbon ceramic electrode prepared by a sol-gel technique and modified with $[Cu(bpy)_2]Br_2$ copper complex was used for determination of bromates (97).

DETERMINATION OF ORGANIC SUBSTANCES

Many interesting applications of CSE are summarized in Table 4. It is possible to prepare tailor-made CSEs for specific tasks by adapting their bulk and/or surface composition. However, their practical utilization is somewhat limited by lower selectivity and sometimes by problems with their passivation. Moreover, many organic compounds gave peaks at the same potential, which requires a preliminary separation step. Interferents, reaction products, and other undesired compounds (e.g., SAS) can passivate the electrode, thus complicating the determination. Problems with passivation can be partially overcome by electrochemical or mechanical cleaning of the electrode or by measurements in flowing medium (2).

Easy reducibility of nitro group enables the determination of nitrated polycyclic aromatic hydrocarbons (NPAH) and nitrated heterocyclic compounds using composite electrodes. Four different electrodes [CAgE, CCE, m-AgSE-CE, metallic silver electrode (AgE)] were used for the determination of 1-nitro-naphtalene (1-NN) (98), 2-nitronaphtalene (2-NN), 6-nitroquinoline (6-NQ), 5-nitro-benzimidazole (5-NBI) (75), and 4-nitrophenol (23). The electrochemical pre-treatment of those electrodes was used to eliminate problems with passivation. The first recording should not be evaluated, which is common for solid electrodes. It is not necessary to eliminate the dissolved oxygen in the cases of AgE, CCE, and CAgE. CAg20 seems to be the most suitable (72, 75). Elimination voltammetry with linear scan (38, 68–70) was used for a detailed study of the electrode reaction. The results with CCE30 and AgCE20 are comparable with those gained using non-composite AgE (72, 75). CAgE20 and CCE30 can be used for the determination of easily reducible azo compounds as demonstrated on the example of Alizarine chrome black PT (74). DPV determination of ascorbic acid at m-AgSA-CE in 0.1 M NaOH gives LDR 10–767 μmol/L and LOD 0.13 μmol/L (41). CCE electrodes are usable for anodic oxidation of aromatic amino compounds or phenols. DPV determination of 2-aminonaphthalene at CCE30 (38) can serve as an example. For surface renovation, wiping with wet filter paper must be applied. Some other interesting applications involve the simultaneous determination of adenine and guanine at CCE30 (38), adenine on m-AgSA-CE (23) (see Fig. 5 for the sake of illustration), of nitrofluorene on m-AgSA-CE (99), of phenylglyoxylic acid (styrene metabolite) in human urine using CCE (11), of 4-chlorophenol and oxalic acid using an expanded graphite-epoxy composite electrode (100), of pyrocatechol at a mechanically renewed electrode made of a graphite-epoxy CSE (101), of hydroquinone using graphite-silicone rubber composite electrode (102), and of phenols using lead(IV) oxide-graphite composite electrodes (103).

SUMMARY

It is possible to conclude that the composite solid electrodes and sensors are applicable in environmental, toxicological, biochemical, food, and pharmaceutical analysis and in many other fields. They can successfully replace mercury electrodes and, in some cases, compete with more frequently used solid and paste electrodes. They offer certain advantages over metallic, glassy carbon electrodes, or other non-composite electrodes; their preparation is simple and non-expensive and their mechanical and electrochemical pretreatment is simple. A well prepared electrode has long-term stability; it can be used for daily measurements without mechanical treatment of the surface for at least one month, unless there are problems with passivation. This difficult problem common to all solid electrodes can be frequently eliminated by a suitable electrochemical pretreatment and/or soft mechanical cleaning. The activation of the electrode surface is achieved by mechanical polishing and by repeated polarization. The following electrochemical activation of the electrode surface is simply realized by repeated cyclic polarization every day before the measurement.

The reproducibility (repeatability) of the results is improved by keeping the electrode potential at a definite value for a definite time interval before each measurement in dependence on analyte and sample matrix. On the other hand, CSEs exhibit some disadvantages typical for all solid electrodes (e.g., worse reproducibility of working surface, relatively shorter lifetimes, and higher LODs compared with mercury electrodes). CSEs can be applied not only for batch analysis using voltammetry or chronopotentiometry, but in flowing systems as well (e.g., HPLC-ED, CZE-ED, FIA-ED). They can be used in the form of disposable electrodes, they can be easily miniaturized and used in the form of mini- or microsensors and grouped together with other electrodes to form a multisensor. Their advantage is the possibility to modify the bulk or the surface of the electrode according to the aim of analysis or investigation. The toxicity of CSEs is negligible and thus they are a very promising alternative for many electroanalytical applications.

ACKNOWLEDGMENT

Financial support of this work was provided by the Grant Agency of the Czech Republic (project No. 203/07/1195), by the Grant Agency of the Academy of Sciences of the CR (Project No. IAA400400806), by the Ministry of Education, Youth, and Sports of the Czech Republic (projects LC 06035 and MSM 0021620857).

ABBREVIATIONS

AB	Acetate buffer
AFM	Atomic force microscopy
AgSA	Silver solid amalgam
ASV	Anodic striping voltammetry
BB	Borate buffer
BR	Britton - Robinson buffer
CCE	Carbon (graphite) composite electrode
CMeE	Carbon (graphite) metallic electrode
CSE	Composite solid electrode
CZE-ED	Capillary zone electrophoresis with electrochemical detection
DC	Direct current
DP	Differential pulse
E_{acc}	Accumulation potential
E_{cl}	Cleaning potential
ECL	Electrogenerated chemiluminiscence
EDX	Energy dispersive X-ray analysis
E_{Reg}	Regeneration potential
FIA-ED	Flow injection analysis with electrochemical detection
HMDE	Hanging mercury drop electrode
HPLC-ED	High performance liquid chromatography with electrochemical detection
LOD	Limit of detection
LOQ	Limit of quantification
MeSA-CE	Solid composite amalgam electrode containing metal “Me” (e.g. Ag)
NBI	Nitrobenzimidazole
NN	Nitronaphtalene
NQ	Nitroquinoline
PB	Phosphate buffer
PSA	Potentiometric stripping analysis
RSD	Relative standard deviation
S.E.	Supporting electrolyte
SAS	Surface active substance
SEM	Scanning electron microscopy
SiGCCE	Silica gel modified carbon (graphite) composite electrode
t_{acc}	Accumulation time
t_{Cl}	Cleaning time
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction.

REFERENCES

1. J. Wang, *Analytical Electrochemistry* (Wiley-VCH, New York, 2006).
2. J. Barek, J. Fischer, T. Navratil, K. Peckova, B. Yosypchuk, and J. Zima, Nontraditional electrode materials in environmental analysis of biologically active organic compounds. *Electroanalysis* 19 (2007):2003–2014.
3. T. Navratil, B. Yosypchuk, and J. Barek, The use of composite electrodes in the analysis of drinking water, in *Progress on Drinking Water Research* eds. M. H. Lefebvre and M. M. Roux, (Nova Science Publishers, New York, 2008).
4. U. A. Kirgoz, S. Marin, M. Pumera, A. Merkoci, and S. Alegret, Stripping voltammetry with bismuth modified graphite-epoxy composite electrodes. *Electroanalysis* 17 (2005):881–886.
5. T. Navratil, J. Barek, and M. Kopanica, Anodic stripping voltammetry using graphite composite electrode. *Collection of Czechoslovak Chemical Communications*, Submitted (2007)
6. S. J. R. Prabakar and S. S. Narayanan, Surface modification of amine-functionalised graphite for preparation of cobalt hexacyanoferrate (CoHCF)-modified electrode: An amperometric sensor for determination of butylated hydroxyanisole (BHA). *Analytical and Bioanalytical Chemistry* 386 (2006):2107–2115.

7. A. Salimi, M. Roushani, B. Haghighi, and S. Soltanian, Amperometric detection of insulin at renewable sol-gel derived carbon ceramic electrode modified with nickel powder and potassium octacyanomolybdate(IV). *Biosensors & Bioelectronics* 22 (2006):220–226.
8. T. Navratil, S. Sebkova, and M. Kopanica, Voltammetry of lead cations on a new type of silver composite electrode in the presence of other cations. *Analytical and Bioanalytical Chemistry* 379 (2004):294–301.
9. T. Navratil and M. Kopanica, Analytical application of silver composite electrode. *Critical Reviews in Analytical Chemistry* 32 (2002):153–166.
10. T. Navratil and M. Kopanica, Lead determination on silver composite electrodes using the effect of underpotential deposition. *Chemicke Listy* 96 (2002):111–116.
11. T. Navratil, Z. Senholdova, K. Shanmugam, and J. Barek, Voltammetric determination of phenylglyoxylic acid in urine using graphite composite electrode. *Electroanalysis* 18 (2006):201–206.
12. M. Serradell, S. Izquierdo, L. Moreno, A. Merkoci, and S. Alegret, Mercury-free PSA of heavy metals using graphite-epoxy composite electrodes. *Electroanalysis* 14 (2002):1281–1287.
13. I. Sestakova, M. Kopanica, L. Havran, and E. Palecek, Constant current chronopotentiometric stripping analysis of Cd-metallothionein on carbon and mercury electrodes. Comparison with voltammetry. *Electroanalysis* 12 (2000):100–104.
14. M. G. Pereira, M. D. Jimenez, M. P. Elizalde, A. Manzo-Robledo, and N. Alonso-Vante, Study of the electrooxidation of ethanol on hydrophobic electrodes by DEMS and HPLC. *Electrochimica Acta* 49 (2004):3917–3925.
15. B. Palenzuela, B. M. Simonet, R. M. Garcia, A. Rios, and M. Valcarcel, Amperometric screening of bacterial food contamination using a composite modified electrode. *Analytica Chimica Acta* 524 (2004):167–174.
16. G. A. Alvarez-Romero, M. E. Palomar-Pardave, and M. T. Ramirez-Silva, Development of a novel nitrate-selective composite sensor based on doped polypyrrole. *Analytical and Bioanalytical Chemistry* 387 (2007):1533–1541.
17. H. Wei and E. Wang, Solid-state electrochemiluminescence of tris(2,2′ -bipyridyl) ruthenium. *Trac-Trends in Analytical Chemistry* 27 (2008):447–459.
18. M. L. Chang and C. M. Chang, Voltammetric determination of sunscreen by convenient epoxy-carbon composite electrodes. *Journal of Food and Drug Analysis* 9 (2001):199–206.
19. R. Santhanam and M. Noel, Effect of solvents on the intercalation/de-intercalation behaviour of monovalent ionic species from non-aqueous solvents on polypropylene-graphite composite electrode. *Journal of Power Sources* 66 (1997):47–54.
20. Z. Hohercakova and F. Opekar, Au/PVC composite—A new material for solid-state gas sensors detection of nitrogen dioxide in the air. *Sensors and Actuators B-Chemical* 97 (2004):379–386.
21. H. Ota, Y. Sakata, A. Inoue, and S. Yamaguchi, Analysis of vinylene carbonate derived SEI layers on graphite anode. *Journal of the Electrochemical Society* 151 (2004):A1659–A1669.
22. M. Luque, A. Rios, and M. Valcarcel, Performance tests and internal quality control activities for the routine analytical use of composite electrodes. *Accreditation and Quality Assurance* 6 (2001):514–520.
23. B. Yosypchuk, T. Navratil, A. N. Lukina, K. Peckova, and J. Barek, Solid amalgam composite electrode as a new sensor for the determination of biologically active compounds. *Chemia Analityczna (Warsaw)* 52 (2007):897–910.
24. M. Kopanica and V. Stara, Silica-gel modified carbon composite electrodes. *Electroanalysis* 3 (1991):13–16.
25. D. E. Tallman and S. L. Petersen, Composite electrodes for electroanalysis—Principles and applications. *Electroanalysis* 2 (1990):499–510.
26. A. Walcarius, D. Mandler, J. A. Cox, M. Collinson, and O. Lev, Exciting new directions in the intersection of functionalized sol-gel materials with electrochemistry. *Journal of Materials Chemistry* 15 (2005):3663–3689.
27. N. Y. Stozhko, N. A. Malakhova, M. V. Fyodorov, and K. Z. Brainina, Modified carbon-containing electrodes in stripping voltammetry of metals. Part II. Composite and microelectrodes. *Journal of Solid State Electrochemistry* 12 (2008):1219–1230.
28. J. W. Fergus, A review of electrolyte and electrode materials for high temperature electrochemical CO_2 and SO_2 gas sensors. *Sensors and Actuators B-Chemical* 134 (2008):1034–1041.
29. J. Barek, K. Peckova, and V. Vyskocil, Adsorptive stripping voltammetry of environmental carcinogens. *Current Analytical Chemistry* 4 (2008):242–249.
30. R. D. O'Neill, J. P. Lowry, G. Rocchitta, C. P. McMahon, and P. A. Serra, Designing sensitive and selective polymer/enzyme composite biosensors for brain monitoring in vivo. *Trac-Trends in Analytical Chemistry* 27 (2008):78–88.
31. F. Cespedes and S. Alegret, New materials for electrochemical sensing: Glucose biosensors based on rigid carbon-polymer biocomposites. *Food Technology and Biotechnology* 34 (1996):143–146.
32. S. L. Petersen and D. E. Tallman, Silver composite electrode for voltammetry. *Analytical Chemistry* 60 (1988):82–86.
33. Thomson_Reuters, ISI Web of Knowledge. http://www.isiknowledge.com. (Accessed 7 February 2009).
34. I. Svancara, K. Vytras, J. Barek, and J. Zima, Carbon paste electrodes in modern electroanalysis. *Critical Reviews in Analytical Chemistry* 31 (2001):311–345.
35. J. Zima, I. Svancara, J. Barek, and K. Vytras, Recent advances in electroanalysis of organic compounds at carbon paste electrodes. *Critical Reviews in Analytical Chemistry* 39 (2009):204–227.
36. M. C. Blanco-Lopez, L. Fernandez-Llano, M. J. Lobo-Castanon, A. J. Miranda-Ordieres, and P. Tunon-Blanco, Voltammetry of diclofenac at graphite, carbon composites, and molecularly imprinted polymer-composite electrodes. *Analytical Letters* 37 (2004):915–927.
37. T. Navratil, M. Kopanica, and J. Krista, Anodic stripping voltammetry for arsenic determination on composite gold electrode. *Chemia Analityczna (Warsaw)* 48 (2003):265–272.
38. S. Sebkova, T. Navratil, and M. Kopanica, Graphite composite electrode in voltammetry. *Analytical Letters* 38 (2005):1747–1758.
39. M. P. Somashekarappa and S. Sampath, Sol-gel derived, silicate-phthalocyanine functionalized exfoliated graphite based composite electrodes. *Analytica Chimica Acta* 503 (2004):195–201.
40. C. Y. Liu, J. F. Hu, J. M. Hu, and H. Tanga, Electrocatalytic oxidation of dopamine at a nanocuprous oxide-methylene blue composite glassy carbon electrode. *Electroanalysis* 18 (2006):478–484.

41. D. Jayasri and S. S. Narayanan, Electrocatalytic oxidation of ascorbic acid by a manganese(II) hexacyanoferrate-modified graphite-wax composite electrode. *Bulletin of Electrochemistry* 21 (2005):537–545.
42. D. Jayasri and S. S. Narayanan, Manganese(II) hexacyanoferrate based renewable amperometric sensor for the determination of butylated hydroxyanisole in food products. *Food Chemistry* 101 (2007):607–614.
43. A. Salimi and S. Pourbeyram, Renewable sol-gel carbon ceramic electrodes modified with a Ru-complex for the amperometric detection of L-cysteine and glutathione. *Talanta* 60 (2003):205–214.
44. A. Salimi, S. Pourbeyram, and H. Haddadzadeh, Sol-gel derived carbon ceramic composite electrode containing a ruthenium complex for amperometric detection of insulin at physiological pH. *Journal of Electroanalytical Chemistry* 542 (2003):39–49.
45. M. Kopanica and V. Stara, Determination of amalgam-forming metals by anodic-stripping voltammetry in solutions containing dissolved-Oxygen. *Electroanalysis* 3 (1991):925–928.
46. D. R. Shankaran, N. Uehara, and T. Kato, Sol-gel derived metal dispersed ceramic-graphite composite electrode for amperometric determination of dopamine. *Analytica Chimica Acta* 478 (2003):321–327.
47. I. Sestakova and P. Mader, Voltammetry on mercury and carbon electrodes as a tool for studies of metallothionein interactions with metal ions. *Cellular and Molecular Biology* 46 (2000):257–267.
48. I. Sestakova and T. Navratil, Voltammetric methods in metallothionein research. *Bioinorganic Chemistry and Applications* 3 (2005):43–53.
49. B. Serra, M. D. Morales, A. J. Reviejo, E. H. Hall, and J. M. Pingarron, Rapid and highly sensitive electrochemical determination of alkaline phosphatase using a composite tyrosinase biosensor. *Analytical Biochemistry* 336 (2005):289–294.
50. L. D. Zhu, Y. X. Li, F. M. Tian, B. Xu, and G. Y. Zhu, Electrochemiluminescent determination of glucose with a sol-gel derived ceramic-carbon composite electrode as a renewable optical fiber biosensor. *Sensors and Actuators B-Chemical* 84 (2002):265–270.
51. C. X. Li, Y. L. Zeng, and C. R. Tang, Glucose biosensor based on carbon/PVC-COOH/ferrocene composite with covalently immobilized enzyme. *Chinese Chemical Letters* 16 (2005):1357–1360.
52. C. H. Liu, K. T. Liao, and H. J. Huang, Amperometric immunosensors based on protein A coupled polyaniline-perfluorosulfonated ionomer composite electrodes. *Analytical Chemistry* 72 (2000):2925–2929.
53. T. Yang, W. Zhang, M. Du, and K. Jiao, A PDDA/poly(2,6-pyridinedicarboxylic acid)-CNTs composite film DNA electrochemical sensor and its application for the detection of specific sequences related to PAT gene and NOS gene. *Talanta* 75 (2008):987–994.
54. C. H. Yang, Y. X. Xu, C. G. Hu, and S. S. Hu, Voltammetric detection of ofloxacin in human urine at a Congo red functionalized water-soluble carbon nanotube film electrode. *Electroanalysis* 20 (2008):144–149.
55. M. Marcinek, X. Y. Song, and R. Kostecki, Microwave plasma chemical vapor deposition of nano-composite C/Pt thin-films. *Electrochemistry Communications* 9 (2007):1739–1743.
56. K. Z. Liang, J. S. Qi, W. J. Mu, and Z. G. Chen, Biomolecules/gold nanowires-doped sol-gel film for label-free electrochemical immunoassay of testosterone. *Journal of Biochemical and Biophysical Methods* 70 (2008):1156–1162.
57. F. Cespedes, E. Martinezfabregas, J. Bartroli, and S. Alegret, Amperometric enzymatic glucose electrode based on an epoxy graphite composite. *Analytica Chimica Acta* 273 (1993):409–417.
58. J. Navarro-Laboulais, J. Trijueque, J. J. Garcia-Jareno, D. Benito, and F. Vicente, Electrochemical impedance spectroscopy of conductor-insulator composite electrodes: Properties in the blocking and diffusive regimes. *Journal of Electroanalytical Chemistry* 444 (1998):173–186.
59. K. D. M. Harris, M. D. Rogers, and C. A. Vincent, A comparison between mixed phase electrode and percolation models for composite electrodes in solid-state cells. *Solid State Ionics* 18-9 (1986):833–837.
60. F. Cespedes and S. Alegret, New materials for electrochemical sensing— II. Rigid carbon-polymer biocomposites. *TrAC, Trends in Analytical Chemistry* 19 (2000):276–285.
61. B. Bas, R. Piech, E. Niewiara, A. Ziemnicka, L. Stobierski, and W. W. Kubiak, TIC working electrode. Voltammetric characteristics and application for determination of lead traces by stripping voltammetry. *Electroanalysis* 20 (2008):1655–1664.
62. G. R. Salazar-Banda, H. B. Suffredini, M. L. Calegaro, S. T. Tanimoto, and L. A. Avaca, Sol-gel-modified boron-doped diamond surfaces for methanol and ethanol electro-oxidation in acid medium. *Journal of Power Sources* 162 (2006):9–20.
63. R. Pauliukaite, A. M. C. Paquim, A. M. O. Brett, and C. M. A. Brett, Electrochemical, EIS and AFM characterisation of biosensors: Trioxysilane sol-gel encapsulated glucose oxidase with two different redox mediators. *Electrochimica Acta* 52 (2006): 1–8.
64. G. Yang, R. Yuan, and Y. Q. Chai, A high-sensitive amperometric hydrogen peroxide biosensor based on the immobilization of hemoglobin on gold colloid/L-cysteine/gold colloid/nanoparticles Pt-chitosan composite film-modified platinum disk electrode. *Colloids Surf B Biointerfaces* 61 (2008):93–100.
65. G. A. Alvarez-Romero, E. Garfias-Garcia, M. T. Ramirez-Silva, C. Galan-Vidal, M. Romero-Romo, and M. Palomar-Pardave, Electrochemical and AFM characterization of the electropolimerization of pyrrole over a graphite-epoxy resin solid composite electrode, in the presence of different anions. *Applied Surface Science* 252 (2006):5783–5792.
66. H. Razmi and H. Heidari, Preparation, electrochemistry, and electrocatalytic activity of lead pentacyanonitrosylferrate film immobilized on carbon ceramic electrode. *Electroanalysis* 20 (2008):2370–2378.
67. O. Dracka, Theory of current elimination in linear scan voltammetry. *Journal of Electroanalytical Chemistry* 402 (1996):19–28.
68. J. Skopalova and T. Navratil, Application of elimination voltammetry to the study of electrochemical reduction and determination of the herbicide metribuzin. *Chemia Analityczna (Warsaw)* 52 (2007):961–977.
69. R. Fadrna, B. Yosypchuk, M. Fojta, T. Navratil, and L. Novotny, Voltammetric determination of adenine, guanine, and DNA using liquid mercury free polished silver solid amalgam electrode. *Analytical Letters* 37 (2004):399–413.

70. S. Sander, T. Navratil, and L. Novotny, Study of the complexation, adsorption and electrode reaction mechanisms of chromium(VI) and (III) with DTPA under adsorptive stripping voltammetric conditions. *Electroanalysis* 15 (2003):1513–1521.
71. L. Trnkova, R. Kizek, and O. Dracka, Application of elimination voltammetry to adsorptive stripping of DNA. *Electroanalysis* 12 (2000):905–911.
72. S. Sebkova, T. Navratil, and M. Kopanica, Comparison of different types of silver composite electrodes to varied amount of silver on example of determination of 2-nitro-naphtalene. *Analytical Letters* 36 (2003):2767–2782.
73. S. Sebkova, Determination of chlorides on composite silver electrodes. *Chemicke Listy* 97 (2003):201–205.
74. S. Sebkova, Voltammetric determination of alizarine chrome black PT using composite electrodes. *Chemicke Listy* 100 (2006):449–454.
75. T. Navratil, J. Barek, and S. Fasinova-Sebkova, Differential pulse voltammetric determination of selected nitro compounds on silver, solid silver composite and solid graphite composite electrodes. *Electroanalysis* 21 (2009):309–315.
76. P. Cizkova, T. Navratil, I. Sestakova, and B. Yosypchuk, Verification of applicability of mercury meniscus modified silver solid amalgam electrode for determination of heavy metals in plant matrices. *Electroanalysis* 19 (2007):161–171.
77. R. Selesovska-Fadrna, M. Fojta, T. Navratil, and J. Chylkova, Brdicka-type processes of cysteine and cysteine-containing peptides on silver amalgam electrodes. *Analytica Chimica Acta* 582 (2007):344–352.
78. R. Selesovska-Fadrna, T. Navratil, and M. Vlcek, Liquid-mercury free solid silver amalgam electrode—Tool for electroanalysis of organic compounds. *Chemia Analityczna (Warsaw)* 52 (2007):911–929.
79. J. Fischer, J. Barek, B. Yosypchuk, and T. Navratil, Voltammetric determination of trace amounts of 2-methyl-4,6-dinitrophenol at a silver solid amalgam electrode. *Electroanalysis* 18 (2006):127–130.
80. B. Yosypchuk, T. Navratil, J. Barek, K. Peckova, and J. Fischer, Amalgam electrodes as sensors in the analysis of aquatic system, in *Progress on Drinking Water Research*, Eds. M. H. Lefebvre and M. M. Roux 143–170 (Nova Science Publishers, New York, 2008).
81. A. Salimi, M. Roushani, and R. Hallaj, Micromolar determination of sulfur oxoanions and sulfide at a renewable sol-gel carbon ceramic electrode modified with nickel powder. *Electrochimica Acta* 51 (2006):1952–1959.
82. A. Salimi, K. Abdi, and G. R. Khayatiyan, Preparation and electrocatalytic oxidation properties of a nickel pentacyanonitrosylferrate modified carbon composite electrode by two-step sol-gel technique: improvement of the catalytic activity. *Electrochimica Acta* 49 (2004):413–422.
83. M. Etienne and A. Walcarius, Evaporation induced self-assembly of templated silica and organosilica thin films on various electrode surfaces. *Electrochemistry Communications* 7 (2005):1449–1456.
84. T. Navratil, B. Yosypchuk, and J. Barek, A multisensor for electrochemical sequential autonomous automatic measurements. *Chemia Analityczna (Warsaw)* 54 (2009):3–17.
85. D. M. Kolb, Physical and electrochemical properties of metal monolayers on metallic substrates, in *Advanced in Electrochemistry and Electrochemical engineering*, Eds. H. Gerischer and C. W. Tobias, (Wiley, New York, 1978), 125–271.
86. J. O. M. Bockris, A. K. N. Reddy, and M. Gamboa-Aldeco, *Modern Electrochemistry* (Kluwer Academic/Plenum Publishers, New York, 2000).
87. S. Carregalo, A. Merkoci, and S. Alegret, Application of graphite-epoxy composite electrodes in differential pulse anodic stripping voltammetry of heavy metals. *Microchimica Acta* 147 (2004):245–251.
88. A. O. Simm, C. E. Banks, S. J. Wilkins, N. G. Karousos, J. Davis, and R. G. Compton, A comparison of different types of gold-carbon composite electrode for detection of arsenic(III). *Analytical and Bioanalytical Chemistry* 381 (2005):979–985.
89. J. Y. Jin, F. Xu, and T. Miwa, Cathodic stripping voltammetry for determination of trace manganese with graphite/styrene-acrylonitrile copolymer composite electrodes. *Electroanalysis* 12 (2000):610–615.
90. Y. A. Zolotov, L. K. Shpigun, N. E. Kopytova, and P. M. Kalimova, Membrane-based electrodes for flow-injection determination of noble metal ions. *Chemia Analityczna* 44 (1999):623–634.
91. N. Y. Stozhko, E. I. Morosanova, L. I. Kolyadina, and S. V. Fomina, Ceramic composite electrode for the determination of selenium(IV) by stripping voltammetry. *Journal of Analytical Chemistry* 61 (2006):158–165.
92. J. B. Jia, L. Y. Cao, Z. H. Wang, and T. X. Wang, Properties of poly(sodium 4-styrenesulfonate)-ionic liquid composite film and its application in the determination of trace metals combined with bismuth film electrode. *Electroanalysis* 20 (2008): 542–549.
93. H. Kahlert and F. Scholz, A graphite silver(I) hexacyanoferrate(III) composite electrode for the determination of iron(III) ions. *Electroanalysis* 9 (1997):922–925.
94. J. Orozco, C. Fernandez-Sanchez, E. Mendoza, M. Baeza, F. Cespedes, and C. Jimenez-Jorquera, Composite planar electrode for sensing electrochemical oxygen demand. *Analytica Chimica Acta* 607 (2008):176–182.
95. S. Da Silva, D. Shan, and S. Cosnier, Improvement of biosensor performances for nitrate determination using a new hydrophilic poly (pyrrole-viologen) film. *Sensors and Actuators B-Chemical* 103 (2004):397–402.
96. S. Sebkova, T. Navratil, and M. Kopanica, Silver composite electrode for voltammetric determination of halogenides. *Analytical Letters* 37 (2004):603–628.
97. A. Salimi, V. Alizadeh, and H. Hadadzadeh, Renewable surface sol-gel derived carbon ceramic electrode modified with copper complex and its application as an amperometric sensor for bromate detection. *Electroanalysis* 16 (2004):1984–1991.
98. K. Peckova, Polarographic and voltammetric determination of trace level of 1-nitro naphtalene. *M.Sc. Thesis*, Charles University in Prague, Prague, 2001.
99. Z. Krejcova, Voltammetric determination of genotoxic 2-nitrofluorene using polished silver solid amalgam composite electrode. *B.Sc. Thesis*, Charles University in Prague, Department of Analytical Chemistry, Prague, 2009.
100. F. Manea, C. Radovan, I. Corb, A. Pop, G. Burtica, P. Malchev, S. Picken, and J. Schoonman, Simultaneous determination of 4-chlorophenol and oxalic acid using an expanded graphite-epoxy composite electrode. *Electroanalysis* 20 (2008):1719–1722.

101. O. V. Karunina, L. I. Skvortsova, and V. N. Kiryushov, Voltammetric determination of pyrocatechol at a mechanically renewed electrode made of a graphite-epoxy composite. *Journal of Analytical Chemistry* 63 (2008):180–183.
102. A. C. de Oliveira, S. X. dos Santos, and E. T. G. Cavalheiro, Graphite-silicone rubber composite electrode: Preparation and possibilities of analytical application. *Talanta* 74 (2008):1043–1049.
103. B. Sljukic, C. E. Banks, A. Crossley, and R. G. Compton, Lead(IV) oxide-graphite composite electrodes: Application to sensing of ammonia, nitrite and phenols. *Analytica Chimica Acta* 587 (2007):240–246.
104. M. L. Chang and C. M. Chang, Simultaneous voltammetric determination of ascorbic acid and its derivatives in cosmetics using epoxy-carbon composite electrodes. *Journal of Food and Drug Analysis* 13 (2005):205–211.
105. J. H. Khorasani, M. K. Amini, H. Ghanei, and S. Tangestaninejad, Flow-injection amperometric determination of ascorbic acid using a graphite-epoxy composite electrode modified with cobalt phthalocyanine. *Iranian Journal of Chemistry & Chemical Engineering-International English Edition* 20 (2001):66–74.
106. J. Saurina, S. Hernandez-Cassou, E. Fabregas, and S. Alegret, Determination of tryptophan in feed samples by cyclic voltammetry and multivariate calibration methods. *Analyst* 124 (1999):733–737.
107. J. Saurina, S. Hernandez-Cassou, E. Fabregas, and S. Alegret, Cyclic voltammetric simultaneous determination of oxidizable amino acids using multivariate calibration methods. *Analytica Chimica Acta* 405 (2000):153–160.
108. R. Aguilar-Sanchez, F. Ahuatl-Garcia, M. M. Davila-Jimenez, M. P. Elizalde-Gonzalez, and M. R. G. Guevara-Villa, Chromatographic and electrochemical determination of quercetin and kaempferol in phytopharmaceuticals. *Journal of Pharmaceutical and Biomedical Analysis* 38 (2005):239–249.
109. R. Aguilar, M. M. Davila, M. P. Elizalde, J. Mattusch, and R. Wennrich, Capability of a carbon-polyvinylchloride composite electrode for the detection of dopamine, ascorbic acid and uric acid. *Electrochimica Acta* 49 (2004):851–859.
110. M. M. Davila, M. P. Elizalde, J. Mattusch, and R. Wennrich, Study of the composite electrodes carbon-polyvinyl chloride and carbon-polyvinyl chloride/Nafion by ex situ and in situ methods. *Electrochimica Acta* 46 (2001):3189–3197.
111. X. H. Sun, X. R. Yang, and E. K. Wang, Evaluation of a sol-gel derived carbon composite electrode as an amperometric detector for capillary electrophoresis. *Journal of Chromatography A* 991 (2003):109–116.
112. T. Selvaraju and R. Ramaraj, Simultaneous detection of ascorbic acid, uric acid and homovanillic acid at copper modified electrode. *Electrochimica Acta* 52 (2007):2998–3005.
113. Y. L. Zeng, C. X. Li, C. R. Tang, X. B. Zhang, G. L. Shen, and R. Q. Yu, The electrochemical properties of Co(TPP), tetraphenylborate modified glassy carbon electrode: Application to dopamine and uric acid analysis. *Electroanalysis* 18 (2006):440–448.
114. D. Jayasri and S. S. Narayanan, Electrocatalytic oxidation and amperometric determination of BHA at graphite-wax composite electrode with silver hexacyanoferrate as electrocatalyst. *Sensors and Actuators B-Chemical* 119 (2006):135–142.
115. R. K. Mendes, P. Cervini, and E. T. G. Cavalheiro, The use of a graphite-castor oil polyurethane composite electrode for the determination of hydroquinone in photographic developers. *Talanta* 68 (2006):708–712.
116. R. A. de Toledo, M. C. Santos, K. M. Honorio, A. B. F. da Silva, E. T. G. Cavalheiro, and L. H. Mazo, Use of graphite polyurethane composite electrode for imipramine oxidation— Mechanism proposal and electroanalytical determination. *Analytical Letters* 39 (2006):507–520.