SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
3 (1997)

RECENT PROGRESS IN THE DEVELOPMENT OF ELECTROCHEMICAL CARBON PASTE SENSORS

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Received December 31, 1997

In this review an overview is given of some recent trends in developing electrochemical sensors that are based on heterogeneous carbon materials. Their main characteristic is a usually non-conducting liquid or solid matrix, into which conductive carbon particles are embedded. Typical representatives of such types of sensors are carbon paste electrodes (CPE), solid carbon composite electrodes (CCE), and screen printed carbon electrodes (SPCE). Main emphasis in this article is put on summarizing trends and strategies of the development of carbon paste sensors during the past few years (365 references).

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Introduction

Electrochemical sensors based on heterogenous carbon materials have attracted enormous interest during the past two decades. Their immanent advantages which make them superior to all other types of electrochemical sensors employing solid or liquid electrode materials is their ease to be modified as well as the low costs of their production.

Electrochemical methods in general which were widely applied in former times in routine analysis have been increasingly replaced by other instrumental methods particularly with respect to the determination of total concentrations of trace elements. Thus, predominantly atomic spectroscopic and mass spectrometric assays are most commonly used for this purpose. Electroanalysis is maintaining and widening its major field of application in the area of sensors. Such devices can be cheap alternatives to expensive, highly sophisticated instrumental equipments and allow portability and field applicability by miniaturization. In many cases they are the base of decentralized testing in environmental, industrial and medical analysis. Even in a simplest design they are extremely valuable just to monitor threshold limits of analytes. In this respect simple and inexpensive production of sensors reduces analytical costs to a minimum. An additional advantage of electrochemical sensors over other instrumental approaches (e.g., atomic spectroscopy, inductively coupled plasma-mass spectrometry) is their ability to detect low and ultra-low concentrations of species rather than elemental concentrations.

Electrochemical, particularly voltammetric and amperometric sensors based on solid homogeneous materials (e.g, graphite, glassy carbon, noble metals such as gold, platinum, palladium) and on mercury suffer from severe disadvantages. In the former case the electrodes require labor-intensive pretreatment of the surface together with time consuming operations if modification is required. Additionally the electrode materials are often rather expensive. Mercury, which is in many electrochemical aspects superior to most other electrode materials, is increasingly repelled from laboratories, especially from the ones dealing with routine analysis. There are various reasons for doing so, such as difficulties in handling a liquid electrode and, moreover, a steadily increasing popular fear of this element (which can influence political decisions in some countries where the use of elemental Hg is forbidden in laboratories).

In this situation, the substitution of conventional electrode materials by others is more than obvious, particularly since the new ones imply more facilities and possibilities. The dominant domain of sensor materials in electroanalysis is nowadays occupied by carbon paste electrodes. As indicated by its name they employ a paste-like substance which consists of electrically conductive carbon powder mixed with a pasting liquid. Other such types of heterogenous materials replace the liquid fraction by a solid one, such as easily meltable organic compounds or polymers. The main advantages of so designed sensors are new physical and chemical properties together with simplest access

to modification, i.e., the introduction of chemically and/or electrochemically reactive functionality at the interface electrode surface and sample solution.

An overview of recent progress in this field of research during the past few years will be given in the article presented here. Since work up to 1993 has been reviewed by us elsewhere [1-6], mainly publications will be considered which appeared thereafter.

Carbon Paste Electrodes

General and Critical Comments

Carbon paste electrodes (CPE), invented by Adams in 1958, were basically designed as an alternative to the dropping mercury electrode [7,8]. Though the concept of a dynamic renewable electrode surface was not successful, it turned out that the material with past-like consistency can be practically employed in voltammetric analysis. After pioneering work of Kuwana [9,10], who actually first modified a CPE by introducing an electrochemically active substance in the material, and after the first chemical modification of an electrode for electrosynthesis [11], modification was soon applied to carbon paste electrodes [12,13]. Finally, Baldwin described the simple method of direct mixing of a solid modifier to the paste [14], which was the starting point of an explodingly increasing research activity in this field.

Quite a few reviews are exclusively devoted to carbon paste electrodes and can be regarded as a good introduction to the subject. The papers comprise carbon pastes in their unmodified and modified forms dealing with their analytical applications [1-5] and their properties and characterization [6]. General designs of electrochemical sensors including carbon pastes and related materials can be found in the literature (e.g., [15]).

In spite of their usefulness carbon pastes exhibit a few disadvantages. Practically, all materials prepared are "individuals" meaning that they can vary slightly in their composition, which is a crucial factor for the performance. Also the roughness of the surface influences the electrochemical behavior so that reproducible treatment of the surface is a necessary prerequisite to obtain coherent results. If the paste is modified, homogeneity problems may occur, especially if particulate substances are used as modifiers. Therefore, some experience is needed to produce and handle pastes adequately. In this respect carbon pastes are often only the primary stage for the development of electrochemical sensors; further approaches are frequently made by transfering the concept from CPEs to more robust sensors, such as thick films (screen printed electrode, SPEs).

Also the nomenclature of the pastes and their modifications is somehow confusing in the literature since apart from some suggestion [16] no obligatory

guidelines exist up to now. This is going to be changed with rules which will be soon worked out by the IUPAC [17].

Unmodified Carbon Pastes

Plain carbon pastes are still subject of fundamental investigations. The choice of components basicly influences the electrochemical behavior of the resulting paste. A microscopic study of various types of materials (graphite and glassy carbon powders mixed with paraffin oil, silicone oil or tricresyl phosphate) revealed that the microstructure of the paste varies significantly with the composition, which will be co-responsible for the electroanalytical performance of the electrode [18]. It is worth to mention that particularly the pasting liquid influences the working potential window of the electrode in voltammetric applications. Usual potential ranges vary between +1.0 to 1.2 V vs. reference at the anodic and -0.7 to -1.0 V at the cathodic end. Tricresyl phosphate was found to extent particularly the anodic range significantly [19-21]. Studies were also performed to check the behavior of CPEs in organic media [22].

Carbon pastes can be a simple alternative to glassy carbon (GC) as a support for film electrodes. Investigations showed that it is possible to plate tricresyl phosphate-derived CPEs with either mercury (exemplary determination of zinc) [23] or gold films (used for the determination of mercury) [24] with comparable properties to conventional metal film electrodes on a GC substrate. The main advantage with CPEs is the fact that there is no need of polishing the surface prior to plating as is the case with solid supports.

Unmodified carbon pastes were employed for the determination of inorganic and organic analytes. Using the voltammetric approach the analytical method was optimized for routine analysis of Cu(II) and Ag(I) [25]. Germanium can be determined *via* adsorptive preconcentration of molybdogermanic heteropoly acid [26]. Palladium preconcentrated under closed circuit conditions gives a well exploitable voltammetric signal probably due to some catalytic wave of hydrogen [27]. A very interesting approach was made by Garcia with adsorptive stripping of colloidal gold which was adopted to an immunoassay by labelling goat anti-human immunoglobulin G with colloidal gold [28].

Thanks to the lipophilic nature of carbon paste, adsorption of organic molecules can advantageously be exploited for all types of stripping techniques. Adsorptive stripping voltammetry was used to determine hydroquinones [29], pyrocatechol [30], flavonoids [31] and pharmaceuticals, such as cephalosporin antibiotics [32], Loprazolam [33], Naltrexone [34] and beta-antagonistic drugs [35].

Indirect voltammetric determination of anionic surfactants is achieved with electroactive ferrocenyl cations *via* ion pair formation and extraction into a carbon paste containing 2-nitrophenyl octyl ether as a pasting liquid [36].

The most promising work in this field was done by Wang's group, who

applied adsorption and potentiometric stripping analysis to a variety of biologically important molecules. Nucleic acids can be determined by adsorption of the analyte directly *via* oxidation of guanine [37-41]; simple amperometric detection of nucleic acids is possible even in flow injection analysis [42]. The potentiometric assay works also with peptide nucleic acids, which are DNA analogs [43]. Such sensors could be the base for the development of very selective sensors to detect specifically diseases such as leukemia (see also chapter "Biosensors"). Successful attempts were made by the authors to transfer the design to thick film carbon strip electrodes. The same group applied also potentiometric stripping with carbon pastes *via* adsorption and oxidation of the tryptophan moieties to the determination of proteins, such as bombesin, neurotensin, luteinizing hormone releasing hormone [44], insulin and myoglobin [45]. In some cases preanodization of the electrode surface is necessary, as was also found for the chemically oxidative preconcentration of adenine and its ensuing voltammetric determination [46]. DNA electrochemical biosensors are reviewed by Wang and coworkers [47]. Most fruitful results can be expected in this area of research (see also paragraph Biosensors).

Modified Carbon Paste Sensors

Modification of carbon paste sensors is easy to perform due to the paste-like consistency of the electrode material. The simplest way of introducing the modifier to the material is direct mixing or dissolving the modifier in the pasting liquid. Particularly when using solid modifying agents, problems with the homogeneity of the paste can arise resulting in poorly reproducible results. Electrochemical activation, especially preanodization, will result in somewhat modified electrodes since the surface characteristics of the electrode and consequently its electro-chemical properties will be changed. By anodic electrochemical treatment insulating layers of the pasting liquid are stripped off and oxygen-containing groups (quinoids, carboxylic and phenolic groups) are generated at the electrode surface which improve the electron transfer characteristics and in many cases lower the overpotential of electrochemical reactions. More demanding procedures of modification involve membrane deposition at the surface (as protective layers, catalysts or anchoring structures for the effective modifier) or even covalent attachment of the modifying agent. Simple modification can also be achieved by adsorption, but in many cases the stability is poor especially if medium exchanges are involved in the analytical procedures. A special form of modification is *in situ* modification where the modifying agent is added directly to the measurement solution and adsorbs to the electrode surface. Thus, the concentration of functional groups is significantly increased there, facilitating the reaction with analyte species.

Main reasons for modification are improving the detection limits (usually

by accumulation of the analyte at the electrode surface), the selectivity and the overall analytical performance of the system. In many cases catalysts or mediators are used, which either lower the overpotential or yield electrochemical responses at all, where there is none otherwise. Preconcentrations are often achieved by direct chemical reaction between the modifier and the target analyte (chemical preconcentration), frequently combined with a medium exchange between test and measuring solutions. Mediated reactions, most commonly found with biosensors, proceed by redox interaction of the mediator and the substrate (analyte), whereupon the original oxidation state of the modifier is reconstituted by electrochemical conversion.

Modified carbon paste electrodes were used for the determination of inorganic and organic analytes. From among the latter, however, the main field of application is their exploitation as biosensors, because CPEs allow very simple, easy and multiple modification with complex and labile systems, such as enzymes.

Inorganic Analytes

A huge variety of modifiers was employed for the preconcentration and voltammetric determination of inorganic analytes, particularly of trace metals. Usually preconcentration is effected by adding complexing ligands or ion exchangers to the paste. Overviews of voltammetric [48] and stripping voltammetric determinations [49] in general can be found in the literature. The determination of noble metals with a broad comparison of various analytical methods was reviewed by Qu [50]. Arrigan gave a good summary on the accumulation of trace metals and organics at modified electrodes [51].

Crown ethers and thioethers were used to quantify Ag(I), Au(III) [52, 53], Pt [53], Cu(II) [54], Pb(II) [53-55], Ni(II), and Co(II) [56]. A description of the use of CPEs, modified with macrocyclic compounds, in voltammetric analysis is given by Ulakhovich and coworkers [57]. Other complexing ligands used as modifiers for CPEs are glyoxal-bis-2-hydroxyanil for the determination of Ag(I) and Hg(II) [58], 2,3-dicyano-1,4-naphthoquinone for Ag(I) and 2,9-dichloro-1,10-phenanthroline for Ag(I) [59,60], oximes for Co(II), Pd(II), Hg(II) [61], Ni(II) [61,62], Cu(II) [63], Pb(II) [64], and Mo(VI) (as a catalytic method with chlorate) [65], 8-hydroxyquinoline for Tl(I) [66] and Tl(III) [67], 1-(2-pyridylazo)-2-naphthol for Co(II) [68] and Mn(II) [69], phenylfluorone for Sb(III) [70], propyl gallate for U(VI) [71], 2,3-diaminonaphthalene for Se(IV) [72,73], Chelite-P for Cu(II) [74], and calixarenes for Pb(II), Cu(II), Hg(II) [75]. The use of the latter substances in electrochemistry is reviewed by Arrigan et al. [76].

Sulphur-containing modifiers are very effective agents for the preconcentration of thiophilic trace metals. Studies were performed on the preconcentration of Ag(I) with 2,2'-dithiopyridine [73], N-benzoyl-N,N'-di-iso-butylthiurea

[77], or 2-mercaptoimidazol [78], of Bi(III) with bismuthiol II-carboxylate [79], of Cu(I) with rubeanic acid [80], of Cu(II) with salicylaldehyde thiosemicarbazone [81], 1,2-bismethyl(2-aminocyclopentene-carbothioate)ethane [82], or 2-salicylidene-aminothiophenol [73], of Hg(II) with a thiolic resin [83] or 2-mercapto-4(3H)-quinazolinone [84], of Pd(II) with thioridazine [85], of Pb(II) with dithizone [86], and of W(VI) with 8-mercaptoquinoline [87].

Ion exchangers are useful tools to accumulate ionic species at the electrode surface. Although they show often the disadvantage of lacking selectivity they can be employed as modifiers for carbon paste electrodes for defined matrices. Amberlite IR 120 [88] and Dowex 50W-8X [89,90] were used for the determination of Cu(II); the latter modifier allows speciation. The cation exchanger HYPHAN can be exploited for the detection of Cd(II), Cu(II), Pb(II), and mercury in drinking water [91].

A point of great interest is natural and artificial clay minerals, which can act as ion exchangers combined with size exclusion effects; various reviews predominantly on zeolites and their use in electrochemistry were published [92-94]. Zeolites as modifiers were used for analytes, such as Cu [95-97], Cd, and Zn [97]. An indirect approach to the determination of electroinactive cations was established by Walcarius using a methyl viologen-loaded zeolite as a modifier which releases the organic electroactive indicator after exposition to the test solution [98]. Vermiculite [99,100] and montmorillonite [101] were used to preconcentrate Cu(II).

Humic substances exhibit also a high ion exchange capacity; they were used for studies with Bi(III) [102], Cu(II), Hg(II), and Pb(II) [103]. Even plant derived materials possess similar properties and can be used to preconcentrate metal ions, to some extent selectively [104].

A special form of accumulation of analytes by ion exchange is ion pair formation, where the charged surfactant is usually added directly to the test solution, which prompts in situ modification of the electrode surface by adsorption. The analyte acts as a counterion and thus forms more or less lipophilic ion pairs, which can be extracted to some extent even into the electrode bulk material. If the modifier is insoluble in the aqueous phase, it can be added directly to the paste as well. Such designs are well applicable to the determination of iodide with cetyltrimethylammonium bromide (CTAB) [105] or cinchonine [106]. In some cases, when metals are determined, complexation of the analyte can have an improving effect, such as Ti(IV) [107], V(V) [108], and Mo(VI) [109] with oxalate in the presence of CTAB. Heptylsulfonic acid can remarkably support the electrochemical deposition of Ag(I) leading to extremely low detection limits in the fmol range [110]. An even simpler approach is made when the pasting liquid (tricresyl phosphate) can take the role of the counterion; a corresponding CPE can successfully be applied to the determination of iodide [111].

Adsorbents can successfully be applied to the accumulation of inorganic analytes; silica can preconcentrate copper from ammoniacal solutions under open

circuit conditions [112]. Electroactivation of the carbon paste improves the electrodeposition of Ag(I) and Cu(II), probably by generation of adsorbant groups at the surface which synergistically support the accumulation [113].

Metal replacement is another approach to preconcentrate analyte species at the electrode surface. A rather insoluble salt or complex acts as modifier, of which the cation is replaced by the analyte due to a lower solubility product or a higher complex formation constant. Thus, Hg(II) can be determined with zinc diethyldithiocarbamate as a modifier [114], Pb(II) with aluminium phosphate [115].

Catalytically active modifiers are quite frequently used for the determination of inorganic species. The active components are mediators rather than real catalysts and react primarily with the substrate in a redox reaction, whereupon they are regenerated electrochemically. Hydrogen peroxide is a particularly interesting substrate since it is often intermediate of enzymatic reactions; therefore many systems working with H_2O_2 are often used for the development of biosensors.

Phthalocyanines were used for electroanalytical studies with H_2O_2 (also a useful transducer for a lactate biosensor) [116], SCN^-, and $SeSCN^-$ [117]. Palladium powder is useful to detect H_2O_2 [118] or NH_2OH [119]. Platinum noble metals in general are rather efficient catalysts for the detection of hydrogen peroxide and are therefore quite frequently used in metal dispersed or metalized form for the development of biosensors [120]. Recently MnO_2 was used as a modifier for CPEs and SPCEs (bulk and film modification) with very low detection limits in the low ppb-range, allowing determinations of H_2O_2 in rain water and other samples [121-124]; work on the development of a glucose biosensor based on this modifier is currently going on. An interesting attempt was made by immobilizing analyte and catalyst at the same time at an ion exchanger-modified CPE. The design was successfully applied to the determination of nitrate [125] and perchlorate [126] using Amberlite LA2 as a modifier and tetrachloro thallate(III) as a catalyst.

Apart from voltammetric and amperometric detections it is also possible to use modified carbon pastes as sensor materials in potentiometric determinations, the modifiers usually playing a role of electroactive ion-exchanging components. The composition of carbon pastes makes it possible to classify the CPEs as ion-selective liquid membrane type electrodes; pasting liquids exhibit usually good extraction ability against ion-associates composed of lipophilic species. This is why they could also be applied to monitor titrations based on ion-pair formation, especially to those applied in determinations of surfactants [360-362]. When compared with ion-selective electrodes based on polymeric membranes which are often used for this purpose [363,364], the CPEs have an advatage of much lower ohmic resistance. Potentiometric titrations of zinc with EDTA were also realized employing 4-(3,5-dichloro-2-pyridyl-azo)- 1,3-diaminobenzene as an ion-exchanger [128]. With a Hg_2HPO_4-modified CPE, it is possible to determine hydrogen phosphate

in concentrated phosphoric acid [127].

Recently, four ion-exchangers were prepared for new perchlorate and fluoroborate ion-selective CPEs which found their applications in direct potentiometric determinations of the two anions as well as monitoring sensors of potentiometric titrations of perchlorate, fluoroborate and iodide using cetylpyridinium chloride as titrant. Simultaneously, it was verified that although the slopes of calibration plots, detection limits as well as selectivity coefficients were similar to those obtainable with commercial liquid/polymeric membrane type ion-selective electrodes, the carbon pastes offered more rapid responses and very low ohmic resistance [365].

Organic Analytes

Preconcentration of organic analytes at modified electrodes is reviewed by Arrigan [51]. Accumulation can be supported by admixing adsorbents or ion exchanger to the paste. Silica enables the preconcentration of Metamitron [129], C-18 bonded silicagel of ephedrine [130], Ioxinyl, and 2-methyl-3-nitroaniline [131]. Sepiolite is effective for ephedrine [132], bentonite for phenols [133-135], Nafion for beta-antagonistic drugs [136], Clenbuterol [137,138], Fenoterol [139], phenytoin (as a competitve immunoassay with cobaltocene-labelled phenytoin) [140], and for the alkaline phosphatase activity *via* preconcentration of a liberated intermediate [141]. Silicone OV-17 is suitable for indole-3-acetic acid [142], a cation exchange resin for phenylephrine [143], and β-cyclodextrine for phenols [144].

Fatty acids and lipids are commonly used as modifiers for carbon paste electrodes for *in vivo* monitoring of mainly dopamine (frequently in brain) in order to eliminate interferences from ascorbic or uric acid. A good overview of this subject is provided by some reviews [145-149]. There are quite diverse opinions in the literature about the applicability of such modified CPEs to *in vivo* measurements; obviously additional modification by albumins and phospholipids occurs due to contact with the brain tissue [150]. Differences in the separation of response potentials of dopamine and ascorbic acid as described in the literature could also be due to a varying viscosity of the paste, which is a crucial factor [151]. Zeolite Y can eliminate ascorbic acid interferences in *in vivo* measurements due to a negative charge barrier, whereas it preferentially incorporates dopamine and epinephrine [152]. Coupling the electrochemical detector for dopamine with microdialysis and additionally with HPLC is reported [153,154]. The lipid treated electrode is also applied to *in vivo* monitoring of ascorbic acid and oxygen in brain [155].

Fatty acids exert also a positive effect on the adsorptive stripping determination of cephalosporin antibiotics [156] and the tricyclic antidepressant Imipramine [157]. The latter together with Amitriptyline can be also detected with poly(N-vinylimidazole) as a modifier [158]. Oleic acid increases the

voltammetric response of estrogens [159]. Surfactants improve the adsorptive stripping of Aceclofenac at ppb levels [160].

Avidin is determinable in an immunoassay with a biotin-modified electrode using daunomycin as an electroactive label [161]. Specific interactions leading to host-guest complexes are exploited for the stripping voltammetric determination of sulfur-containing amino acids with crown ethers [162].

Inorganic insoluble salts seem to be promising modifiers for the accumulation of organic acids, if the resulting salt is less soluble than the modifying agent. Oxalate can thus be preconcentrated with $PbSO_4$ [163].

Analytical methods for organic species quite frequently exploit the catalytic effects of a mediator. Phthalocyanines were used for the determination of *t*-butyl hydroxyanisole [164], *t*-butyl hydroxytoluene [165], Thiram, Disulfiram [166], glutathione [167], thiols (microelectrodes) [168], Thiram and Disulfiram (with accumulation) [169], Cu(II)-porphyrin for sugar [170]. Ruthenium dioxide allows detection of amino acids in flow systems [171] and can even be used for the direct determination of glucose [172]. Trioctylamine is able to serve as an anchoring modifier for hexacyanoferrate as a catalyst for ascorbic acid, which can simultaneously be accumulated [173]. The same analyte shows improved response in the presence of tetrathiafulvalene [174] or Methylene Green [175]. The latter modifier is also very suitable to catalyze the oxidation of NADH [176,177], a task which can also be performed by Meldola's Blue [178] or by coatings of poly(*o*-aminophenol) or poly(*o*-phenylenediamine) [179].

Lipophilic mediators dissolved in the pasting liquid are exploitable to indicate peroxidase and lactase activity in solutions *via* liberated hydrogen peroxide [180]. Palladium powder dispersed in a carbon paste can effectively catalyze the reduction of aliphatic aldehydes [181].

Strictly speaking, also electrochemical activation, in particular with highly positive potentials, can be regarded as modification ("electrochemical modification"). Such electrode pretreatments have often an improving effect on potentiometric nucleic acid probes [37-45], preanodization generates carbon-oxygen compounds at the electrode surface, which still possess potential oxidizing capability. This can be exploited for the accumulation of adenine in its oxidized form under open circuit conditions with ensuing voltammetric determination [46]. Oxidative electrode pretreatment also facilitates the determination of uric acid, xanthine and hypoxanthine which allows even their simultanous quantitation in biological fluids [182,183].

Biosensors

Most work on modified carbon paste electrodes deals with the development of biosensors. A sensor in general is a device which recognizes more or less

specifically molecules or ions, whereupon a transducer converts the information of recognition into an exploitable signal. Biosensors in a strict sense are detectors whose substrate recognition depends on biological entities (enzymes, nucleic acids, tissues) integrated in the sensor. If the transducer is based on electrochemical principles, voltammetry can be applied, but in most cases amperometry is the method of choice because it allows quick monitoring of the response signal even in flow (e.g., high performance liquid chromatography HPLC, capillary electrophoresis CE, flow injection analysis FIA) or batch systems (chronoamperometry CA, batch injection analysis BIA) as well as on-line monitoring in dynamic or static processes.

Electrochemical biosensors are mainly restricted to redox enzymes since they provide an optimal base for electrochemical conversion of intermediates or products. Most frequently used enzymes are oxidases and dehydrogenases. Some general working principles as exploited with redox enzymes are sketched in Fig.1. With respect to oxidation of a substrate, the enzyme can, be in the simplest case, reoxidized directly at the electrode surface which is exploited with mediatorless biosensors (Fig. 1A). In most cases lies, however, the redox moiety of the enzyme inside the protein structure, which makes it inaccessible to direct electron transfer. Thus usually an electron messenger (mediator) is required to link the redox-conversion of the enzyme to the electron transfer at the electrode interface. The electron acceptor may penetrate directly into the enzyme and interact with its redox moiety (direct mediation, Fig. 1B), or oxygen performs this task, producing hydrogen peroxide as an intermediate (Fig. 1C). A similar sketch holds for nicotineamide adenine dinucleotide (NAD^+), which is also a frequent co-substrate in enzymatic oxidation reactions yielding the reduced form NADH. H_2O_2 exhibits a relatively high overpotential at carbon paste electrodes, so that its mediated detection is preferable. As it can act as an oxidant and as a reductant, mediated monitoring of H_2O_2 is possible in two alternatives (Fig. 1C, a and b). As a mediator even horseradish peroxidase (HRP) can be used either directly (following scheme b) or with mediation yielding bienzyme electrodes.

An excellent review on carbon paste biosensors was given by Gorton covering publications up to 1993 [184]. Therefore in this paper only recent works will be considered. Quite a few reviews appeared which give a good general introduction to the current trends in the development of biosensors [185-190], including mediated amperometric biosensors [191], concepts for transducers and direct electron transfer [192], peroxidase-modified electrodes [193], metalloenzymes [194], metallized carbon amperometric biosensors [120], DNA electrochemical biosensors [47], polymeric films in biosensors [195] as well as applications to flow systems (HPLC, FIA, CE) [196].

Most of the investigations on carbon paste biosensors deal with the development of sensors for sugars [197-238], in particular of glucose [197-233], due to the fact that there is an enormous need for quick and reliable determination of this analyte mainly in diabetes patients and food products. The

studies are generally based on incorporation of the corresponding oxidase or dehydrogenase and deal preferentially to improve detection by new mediators or by increasing the robustness, sensitivity or shelf life stability of sensors. The enzymes are immobilized either directly, by adsorption, entrapped in membranes, or cross-linked with glutaraldehyde. Interferences from ascorbic or

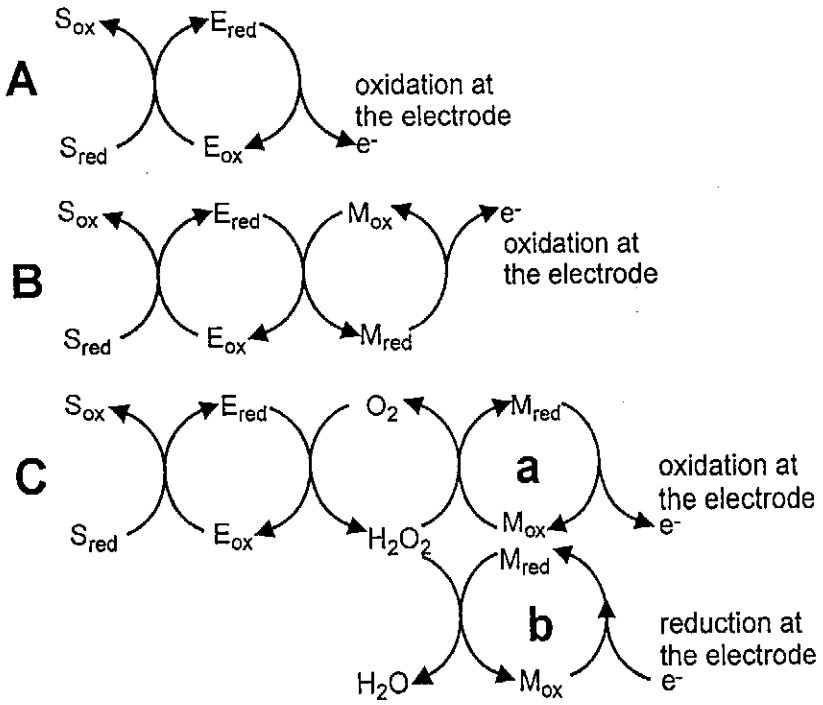

Fig.1 Amperometric detection possibilities of redox enzyme reactions (oxidation of a substrate) in electrochemical biosensors (S substrate, M mediator, E enzyme; index ox indicates the oxidized form, red the reduced). A - mediatorless direct electrochemical oxidation of the reduced enzyme system; B - direct mediation with M acting as an electron acceptor; C - mediated detection of hydrogen peroxide which can act as a reducing (a) or oxidizing (b) agent

uric acid can be eliminated with protective membranes, preferentially of cellulose acetate or Nafion. General concepts of reagentless oxidoreductase biosensors are sketched by Schmidt and Schuhmann [197], oxidase based biosensors on rhodinized carbon pastes and anti-interference layers are described by Wang et al. [198] who also give a critical comparison of metallized and mediator-based biosensors [199].

The determination of glucose is mostly based on the use of glucose oxidase (GOx) with various mediators, such as rhodium [200,201] or iridium in

dispersed form [202], osmium complexes or redox polymers [203-207], ferrocenes [208-218], cobaltocenes [219] Cu-bis(bathophenanthroline) [220], quinones [221-225], ubiquinone [226], tetracyanoquino-dimethane [227], Toluidine Blue [228], Methylene Green [229], viologens [230], and Meldola's Blue [231]; aldose dehydrogenase can be used in general for the detection of aldoses [208,209]. Assays for glucose microelectrodes [232,233], biosensors arrays [234] and dual working electrodes [235,236] were reported. Sucrose can be determined *via* glucose by multiple enzyme modification with invertase, mutarotase and glucose oxidase [235,237]. GOx shows a surprisingly high thermal stability and can stand temperature stress (>50° C) over a long period of time (up to 4 months) [238].

Similar attempts as with glucose were realized for fructose employing fructose dehydrogenase either mediatorless with polyethyleneimine [239] or mediated with Meldola's Blue [240], for galactose with galactose oxidase on platinized carbon [241], and for lactose with β-galactosidase and glucose oxidase, which can be used for the simultaneous determination of galactose and glucose with a dual working electrode arrangement [242].

Anti-digoxin antibodies are detectable with an immunoassay employing digoxin-conjugated glucose oxidase modified with ferrocene, which shows less electrochemical reactivity upon formation of the antibody immunocomplex due to steric hindrance [243].

Lactate is also rather a popular analyte and can be determined in its D- as well as in its L-form when using the appropriate enzyme lactate dehydrogenase [244-257]. As mediators HRP [244-246], ferrocenes [247], Toluidine Blue O [248], dispersed ruthenium [249], lipophilic cobalt phthalo-cyanine [250], cytochrome c (in combination with asolectine) [251], tetrathia-fulvalene (TTF) [252], or polymers [253-256] are used often with direct mixing of the co-substrate NAD^+. *Paracoccus denitrificans* is a suitable modifier, either as membrane vesicles or whole cells, for a microbial biosensor for the determination of lactate and succinate [257].

Ethanol can be conveniently detected with alcohol dehydrogenase (ADH) [258-268] in combination with NAD^+ mediated by HRP (also wired with Os redox hydrogel) [258-260], by Meldola's Blue or other redox dyes [261-264], or by polymers [254,265]. Pectin is determinable *via* methanol with a CPE modified with ADH and an attached orange peel which is a source of pectinesterase de-esterfying pectin and releasing CH_3OH [269]. Methanol dehydrogenase with phenazine methosulfate as a mediator can be used for indirect monitoring of NH_3, which acts as an enzyme activator [270].

Phenolic compounds are oxidized by tyrosinase, which can be employed as a modifier for carbon paste sensors, where conveniently the quinoid response is monitored [271-282]. The quinone product can also be accumulated by conducting the enzymatic reaction under open circuit conditions [275]. Studies were made to investigate the influence of mediators [276], binders [277], and additives [278] on tyrosinase-modified electrodes. The enzyme can serve for

indirect detection of hydrazines by reversible competitive inhibition [282]. Mushroom [283] or potato tissue [284] can serve as a source for polyphenol oxidase in order to oxidize phenols; potato tissue was also applied to the determination of dopamine. Another approach exploits the enzymatic regeneration of electrochemically oxidized phenolic compounds by quinoprotein glucose dehydrogenase, which oxidizes glucose in the substrate (thus, the phenolic analyte acts as a mediator) [285]. It is also possible to monitor the response towards phenoxy radicals formed during enzymatic oxidation of phenols by HRP in the presence of H_2O_2 [286], but in this case solid graphite electrodes are preferable.

Other biologically important analytes which can be determined by enzymatic oxidation are L/D-amino acids with L/D-amino acid oxidase [287, 288], L-glutamate by thermophilic glutamate dehydrogenase and Toluidine Blue [289] or by glutamate oxidase and TTF [290], L-glutaminate by glutaminase in combination with glutamate oxidase [290], and L-malate with L-malate dehydrogenase and Toluidine Blue [228]. Salicylate hydroxylase allows the determination of salicylate [291-293], but shows some chaotic regime [293]. Uricase together with HRP facilitates the detection of uric acid [294]. Biosensors containing poly(ethylene glycol)-modified choline oxidase and ferrocene can monitor choline [295]. Adenosine triphosphate (ATP) is detectable *via* H_2O_2 using glycerol kinase and glycerol-3-phosphate oxidase as enzyme modifiers and Pt as a mediator [296]. Oxidative hydroxylation of nicotinic acid by bacterial cells of *Pseudomonas fluorescens* gives an electrochemical response with mediation of p-benzoquinone in the electrode bulk or in solution [297, 298].

Photocurrent studies were performed with intact cells of cyanobacteria and diaminodurene as a mediator [299], investigations on the photooxidation of water were done with the photosystem II of spinach chloroplasts [300].

Also inorganic analytes can be determined by biosensors. Thus, HRP is useful to monitor hydrogen peroxide and other types of peroxides (e.g., butanone peroxide) [301-309]; various mediators and stabilization procedures were investigated. Microperoxidase [310] or even asparagus tissue [311] can be used instead of HRP. The enzyme also gives exploitable amperometric responses with FIA [312]. Cyanide can be determined indirectly by inhibition of cytochrome c oxidase [313].

The most interesting approach for the specific detection of DNA was done on voltammetric base by Millan et al. [314] and was developed further with chronopotentiometry and potentiometric stripping by Wang's group [47,315-319]. Single stranded oligonucleotides [314-317] or peptide nucleic acids (DNA analogs) [318,319] are immobilized on the sensor and undergo specific hybridization with the analyte while detection is achieved by an electroactive indicator (usually a Co(III)-complex). Thus, assays for detection of cystic fibrosis [314], *Mycobacterium tuberculosum* [316] and HIV-1 DNA [317] were realized. Fabrication as thick film sensor which responds towards *Escherichia coli* is possible [320]. DNA probes can be also employed for the

determination of hydrazines [321] and phenothiazines [322].

Occasionally, adsorption of proteins was applied to modify carbon paste electrodes. The catalytic properties of plasmin adsorbed onto carbon pastes were studied with an electrogenic substrate [323-325]; fibrinogen was used with a ferro/ferricyanide probe [326,327]. CPEs modified with bovine serum albumin and polycations were characterized by Gorton's group [328].

Carbon Pastes with Incorporated Analytes and Electroactive Components

Carbon pastes are an ideal matrix to incorporate electroactive species, particularly if they are not, or only slightly, soluble in the aqueous sample solution. The role and exploitation of paste additives as mediator in modified sensor was sketched already in the previous chapters. But incorporation of such substances opens also a simple way to characterize them with respect to their electrochemical behavior and to perform interaction, dissolution and leaching studies. Some approaches even incorporate the whole sample matrix into the paste in order to quantify electrochemically active components in analogy to abrasive stripping voltammetry [329]. The binder of pastes can be either of non-electrolytic type as in conventional CPEs or of electrolytic nature, often strongly acidic or alkaline.

Most applications in this field deal with inorganic compounds. Copper(I,II)-salts and oxides were investigated in corrosion studies with azole as a corrosion inhibitor [330]; the Cu(II)/Cu(III) ratio in superconductors can be determined in this way [331]. Copper and silver compounds were used for interaction studies with humic acids [332]. Copper ferrite was electrochemically characterized together with the corresponding copper and iron salts with a CPE based on an electrolytic binder [333]. The electrochemical behavior of Fe(II),Fe(III) compounds including magnetite [334], the oxidation of FeAsS [335] in acidic solutions and the dissolution of ilmenite [336] were studied. Galena [337], manganese oxides [338], spheralites [339,340], vanadium compounds [341,342], chalcopyrite [343], Cu, Pb and Bi in various oxidation states [344], Ni-complexes [345,346], and metallic powders [347] were subject to electrochemical investigations. Zeolite served as an adsorbant for electroactive species, such as Methyl Viologen [348], Ag(I), Cu(II) and complexes of cobalt, iron [349] and ruthenium [350]. Alizarine S can be added to carbon paste after adsorption onto alumina [351] or circonia [352]; Zr(IV)-phosphate is a proper sorbent for Methylene Blue [353]. Diphenylcarbazone, diphenylcarbazide [354], α-tocopherol [355], and polyamides containing disulfide bonds [356] were mixed directly to the paste for their electrochemical characterization.

Lipid peroxides in oils [357], electroactive constituents of sesame oil, such as sesaminol and sesamol [358], as well as piroxicam in pharmaceutical formulations [359] can be determined quantitatively by adding the sample to the paste.

Prospectives

The huge number of publications dealing with carbon paste electrodes underlines clearly that this electrode material is an indispensable tool in electrochemical research nowadays. Particularly the ease of preparation as well as modification even with very labile systems and also in multiple form make it ideally suited for designing electrochemical sensors based on voltammetric, amperometric or potentiometric transduction. In this context carbon pastes will still be an extremely fruitful area of research in the future.

But according to our opinion they do not represent the final state of the art, since also quite a lot of problems are connected with them concerning reproducibility and stability. We think that other types of sensors, in particular solid composite electrodes and one-shot strip-type thick films are finally superior to carbon pastes, simply due to the fact that they can be produced in large quantities in a very reproducible manner, showing usually also increased robustness and shelf-life stabilities. In this context carbon pastes will be a necessary but in some respects transient tool for developing sensors which will be applied on a large scale.

Acknowledgements

The authors appreciate support for this work from the Austrian Fonds zur Förderung der wissenschaftlichen Forschung (project P11172-CHE) and from the AKTION Austrian Czech Academic Exchange program (project 5p1). H.A. acknowledges financial support by an individual scholarship from the Austrian government.

References

1. Kalcher K.: Electroanalysis **2,** 419 (1990).
2. Kalcher K., Kauffmann J.-M., Wang J., Švancara I., Vytřas K., Neuhold C., Yang Z.: Electroanalysis **7,** 5 (1995).
3. Kalcher K., Cai X., Kölbl G., Švancara I., Vytřas K.: Sb. Věd. Prací, Vys. Škola Chem. Technol., Pardubice **57,** 5 (1994).
4. Švancara I., Vytřas K., Renger F., Smyth M.R.: Sb. Věd. Prací, Vys. Škola Chem. Technol., Pardubice **56,** 21 (1992/93).
5. Vytřas K., Švancara I.: Chem. Listy **88,** 412 (1994).
6. Švancara I., Vytřas K.: Chem. Listy **88,** 138 (1994).
7. Adams R.N.: Anal. Chem. **30,** 1576 (1958).
8. Adams R.N.: *Electrochemistry at Solid Electrodes,* 1st ed., Marcel Dekker, New York 1969.

9. Kuwana T., French W.G.: Anal. Chem. **36,** 241 (1964).
10. Schultz F.A., Kuwana T.: J. Electroanal. Chem. **10,** 95 (1965).
11. Walkins B.F., Sehling J.R., Kariv E., Miller L.L.: J. Amer. Chem. Soc. **97,** 3549 (1975).
12. Cheek G.T., Nelson R.F.: Anal. Lett. **A11,** 393 (1978).
13. Yao T., Musha S.: Anal. Chim. Acta **110,** 203 (1979).
14. Ravichandran K., Baldwin R.P.: J. Electroanal. Chem. **126,** 293 (1981).
15. Campanella L., Tomassetti M.: Bull. Electrochem. **8,** 229 (1992).
16. Durst R.A., Bäumer A.J., Murray R.W., Buck R.P., Andrieux C.P.: Pure Appl. Chem. **69,** 1317 (1997).
17. Nachr. Chem. Tech. Lab. **45,** 1219 (1997).
18. Švancara I., Hvízdalová M., Vytřas K., Kalcher K., Novotný R.: Electroanalysis **8,** 61 (1997)
19. Vytřas K., Švancara I., Renger F., Srey M., Vaňková R., Hvízdalová M.: Collect. Czech. Chem. Commun. **58,** 2039 (1993).
20. Švancara I., Vytřas K.: Anal. Chim. Acta **273,** 195 (1993).
21. Švancara I., Kalcher K., Diewald W., Vytřas K.: Electroanalysis **8,** 336 (1996).
22. Kelepouris L., Plaush A.: Abstr. Pap. Amer. Chem. Soc. **211,** 176 (1996).
23. Švancara I., Pravda M., Hvízdalová M., Vytřas K., Kalcher K.: Electroanalysis **6,** 63 (1994).
24. Švancara I., Matoušek M., Sikora E., Schachl K., Kalcher K., Vytřas K.: Electroanalysis **9** (1997) 827.
25. Labar C., Lamberts L.: Talanta **44,** 733 (1997).
26. Osipova E.A., Prokhorova G.V., Gurentsova O.I., Kopytova N.E.: Industr. Lab. **60,** 82 (1994).
27. Lubert K.H., Guttmann M., Beyer L.: Electroanalysis **8,** 320 (1996).
28. Garcia M.B.G., Garcia A.C.: Bioelectrochem. Bioenerg. **38,** 389 (1995).
29. Wang L.H.: Analyst **120,** 2241 (1995).
30. Eskinja I., Grabaric Y., Grabaric B.S.: Atm. Environm. **29,** 1165 (1995).
31. Zoulis N.E., Efstathiou C.E.: Anal. Chim. Acta **320,** 255 (1996).
32. El-Maali N.A. Ghandour M.A., Kauffmann J.-M.: Bioelectrochem. Bioenerg. **38,** 91 (1995).
33. Arenaza M.J., Gallo B., Berrueta L.A, Vicente F.: Anal. Chim. Acta **305,** 91 (1995).
34. Fernandez Abedul M.T., Velazquez Rodriguez M.S.: Anal. Lett. **30,** 1491 (1997).
35. Boyd D., Rodriguez J.R.B., Ordieres A.J.M, P. Tuñón-Blanco, M.R. Smyth: Analyst **119,** 1979 (1994).
36. Hattori T., Kato M., Tanaka S., Hara M.: Electroanalysis **9** (1997) 722.
37. Wang J., Cai X., Wang J.Y., Jonsson C., Paleček E.: Anal. Chem. **67,** 4065 (1995).
38. Cai X., Rivas G., Farias P.A.M., Shiraishi H., Wang J.: Bioelectrochem.

Bioenerg. **40,** 41 (1996).
39. Cai X., Rivas G., Farias P.A.M., Shiraishi H., Wang J., Paleček E.: Electroanalysis **8,** 753 (1996).
40. Wang J., Cai X., Jonsson C., Balakrishnan M.: Electroanalysis **8,** 20 (1996).
41. Cai X., Rivas G., Shiraishi H., Farias P., Wang J., Tomschik M., Jelen F., Paleček E.: Anal. Chim. Acta **244,** 65 (1997).
42. Wang J., Chen L., Chicharro M.: Anal. Chim. Acta **319,** 347 (1996).
43. Wang J., Rivas G., Cai X., Chicharro M., Dontha N., Luo D.B., Palecek E., Nielsen P.E.: Electroanalysis **9,** 120 (1997).
44. Cai X., Rivas G., Farias P.A.M., Shiraishi H., Wang J., Paleček E.: Anal. Chim. Acta **332,** 49 (1996).
45. Wang J., Rivas G., Cai X., Chicharro M., Farais P.A.M. Paleček E.: Electroanalysis **8,** 902 (1996).
46. Cai X., Ogorevc B., Kalcher K.: Electroanalysis **7,** 1126 (1995).
47. Wang J., Rivas G., Cai X., Paleček E., Nielsen P., Shiraishi H., Dontha N., Luo D., Parrado C., Chicharro M., Farias P.A.M., Valera F.S., Grant D.H., Oszoz M., Flair M.N.: Anal. Chim. Acta **347,** 1 (1997).
48. Ulakhovich N.A., Medyantseva E.P., Budnikov G.K.: J. Anal. Chem. (Transl. Zh. Anal. Khim.) **48** (1993) 682.
49. Kalvoda R.: Fresenius J. Anal. Chem. **349,** 565 (1994).
50. Qu Y.B.: Analyst **121,** 139 (1996).
51. Arrigan D.W.M.: Analyst **119,** 1953 (1994).
52. Troyanski E.I., Pogosyan M.S., Samoshina N.M., Nikishin G.I.: Mendeleev Comm. **1996,** 1.
53. Shaidarova L.G., Algakhri M.A., Ulakhovich N.A., Zabirov N.G., Budnikov G.K.: J. Anal. Chem. (Transl. Zh. Anal. Khim.) **49,** 452 (1994).
54. Ulakhovich N.A., Algakhri M.A., Shaidarova L.G.: Industr. Lab. **60,** 148 (1994).
55. Shaidarova L.G., Ulakhovich N.A., Algakhri M.A., Budnikov G.K.: Izv. Vys. Uch. Zav., Khim. Khim. Tekhnol. **36,** 51 (1996).
56. Shaidarova L.G., Ulakhovich N.A., Fedorova I.L., Galyamedtinov Y.G.: J. Anal. Chem. (Transl. Zh. Anal. Khim.) **51,** 687 (1996).
57. Shaidarova L.G., Ulakhovich N.A., Algakhri M.A., Budnikov G.K.: J. Anal. Chem. (Transl. Zh. Anal. Khim.) **50,** 692 (1995).
58. Won M.S., Moon D.W., Shim Y.B.: Electroanalysis **7,** 1171 (1995).
59. Khodari M., Aboukrisha N.M., Fandy R.: Talanta **41,** 2179 (1994).
60. Hunag S.S., Cheng Z.G., Li B.F., Lin H.G., Yu R.Q.: Analyst **119,** 1859 (1994).
61. Zhang Z.Q., Liu H., Li Y.F.: Anal. Chim. Acta **333,** 119 (1996).
62. Jimoh M.A., Scholz F.: Fresenius J. Anal. Chem. **356,** 202 (1996).
63. Peng T.Z., Sheh L.Q., Wang G.S.: Mikrochim. Acta **122,** 125 (1996).
64. Peng T.Z., Tang Z., Wang G.S., Shen B.E.: Electroanalysis **6,** 597 (1994).
65. Gao Z.Q., Siow K.S., Ng A.: Electroanalysis **8,**1183 (1996).

66. Cai Q.T., Khoo S.B.: Electroanalysis **7,** 379 (1995).
67. Cai Q.T., Khoo S.B.: Analyst **120,** 1047 (1995).
68. Bae Z.U., Park Y.C., Lee S.H., Jeon W.S., Chang H.Y.: Bull. Korean Chem. Soc. **17,** 995 (1996).
69. Khoo S.B., Soh M.K., Cai Q.T., Khan M.R., Guo S.X.: Electroanalysis **9,** 45 (1997).
70. Khoo S.B., Zhu J.: Analyst **121,** 1983 (1996).
71. Wang J., Lu J.M., Larson D.D., Olsen K.: Electroanalysis **7,** 247 (1995).
72. Ferri T., Guidi F., Morabito R.: Electroanalysis **6,** 1087 (1994).
73. Sugawara K.: Bunseki Kagaku **43,** 95 (1994).
74. Agraz R., Demiguel J., Sevilla M.T., Hernandez L.: Electroanalysis **8,** 565 (1996).
75. Arrigan D.W.G., Svehla G., Harris S.J., McKervey M.A.: Electroanalysis **6,** 97 (1994).
76. Oconnor K.M., Arrigan D.W.M, Svehla G.: Electroanalysis **7,** 205 (1995).
77. Guttmann M., Lubert K.H.: Fresenius J. Anal. Chem. **356,** 263 (1996).
78. Cai X., Kalcher K., Neuhold C., Goessler W., Grabec I., Ogorevc B.: Fresenius J. Anal. Chem. **348,** 736 (1994).
79. Ferri T., Paci S., Morabito R.: Ann. Chim. **86,** 245 (1996).
80. Won M.S., Kim M.J., Shim Y.B.: Bull. Korean Chem. Soc. **17,** 1142 (1996).
81. Chang C.H., Liu C.Y.: J. Chin. Chem. Soc. **44,** 231 (1997).
82. Safavi A., Pakniat M., Maleki N.: Anal. Chim. Acta **335,** 275 (1996).
83. Agraz R., Sevilla M.T., Hernandez L.: J. Electroanal. Chem. **390,** 47 (1995).
84. Cai X., Kalcher K., Lintschinger J., Neuhold Ç.: Mikrochim. Acta **112,** 135 (1993).
85. Raber G., Kalcher K., Neuhold C.G., Talaber C., Kölbl G.: Electroanalysis **7,** 138 (1995).
86. Molina Holgado T., Pinilla Macias J.M., Hernandez Hernandez L.: Anal. Chim. Acta **309,** 117 (1995).
87. Shumilova M.A., Trubachev A.V., Kurbatov D.I.: J. Anal. Chem. (Transl. Zh. Anal. Khim.) **52,** 753 (1997).
88. Wu W.S., Uddin M.S., Chi H., Hidajat K.: J. Appl. Electrochem. **24,** 548 (1994).
89. Labuda J., Korgova H., Vaníčkova M.: Anal. Chim. Acta **305,** 42 (1995).
90. Labuda J., Korgova E., Vaníčkova M., Tarapcik P.: Chem. Anal. (Warsaw) **41,** 865 (1996).
91. Helms I., Scholz F.: Fresenius J. Anal. Chem. **356,** 237 (1996).
92. Rolison D.R.: Stud. Surf. Sci. Catal. **85,** 543 (1994).
93. Bedioui F., Roue L., Briot E., Devynck J., Bell S.L., Balkus K.J.: J. Electroanal. Chem. **373,** 19 (1994).
94. Walcarius A.: Electroanalysis **8,** 971 (1996).
95. Walcarius A., Barbaise T., Bessiere J.: Anal. Chim. Acta **340,** 61 (1997).
96. Chen B., Goh N.K., Chia L.S.: Electrochim. Acta **42,** 595 (1997).

97. Bing C., Kryger L.: Talanta **43,** 153 (1996).
98. Walcarius A., Lamberts L., Derouane E.G.: Electroanalysis **7,** 120 (1995).
99. Grabec-Svegl I., Ogorevc B., Hudnik V.: Fresenius J. Anal. Chem. **354,** 770 (1996).
100. Ogorevc B., Cai X., Grabec I.: Anal. Chim. Acta **305,** 176 (1995).
101. Kula P., Navratilova Z.: Fresenius J. Anal. Chem. **354,** 692 (1996).
102. Wang C.M., Sun Q.Y., Li H.L.: Electroanalysis **9,** 645 (1997).
103. Jeong E.D., Won M.S., Shim Y.B.: Electroanalysis **6,** 887 (1994).
104. Drake L.R., Rayson G.D.: Anal. Chem. **68,** A22 (1996).
105. Lu G.H., Yang M., Zheng Q.F., Wang A.L., Jin Z.X.: Electroanalysis **7,** 591 (1995).
106. Kwak M.K., Park D.S., Won M.S., Shim Y.B.: Electroanalysis **8,** 680 (1996).
107. Stadlober M., Kalcher K., Raber G.: Talanta **43,** 1915 (1996).
108. Stadlober M., Kalcher K., Raber G.: Electroanalysis **9,** 225 (1997).
109. Stadlober M., Kalcher K., Raber G.: Anal. Chim. Acta **350,** 318 (1997).
110. Švancara I., Kalcher K., Diewald W., Vytřas K.: Electroanalysis **8,** 336 (1996).
111. Švancara I., Konvalina J., Schacjl K., Kalcher K., Vytřas K.: Electroanalysis, submitted for publication.
112. Walcarius A., Bessiere J.: Electroanalysis **9,** 707 (1997).
113. Rivas G.A., Ortiz P.I.: Anal. Lett. **27,** 751 (1994).
114. Khoo S.B., Cai Q.T.: Electroanalysis **8,** 549 (1996).
115. Abdollahi S.: Anal. Chim. Acta **304,** 381 (1995).
116. Mizutani F., Yabuki S., Iijima S.: Electroanalysis **7,** 706 (1995).
117. Cookeas E.G., Efstathiou C.E.: Analyst **119,** 1607 (1994).
118. Cai X., Kalcher K., Kölbl G., Neuhold C., Diewald W., Ogorevc B.: Electroanalysis **7,** 340 (1995).
119. Cai X., Kalcher K., Lintschinger J., Neuhold C., Tykarski J., Ogorevc B.: Electroanalysis **7,** 556 (1995).
120. Wang J., Lu F., Angnes L., Liu J., Sakslund H., Chen Q., Pedrero M., Chen L., Hammerich O.: Anal. Chim. Acta **305,** 3 (1995).
121. Schachl K., Alemu H., Kalcher K., Ježková J., Švancara I., Vytřas K.: Analyst **122,** 985 (1997).
122. Schachl K., Alemu H., Kalcher K., Ježková J., Švancara I., Vytřas K.: Anal. Lett. **30,** 2655 (1997).
123. Schachl K., Alemu H., Kalcher K., Moderegger M., Švancara I., Vytřas K.: Fresenius J. Anal. Chem., submitted for publication.
124. Schachl K., Alemu H., Kalcher K., Ježková J., Švancara I., Vytřas K.: Sci. Pap. Univ. Pardubice Ser. A **3,** 41 (1997).
125. Neuhold C., Kalcher K., Diewald W., Cai X., Raber G.: Electroanalysis **6,** 227 (1994).
126. Neuhold C., Kalcher K., Cai X., Raber G.: Anal. Lett. **29,** 1685 (1996).

127. Elmaslout A., Benayada A., Oudda H., Bessiere J., Pillet Y.: Analusis **24,** 182 (1996).
128. Raba J., Fontan C.A., Cortinez V.A.: Talanta **41,** 273 (1994).
129. Arranz A., Villalba M.F., Debetono S.F., Moreda J.M., Arranz J.F.: Fresenius J. Anal. Chem. **357,** 768 (1997).
130. Chicharro M., Zapardiel A., Bermejo E., Perez J.A., Hernandez L.: Anal. Lett. **27,** 1809 (1994).
131. Faller C., Meyer A., Henze G.: Fresenius J. Anal. Chem. **356,** 279 (1996).
132. Chicharro M., Zapardiel A., Bermejo E., Perezlopez J.A., Hernandez L.: Analusis **23,** 131 (1995).
133. Rodriguez I.N., Leyva J.A.M., Decisneros J.L.H.H.: Analyst **122,** 601 (1997).
134. Rodriguez I.N, Zamora M.B., Salvador J.M.B., Leyva J.A.M., Hernandezartiga M.P., Decisneros J.L.H.H.: Mikrochim. Acta **126,** 87 (1997).
135. Rodriguez I.N., Leyva J.A.M., Decisneros J.L.H.H.: Anal. Chim. Acta **344,** 167 (1997).
136. Boyd D., Rodriguez J.R.B., Ordieres A.J.M., Tuñón-Blanco P., Smyth M.R.: Analyst **119,** 1979 (1994).
137. Moane S., Smyth M.R., Okeffe M.: Analyst **121,** 779 (1996).
138. Moane S., Rodriguez J.R.B., Ordieres A.J.M., Tuñón-Blanco P., Smyth M.R.: J. Pharm. Biomed. Anal. **14,** 57 (1995).
139. Boyd D., Rodriguez J.R.B., Tuñón-Blanco P., Smyth M.R.: J. Pharm. Biomed. Anal. **12,** 1069 (1994).
140. Rapicault S., Limoges B., Degrand C.: Anal. Chem. **68,** 930 (1996).
141. Rapicault S., Limoges B., Degrand C.: Electroanalysis **8,** 880 (1996).
142. Hernandez P., Galan F., Nieto O., Hernandez L.: Electroanalysis **6,** 577 (1994).
143. Perlado J.C., Zapardiel A., Bermejo E., Perez J.A., Hernandez L.: Anal. Chim. Acta **305,** 83 (1995).
144. Kim S.H., Won M.S., Shim Y.B.: Bull. Korean Chem. Soc. **17,** 342 (1996).
145. Oneill R.D.: Analyst **119,** 767 (1994).
146. Rebec G.V., Pierce R.C.: Progr. Neurobiol. **43,** 537 (1994).
147. Pantano P., Kuhr E.G.: Electroanalysis **7,** 405 (1995).
148. Oneill R.D., Lowry J.P.: Behaviour. Brain Res. **71,** 33 (1995).
149. Blaha C.D., Phillips A.G.: Behaviour. Pharmacol. **7,** 675 (1996).
150. Blaha C.D., Liu D., Phillips A.G.: Biosensors Bioelectr. **11,** 63 (1996).
151. Petit C., Gonzalez Cortes A., Kauffmann J.M.: Bioelectrochem. Bioenerg. **41,** 101 (1996).
152. Wang J., Walcarius A.: J. Electroanal. Chem. **407,** 183 (1996).
153. Diciano P., Blaha C.D., Phillips A.G.: Behaviour. Pharmacol. **7,** 714 (1996).
154. Diciano P., Coury A., Deporteere R.Y., Egilmez Y., Lane J.D.,

Emettoglesby M.W., Lepiane F.G., Phillips A.G., Blaha C.D.: Behaviour. Pharmacol. **6**, 311 (1995).
155. Lowry J.P., Boutelle M.G., Oneill R.D., Fillenz M.: Analyst **121**, 761 (1996).
156. Elmaali N.A., Ghandour M.A., Kauffmann J.M.: Bioeletrochem. Bioenerg. **38**, 91 (1995).
157. Khodari M., Mansour H., Eldin H.S.: Anal. Lett. 30, 1909 (1997).
158. Biryol I., Uslu B., Kucukyavuz Z.: J. Pharm. Biomed. Anal. **15**, 371 (1996).
159. Hu S.S., Guo M.D., Hu G.Z., Jiang M.: Anal. Lett. **28**, 1993 (1995).
160. Posac J.R., Vazquez M.D., Tascón M.L., Acuña J.A., Delafuente C., Sanchez Batanero P.: Talanta **42**, 293 (1995).
161. Sugawara K., Tanaka S., Nakamura H.: Anal. Chem. **67**, 299 (1995).
162. Shaidarova L.G., Fedorova I.L., Ulakhovich N.A., Budnikov G.K.: J. Anal. Chem. (Transl. Zh. Anal. Khim.) **52**, 238 (1997).
163. Cai X., Ogorevc B., Tavcar G., Kalcher K.: Electroanalysis **7**, 639 (1995).
164. Ruiz M.A, Calvo M.P., Pingarron J.M.: Talanta **41**, 289 (1994).
165. Ruiz M.A., Yanezsedeno P., Pingarron J.M.: Electroanalysis **6**, 475 (1994).
166. Fernandez C., Riviejo A.J, Pingarron J.M.: Analusis **23**, 319 (1995).
167. Hart J.P., Wring S.A.: Anal. Proc. **28**, 4 (1991).
168. Oshea T.J., Lunte S.M.: Anal. Chem. **66**, 307 (1994).
169. Fernandez C., Riviejo A.J., Pingarron J.M.: Analusis **23**, 319 (1995).
170. Sugawara K., Yamamoto F., Tanaka S., Nakamura H.: J. Electroanal. Chem. **394**, 263 (1995).
171. Wang J., Lin Y.H.: Electroanalysis **6**, 125 (1994).
172. Lyons M.E.G., Fitzgerald C.A., Smyth M.R.: Analyst **119**, 855 (1994).
173. Labuda J., Hudakova M.: Electroanalysis **9**, 239 (1997).
174. Murthy A.S.N., Anita: Biosensors Bioelectr. **11**, 191 (1996).
175. Yu A.M., He C.X., Zhou J., Chen H.Y.: Fresenius J. Anal. Chem. **357**, 84 (1997).
176. Chi Q.J., Dong S.J.: Anal. Chim. Acta **285**, 125 (1994).
177. Chen H.Y., Yu A.M., Han J.L., Mi Y.Z.: Anal. Lett. **28**, 1579 (1995).
178. Kubota L.T., Gouvea F., Andrade A.N., Milagres B.G., Neto G.D.: Electrochim Acta **41**, 1465 (1996).
179. Lobo MJ., Miranda A.J., Lopesfonseca J.M., Tuñón-Blanco P.: Anal. Chim. Acta **325**, 33 (1996).
180. Kulys J., Drungiliene A., Wollenberger U., Krikstopaitis K., Scheller F.: Electroanalysis **9**, 213 (1997).
181. Cai X., Kalcher K.: Electroanalysis **6**, 397 (1994).
182. Cai X., Kalcher K., Neuhold C.: Fresenius J. Anal. Chem. **348**, 660 (1994).
183. Cai X., Kalcher K., Ogorevc B.: Talanta **41**, 407 (1994).
184. Gorton L.: Electroanalysis **7**, 23 (1995).
185. Hall E.A.H.: Int. J. Biochem. **20**, 357 (1988).

186. Vadgama P., Crump P.V.: Analyst **117**, 1657 (1992).
187. Hall E.A.H., Gooding J.J., Hall C.E.: Mikrochim. Acta **121**, 119 (1995).
188. Ikeda T.: Bunseki Kagaku 44, 333 (1995).
189. Wollenberger U.: Biotechnol. Gen. Eng. Rev. 13, 237 (1996).
190. Skladal P., Macholan L.: Chem. Listy **91**, 105 (1997).
191. Stoecker P.W., Yacynych A.M.: Bull. Electrochem. **8**, 181 (1992).
192. Ghindilis A.L., Atanasov P., Wilkins E.: Electroanalysis **9**, 661 (1997).
193. Ruzgas T., Csoregi E., Emneus J., Gorton L., Markovarga G.: Anal. Chim. Acta **330**, 123 (1996).
194. Hill H.A.O., Hunt N.I.: Meth. Enzymol. **227**, 501 (1993).
195. Emr S.A., Yacynych A.M.: Electroanalysis **7**, 913 (1995).
196. Emneus J., Marko-Varga G.: J. Chromatogr. **A 703**, 191 (1995).
197. Schmidt H.L., Schuhmann W.: Biosensors Bioel. **11**, 127 (1996).
198. Wang J., Chen L., Liu J., Lu F.: Electroanalysis **8**, 1127 (1996).
199. Wang J., Chen L., Liu J.: Electroanalysis **9**, 298 (1997).
200. Wang J., Liu J., Chen L., Lu F.: Anal. Chem. **66**, 3600 (1994).
201. Wang J., Walcarius A.: J. Electroanal. Chem. **405**, 117 (1996).
202. Wang J., Rivas G., Chicharro M.: Electroanalysis **8**, 434 (1996).
203. Parellada J., Narvaez A., Dominguez E., Katakis I.: Biosensors Bioel. **12**, 267 (1997).
204. Hedenmo M., Narvaez A., Dominguez E., Katakis I.: Analyst **121**, 1891 (1996).
205. Csoregi E., Laurell T., Katakis I., Heller A., Gorton L.: Mikrochim. Acta **121**, 31 (1995).
206. Pravda M., Adeyoju O., Iwuoha E.I., Vos J.G., Smyth M.R., Vytřas K.: Electroanalysis **7**, 619 (1995).
207. Ježková J., Iwuoha E.I., Smyth M.R., Vytřas K.: Electroanalysis **9**, 978 (1997).
208. Smolander M., Gorton L., Lee H.S., Skotheim T., Lan H.L.: Electroanalysis **7**, 941 (1995).
209. Smolander M., Markovarga G., Gorton L.: Anal. Chim. Acta **302**, 233 (1995).
210. Losada J., Cuadrado I., Moran M., Casado C.M., Alonso B., Barranco M.: Anal. Chim. Acta **338**, 191 (1997).
211. Milagres B.G., Kubota L.T., Neto G.D.: Electroanalysis **8**, 489 (1996).
212. Martens N., Hindle A., Hall E.A.H.: Biosensors Bioel. **10**, 393 (1995).
213. Yabuki S., Mizutani F.: Biosensors Bioel. **10**, 353 (1995).
214. Saby C., Mizutani F., Yabuki S.: Anal. Chim. Acta **304**, 33 (1995).
215. Bu H.Z., Mikkelsen S.R., English A.M.: Anal. Chem. **67**, 4071 (1995).
216. Mizutani F., Yabuki S., Katsura T.: ACS Symp. Ser. **556**, 41 (1994).
217. Wang J., Naser N.: Electroanalysis **6**, 571 (1994).
218. Andrieux C.P., Audebert P., Bacchi P., Divisiablohorn B.: J. Electroanal. Chem. **394**, 141 (1995).

219. Mizutani F., Yabuki S., Iijima S.: Anal. Chim. Acta **300**, 59 (1995).
220. Labuda J., Hudakova M.: Chem. Anal. (Warsaw) **42**, 435 (1997).
221. Kaku T., Okamoto Y., Charles L., Holness W., Karan H.I.: Polymer **36**, 2813 (1995).
222. Elatrash S.S., Oneill R.D.: Electrochim. Acta **40**, 2791 (1995).
223. Tessema M., Ruzgas T., Gorton L., Ikeda T.: Anal. Chim. Acta **310**, 161 (1995).
224. Lan H.L., Kaku T., Karan H.I., Okamoto Y.: ACS Symp. Ser. **556**, 124 (1994).
225. Motta N., Guadelupe A.R.: Anal. Chem. **66**, 566 (1994).
226. Kawakami M., Uriuda N., Koya H., Gonda S.: Anal. Lett. **28**, 1555 (1995).
227. Sun C.Q., Song W.B., Zhao D., Gao Q., Xu H.D.: Microchem. J. **53**, 296 (1996).
228. Huan Z.W., Persson B., Gorton L., Sahni S., Skotheim T., Bartlett P.: Electroanalysis **8**, 575 (1996).
229. Kulys J., Wang L., Hansen H.E., Buchrasmussen T., Wang J., Oszoz M.: Electroanalysis **7**, 92 (1995).
230. Karan H.I., Lan H.L., Okamoto Y.: ACS Symp. Ser. **556**, 169 (1994).
231. Kulys J., Hansen H.E., Buchrasmussen T., Wang J., Oszot M.: Anal. Chim. Acta **288**, 193 (1994).
232. Oshea T.J., Lunte S.M.: Anal. Chem. **66**, 307 (1994).
233. Gasparini R., Scarpa M., Vianello F., Mondovi B., Rigo A.: Anal. Chim. Acta **294**, 299 (1994).
234. Kulys J., Hansen H.E.: Biosensors Bioel. **9**, 491 (1994).
235. Zhang X.N., Rechnitz G.A.: Electroanalysis **6**, 361 (1994).
236. Kulys J., Hansen H.E.: Anal. Chim. Acta **303**, 285 (1995).
237. Zhang X.N., Rechnitz G.A.: Electroanalysis **6**, 361 (1994).
238. Wang J., Liu J., Cepra G.: Anal. Chem. **69**, 3124 (1997).
239. Parellada J., Dominguez E., Fernandez V.M.: Anal. Chim. Acta **330**, 71 (1996).
240. Garcia C.A.B., Neto G.D., Kubota L.T., Grandin L.A.: J. Electroanal. Chem. **418**, 147 (1996).
241. Manowitz P., Stoecker P.W., Yacynych A.M.: Biosensor Bioel. **10**, 359 (1995).
242. Katsu T., Zhang X.N., Rechnitz G.A: Talanta **41**, 843 (1994).
243. Suzawa T., Ikariyama Y., Aizawa M.: Anal. Chem. **66**, 3889 (1994).
244. Spohn U., Narasaiah D., Gorton L.: Electroanalysis **8**, 507 (1996).
245. Spohn U., Narasaiah D., Gorton L.: Anal. Chim. Acta **319**, 79 (1996).
246. Narasaiah D., Spohn U., Gorton L.: Anal. Lett. **29**, 181 (1996).
247. Boujtita M., Chapleau M., Elmurr N.: Electroanalysis **8**, 485 (1996).
248. Shu H.C., Mattiasson B., Persson B., Nagy G., Gorton L., Sahni S., Geng L., Boguslavsky L., Skotheim T.: Biotechnol. Bioeng. **46**, 270 (1995).
249. Wang J., Chen Q., Pedrero M.: Anal. Chim. Acta **304**, 41 (1995).

250. Mizutani F., Yabuki S., Iijima S.: Electroanalysis **7**, 706 (1995).
251. Amine A., Deni J., Kauffmann J.-M.: Bioelectrochem. Bioenerg. **34**, 123 (1994).
252. Mulchandani A., Bassi A.S., Nguyen A.: J. Food Sci **60**, 74 (1995).
253. Lobo-Castañón M.J., Miranda-Ordieres A.J., Tuñón-Blanco P.: Anal. Chim. Acta **346**, 165 (1997).
254. Lobo M.J., Miranda A.J., Lopez Fonseca J.M, Tuñón-Blanco P.: Anal. Chim. Acta **325**, 33 (1996).
255. Shu H.C., Gorton L., Persson B., Mattiasson B.: Biotechnol. Bioeng. **46**, 280 (1995).
256. Narasaiah D., Spohn U., Gorton L.: Anal. Lett. **29**, 181 (1996).
257. Kalab T., Skladal P.: Electroanalysis **6**, 1004 (1994).
258. Johansson K., Jonssonpettersson G., Gorton L., Markovarga G., Csoregi E.: J. Biotechnol. **31**, 301 (1993).
259. Marko-Varga G., Johansson K., Gorton L.: J. Chromatogr., **A 660**, 153 (1994).
260. A.R. Vijayakumar, E. Csoregi, A. Heller, L. Gorton: Anal. Chim. Acta **327**, 223 (1996).
261. Mullor S.G., Sanchez Cabezudo M, Miranda-Ordieres A.J., Ruiz B.L.: Talanta **43**, 779 (1996).
262. Lobo M.J., Miranda A.J., Tuñón-Blanco P.: Electroanalysis **8**, 591 (1996).
263. Lobo M.J., Miranda A.J., Tuñón-Blanco P.: Electroanalysis **8**, 932 (1996).
264. Chi Q.J., Dong S.J.: Anal. Chim. Acta **285**, 125 (1994).
265. Lobo-Castañón M.J., Miranda-Ordieres A.J., Tuñón-Blanco P.: Biosensors Bioel. **12**, 511 (1997).
266. Boujtita M., Chapleau M., Elmurr N.: Anal. Chim. Acta **319**, 91 (1996).
267. Boujtita M., Elmurr N.: J. Food Sci. **60**, 201 (1995).
268. Wang J., Liu J.: Anal. Chim. Acta **284**, 385 (1993).
269. Horie H., Rechnitz G.SA.: Anal. Chim. Acta **306**, 123 (1995).
270. Suye S.I., Nakamura Y., Inuta S., Ikeda T., Senda M.: Biosensors Bioel. **11**, 529 (1996).
271. Marko-Varga G., Burestedt E., Svensson C.J., Emneus J., Gorton L., Ruzgas T., Lutz M., Unger K.K.: Electroanalysis **8**, 1121 (1996).
272. Burestedt E., Narvaez A., Ruzgas T., Gorton L., Emneus J., Dominguez E., Marko-Varga G.: Anal. Chem. **68**, 1605 (1996).
273. Cosnier S., Popescu I.C.: Anal. Chim. Acta **319**, 145 (1996).
274. Lindgren A., Ruzgas T., Emneus J., Csoregi E., Gorton L., Marko-Varga G.: Anal. Lett. **29**, 1055 (1996).
275. Wang J., Chen Q.: Electroanalysis **7**, 746 (1995).
276. Hedenmo M., Narvaez A., Dominguez E., Katakis I.: J. Electroanal. Chem. **425**, 1 (1997).
277. Wang J., Lu F, Kane S.A., Choi Y.K., Rogers K.: Abstr. Pap. ACS **213**, 60 (1997).

278. Lutz M., Burestedt E., Emneus J., Liden H., Gobhadi S., Gorton L., Marko-Varga G.: Anal. Chim. Acta 305, **8** (1995).
279. Burestedt E., Emneus J., Gorton L., Marko-Varga G., Dominguez E., Ortega F., Narvaez A., Irth H., Lutz M., Puig D., Barcelo D.: Chromatographia **41**, 207 (1995).
280. Ortega F., Dominguez E., Burestedt E., Emneus J., Gorton L., Marko-Varga G.: J. Chromat. **A 675**, 65 (1994).
281. Wang J., Lu F., Lopez D.: Biosensors Bioel. **9**, 9 (1994).
282. Wang J., Chen L.: Anal. Chem. **67**, 3824 (1995).
283. Oszoz M., Erdem A., Kilinc E., Gokgunnec L.: Electroanalysis **8**, 147 (1996).
284. Forzani E.S., Rivas G.A., Solis V.M.: J. Electroanal. Chem. **382**, 33 (1995).
285. Wollenberger U., Neumann B.: Electroanalysis **9**, 366 (1997).
286. Ruzgas T., Emneus J., Gorton L., Marko-Varga G.: Anal. Chim. Acta **311**, 245 (1995).
287. Kacaniklic V., Johansson K., Marko-Varga G., Gorton L., Jonsson-Pettersson G., Csoregi E.: Electroanalysis **6**, 381 (1994).
288. Rivas G.A., Maestroni B.: Anal. Lett. **30**, 489 (1997).
289. Jeffries C., Pasco N., Baronian K., Gorton L.: Biosensors Bioel. **12**, 225 (1997).
290. Mulchandani A., Bassi A.S.: Biosensors Bioel. **11**, 271 (1996).
291. Kubota L.T., Migraes B.G., Gouvea F., Neto G.D.: Anal. Lett. **29**, 893 (1996).
292. Zhou D.M., Nigam P., Jones J., Marchant R.: J. Chem. Technol. Biotechnol. **64**, 331 (1995).
293. Kubota L.T., Kleinke M.U., Mello C., Bueno M.I., Neto G.D.: Chem. Phys. Lett. **264**, 662 (1997).
294. Miland E., Ordieres A.J.M., Tuñón-Blanco P., Smyth M.R., Fagain C.O.: Talanta **43**, 785 (1996).
295. Yabuki S., Mizutani F., Katsura T.: Sensors Actuators B - Chem. **20**, 159 (1994).
296. Katsu T., Yang X.R., Rechnitz G.A.: Anal. Lett. **27**, 1215 (1994).
297. Takayama K., Kurosaki T., Ikeda T., Nagasawa T.: J. Electroanal. Chem. **381**, 47 (1995).
298. Takayama K., Ikeda T., Nagsawa T.: Electroanalysis **8**, 765 (1996).
299. Martens N, Hall E.A.H.: Photochem. Photobiol. **59**, 91 (1994).
300. Amako K., Yanai H., Ikeda T., Shiraishi T., Takahashi M.: J. Electroanal. Chem. **362**, 71 (1993).
301. Vijayakumar A., Csoregi E., Ruzgas T., Gorton L.: Sensors Actuators B - Chem. **37**, 97 (1996).
302. Liu H.Y., Zhang Z.N., Fan Y.B., Dai M., Zhang X.L., Wie J.J., Qiu Z.N., Li H.B., Wu X.X., Deng J.Q., Di D.Y.: Fresenius J. Anal. Chem. **357**, 297

(1997).
303. Wuo W.L., Liu H.Y., Deng H.H., Sun K., Zhao C.H., Qi D.Y., Deng J.Q.: Anal. Lett. **30**, 205 (1997).
304. Li J., Tan S.N., Ge H.L.: Anal. Chim. Acta **335**, 137 (1996).
305. Ciszewski A., Gorski Z.: Electroanalysis **7**, 495 (1995).
306. Popescu I.C., Zetterberg G., Gorton L.: Biosensors Bioel. **10**, 443 (1995).
307. Charpentier L., Elmurr N.: Analusis **23**, 265 (1995).
308. Rajendran V., Csoregi E., Okamoto Y., Gorton L.: Abstr. Pap. ACS **213**, 43 (1997).
309. Popescu I.C., Csoregi E., Gorton L.: Electroanalysis **8**, 1014 (1996).
310. Razumas V., Kazlauskaite J., Vidziunaite R.: Bioelectrochem. Bioenerg. **39**, 139 (1996).
311. Oungpipat W., Alexander P.W., Southwellkeely P.: Anal. Chim. Acta **309**, 35 (1995).
312. Dominguez Sanchez P., Osullivan C.K., Miranda Ordieres A.J., Tuñón-Blanco P., Smyth M.R.: Anal. Chim. Acta **291**, 349 (1994).
313. Amine A., Alafandy M., Kauffmann J.M., Pekli M.N.: Anal. Chem. **67**, 2822 (1995).
314. Millan K.M., Saraullo A., Mikkelsen S.R.: Anal. Chem. **66**, 2943 (1994).
315. Wang J., Cai X., Rivas G., Shiraishi H.: Anal. Chim. Acta **326**, 141 (1996).
316. Wang J., Rivas G., Cai X., Dontha N., Shiraishi H., Luo D.B., Valera F.S.: Anal. Chim. Acta **337**, 41 (1997).
317. Wang J., Cai X., Rivas G., Shiraishi H., Farias P.A.M., Dontha N.: Anal. Chem. **68**, 2629 (1996).
318. Wang J., Paleček E., Nielsen P.E., Rivas G., Cai X., Shiraishi H., Dontha N., Luo D.B., Farias P.A.M.: J. Amer. Chem. Soc. **118**, 7667 (1996).
319. Wang J., Rivas G., Cai X., Chicharro M., Parrado C., Dontha N., Begleiter A., Mowat M., Paleček E., Nielsen P.E.: Anal. Chim. Acta **344**, 111 (1997).
320. Wang J., Rivas G., Cai X.: Electroanalysis **9**, 395 (1997).
321. Wang J., Chicharro M., Rivas G., Cai X., Dontha N., Farias V, Shiraishi H.: Anal. Chem. **68**, 2251 (1996).
322. Wang J., Rivas G., Cai X., Shiraishi H., Farias P.A.M., Dontha N., Luo D.B.: Anal. Chim. Acta **332**, 139 (1996).
323. Longchamp S., Randriamahazaka H.N., Nigretto J.M.: J. Electroanal. Chem. **412**, 31 (1996)
324. Longchamp S., Randriamahazaka H.N., Nigretto J.M.: Electroanalysis **8**, 20 (1996).
325. Longchamp S., Randriamahazaka H.N., Nigretto J.M.: J. Colloid Interf. Sci. **166**, 444 (1994).
326. Elrhazi M., Randriamahazaka H.N., Nigretto J.M.: Electroanalysis **9**, 403 (1997).

327. Arkoub I.A., Randriamahazaka H., Nigretto J.M.: Anal. Chim. Acta **340**, 99 (1997).
328. Kulys J., Gorton L., Dominguez E., Emneus J., Jarskog H.: J. Electroanal. Chem. **372**, 49 (1994).
329. Scholz F., Meyer B.: Chem. Soc. Rev. **23**, 341 (1994).
330. Lakshminarayanan V., Kannan R., Rajagopalan S.R.: J. Electroanal. Chem. **364**, 79 (1994).
331. Vidal J.C., Vera A., Castillo J.R.: Anal. Sci. **12**, 109 (1996).
332. Kula P., Navratilova Z.: Electroanalysis **6**, 1009 (1994).
333. Bachiller P.E., Garcia M.L.T., Barbado M.D.V.: J. Electroanal. Chem. **367**, 99 (1994).
334. Encinas P., Lorenzo L., Tascon M.L., Vazquez M.D., Sanchez Batanero P.: L. Electroanal. Chem. **372**, 161 (1994).
335. Lazaro I., Cruz R., Gonzalez I., Monry M.: Int. J. Miner. Proc. **50**, 63 (1997).
336. Marinovich Y., Bailey S., Avraamides J., Jayasekera S.: J. Appl. Electrochem. **25**, 823 (1995).
337. Ahlberg E., Asbjornsson J.: Hydrometallurgy **34**, 171 (1993).
338. Gonzalez C., Gutierrez J.I., Gonzalezvelasco J.R., Cid A., Arranz A., Arranz J.F.: J. Therm. Anal. **47**, 93 (1996).
339. Ahlberg E., Asbjornsson J.: Hydrometallurgy **36**, 19 (1994).
340. Richardson P.E., Hu Q., Finkelstein N.P., Yoon R.H.: Int. J. Miner. Proc. **41**, 71 (1994).
341. Barrado E., Pardo R., Castrillejo Y., Vega M.: J. Electroanal. Chem. **427**, 35 (1997).
342. Strappazzon R., Lamberts L.: Analysis **22**, 263 (1994).
343. Lazaro L., Martinez Medina N, Rodriguez I., Arce E., Gonzalez I.: Hydrometallurgy **38**, 277 (1995).
344. Espinosa A.M., Tascon M.L., Encinas P., Vazquez M.D., Sanchez Batanero P.: Electrochim. Acta **40**, 1623 (1995).
345. Tommasino J.B., Pomarede B., Medus D., Demontauzon D., Cassoux P., Fabre P.L.: Mol. Cryts. Liqu. Cryst. Sci. Technol. Sect. A - Mol. Cryst. Liqu. Cryst. **237**, 445 (1993).
346. Encinas P., Lorenzo L., Tascon M.L., Vazquez M.D., Sanchez Batanero P.: J. Electroanal. Chem. **371**, 161 (1994).
347. Galová M., Markušová K., Lux L., Zezula I., Orinakova R.: Chem. Pap. (Chem. Zvesti) **51**, 5 (1997).
348. Yoon K.B., Park Y.S., Kochi J.K.: J. Amer. Chem. Soc. **118**, 12710 (1998).
349. Senaratne C., Zhang J., Baker M.D., Bessel C.A., Rolison D.R.: J. Phys. Chem. **100**, 5849 (1996).
350. Walcarius A., Lamberts L.: J. Electroanal. Chem. **422**, 77 (1997).
351. Navarro P., Jambon C., Vittori O.: Fresenius J. Anal. Chem. **356**, 476

(1996).
352. Bennoua A., Durand B., Vittori G., Chassagneux F., Kheribech K.: Ann. Chim. - Sci. Mater. **21**, 557 (1996).
353. Passoa C.A., Gushikem Y., Kubota L.T.: Electroanalysis **9**, 800 (1997).
354. Ramirez M.T., Morales Perez A., Rojas Hernadez A., Gonzalez I.: J. Electroanal. Chem. **410**, 203 (1996).
355. Kim O.S., Kusuda K.: Bioelectrochem. Bioener. **33**, 61 (1994).
356. Tsutsumi H., Okada K., Oishi T.: Electrochim. Acta **41**, 2657 (1996).
357. Kim O.S., Maekawa K., Kusuda K.: J. Amer. Oil Chem. Soc. **72**, 299 (1995).
358. Shiragami S., Kim O.S., Kusuda K.: J. Electroanal. Chem. **379**, 315 (1994).
359. Paniagua A.R., Vazquez M.D., Tascon M.L., Sanchez Batanero P.: Electroanalysis **6**, 265 (1994).
360. Vytřas K., Ježková J., Kalous J., Švancara I. in *XXVIII. seminár o tenzidoch a detergentoch*, p. 35, Sloveca, Nováky 1994.
361. Vytřas K., Ježková J., Kalous J. in *XXIX. seminář o tenzidech a detergentech*, p. 117, University Press Centre, Pardubice 1995.
362. Vytřas K., Kalous J., Ježková J.: Egypt. J. Anal. Chem.**6**, 107 (1997).
363. Vytřas K.: Ion-Sel. Electrode Rev. 7, 77 (1985).
364. Vytřas K.: Electroanalysis **3**, 343 (1991).
365. Ježková J., Musilová J., Vytřas K.: Electroanalysis **9**, 1433 (1997).