VERSITA

Cent. Eur. J. Chem. • 7(4) • 2009 • 598–656
DOI: 10.2478/s11532-009-0097-9

Central European Journal of **Chemistry**

Carbon paste electrodes in the new millennium

Invited Review

Ivan Švancara[1]*, Alain Walcarius[2], Kurt Kalcher[3], Karel Vytřas[1]

[1]*Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, CZ-532 10 Pardubice, Czech Republic*

[2]*Laboratory of Physical Chemistry and Microbiology for the Environment, 54600 Villers-les-Nancy, France*

[3]*Institute of Chemistry – Analytical Chemistry, Karl-Franzens-University of Graz, A-3000 Graz, Austria*

Received 14 May 2009; Accepted 9 July 2009

Abstract: In this review (with 500 refs), both electrochemistry and electroanalysis with carbon paste-based electrodes, sensors, and detectors are of interest, when attention is focused on the research activities in the years of new millennium. Concerned are all important aspects of the field, from fundamental investigations with carbon paste as the electrode material, via laboratory examination of the first electrode prototypes, basic and advanced studies of various electrode processes and other phenomena, up to practical applications to the determination of inorganic ions, complexes, and molecules. The latter is presented in a series of extensive tables, offering a nearly complete survey of methods published within the period of 2001-2008. Finally, the latest trends and outstanding achievements are also outlined and future prospects given.

Keywords: *Carbon paste electrodes • Electrochemistry • Electroanalysis • New millennium (2001-2008)*

1. Introduction

1.1. Electrochemistry and electroanalysis with carbon paste electrodes in the light of Nobel Prize winner Jaroslav Heyrovský and his polarography

The year of 2009 comprises an anniversary celebrating exactly fifty years that have passed since Professor Jaroslav Heyrovský (1890-1967) won the Nobel Prize for Chemistry as an award for the discovery of polarographic method, its principal development, and popularisation worldwide [1]. Coincidentally, the same year also represents a break-point that indicates the start of a new half-a-century of existence of carbon paste as the electrode material [2].

It is to be noted that both seemingly distant fields – *i.e.*, polarography with the dropping mercury electrode (DME) and electrochemistry with carbon paste electrodes (CPEs) – are somehow associated as the configuration of classical DME has become an inspiration for similarly functioning electrode variant based on carbon dispersion. This linking point had appeared in the late 1950s, when Professor Ralph Norman Adams (1924-2002) and his students were testing a new "dropping carbon electrode" (DCE) as an alternative to the DME for anodic oxidations of organic compounds, where the mercury drop could not be used. Although such a concept had finally failed, a thicker mixture of softer consistence, carbon paste [3], was found to be capable of replacing satisfactorily the originally intended DCE configuration [4].

There is yet another link between carbon pastes and polarography – it is the first review on CPEs, written again by Adams [5] that had appeared in a Japanese bulletin Review of Polarography. In view of present day's classification, it was rather unusual

* *E-mail: Ivan.Svancara@upce.cz*

choice as the referred CPEs representing solid-like sensors, with invariable surface, and of non-mercury character could not be operated in the polarographic regime, but voltammetrically. (At that time, however, voltammetric experiments had sometimes been reported as polarographic measurements – see *e.g.* [6] and the authentic citation withdrawn from the abstract, "...*The carbon paste electrode recommended by Adams for polarographic oxidation of various organic substances*...", published in Nature – one of the most prestigious scientific journals.)

Finally, polarography with DME and the CPEs themselves share quite similar fates when taking into account their more-or-less accidental discoveries, as well as the resultant position achieved in modern electrochemistry. Whereas polarographic *I-E* curves were first registered during investigations with electrocapillary phenomena at the DME [7], carbon paste was a "side-product" coming from unsuccessful experimentation with the above-mentioned DCE [4,5]. Some decades later, when polarography had already become the worldwide-renowned scientific discipline [1], the electrochemistry with CPEs also started to play a role of highly respected field that would spread over the globe, spawning about 2 000 scientific papers and having touched almost each area of theoretical and applied electrochemistry [2].

1.2. The state of art in the new millennium

Since their invention in 1958, carbon paste electrodes (CPEs) underwent a very impressive development, pursuing the progress in electrochemistry, electroanalysis, and instrumental analysis as such. The respective history illustrated *via* the individual periods and milestones has already been summarised, when practically each aspect, feature, or particular area were of interest in the past five decades. Also, some significant periods of research work with CPEs were the subject of exclusively oriented reviews and related reports (see [1,2] and refs. therein).

Herein, for the reader's comfort, it is possible to briefly point out the respective bibliographic sources published to date and given below in a chronological order: (i) the early era of CPEs has been evaluated by Adams himself [4,5]; the key contributions from the 1960s concerning initial characterisations of CPEs coming also from his laboratories [8-10], as well as from some other pioneers in the U.S. and Europe [11-15]; (ii) typical achievements during the 1970s can then be withdrawn from some original reports (*e.g.* [16-20]); (iii) the starting era of chemically and biologically modified carbon paste electrodes (CMCPEs and CP-biosensors, respectively) initiated by a series of key studies [21-25] and spread over the entire 1980s is documented by a triad of contemporary reviews [26-28]; (iv) the beginning of 1990s and the following years are covered in the remaining reviews articles [29-39], including some specialised areas [34,35]. Finally, there are also two attempts to overview the field in its entirety. The first accomplishment of this kind is a 250-pages-lengthy chapter published in the Encyclopedia Of Sensors *(EOS)* series [40]; the second being a brand new review made on the occasion of the half-centurial jubilee of carbon paste [2]. As seen, the last review devoted to a particular period of the field was the article published by our group in 2001 [36].

In an effort to specify the latest achievements and trends, we have prepared this new review focused on the years after the commencement of the new millennium – for the period of 2001-2008. In some respect, it can be considered as a continuation of the above-mentioned review covering the years of 1996-2000 [36], together with its forerunners having dealt with the preceding half-decade of 1991-1995 [29,30]. However, compared to these compilations, there is one distinct difference – this review and its sections concerning electroanalytical applications are concentrated on inorganic analysis only and the determinations of organic substances, environmental pollutants, pharmaceuticals, and biologically important compounds are not considered, except for single mentions dealing with new groups of CPEs or in association with latest achievements with some particular techniques. The reason for such a selection is a special review [41] covering the recent advances in organic and biological electroanalysis with CPEs and appearing soon in an article dedicated also to the 50th anniversary of Heyrovský's Nobel Prize and concerning predominantly organic electrochemistry.

Last but not least, here is only a little overlay with the above-mentioned book-chapter [40], having also reviewed a number of publications from the first years of the new millennium. This text is focused exclusively on latest trends and summarises additionally more than two hundred new publications that have appeared in the last three years – *i.e.*, after the release of the review in *EOS*.

2. Electrochemical research with carbon paste electrodes in the period of 2001-2008

2.1. Classical carbon pastes and some advances in their characterisation

Similarly as in previous decades, mixtures made of commercially available spectroscopic graphite powders (as a carbon moiety) and of either paraffin (mineral) oils

or silicone fluids (in the role of pasting liquid or binder, respectively) have also dominated over the years of the new millennium and it can be expected that such mixtures might represent about 75% among all carbon pastes employed [2]. Apart from their actual use – *i.e.*, if the resultant CPEs were employed in the bare configuration or as chemically modified carbon paste electrodes, CMCPEs –, this statement reflects the fact that traditional carbon paste compositions may still offer attractive properties and versatile use. Their wide applicability, as well as compatibility with new procedures and materials, is then documented throughout this text and, especially, in sections **3** and **4**, summarising the individual methods of inorganic electroanalysis reported over the period 2001-2008.

The continuing interest in traditional carbon pastes has then resulted in some valuable contributions to the basic characterisation of CPEs, CMCPEs, or carbon paste-based electrode substrates, which could be achieved with the aid of (i) new instrumentation, (ii) hitherto-unused approaches, or initiated by (iii) actual demands.

(i) Among newly used instrumental techniques for characterisation measurements, one can mention studies on the carbon paste structure with atomic force microscopy (AFM [42]), scanning electrochemical microscopy (SECM [43]), or surface screening with electrochemical impedance spectroscopy (EIS [44]) and spectroelectrochemistry (SEC [45]).

(ii) One of the unpublished approaches to the characterisation of CPEs is newly described in a report [46], dealing with the electrical resistance of carbon paste mixtures. The respective studies have helped to explain long-time unclear reasons for excellent conductivity of common carbon pastes (see *e.g.* [39,40]), which could be accomplished *via* experimental verification of a new hypothesis – "Model of the tightest arrangement of carbon particles".

(iii) As a typical example of an actual demand that influences the orientation of modern electrochemical research and applied electroanalysis, it is possible to quote the increasing popularity of the so-called "green analytical chemistry" [47]. Carbon paste as completely non-toxic and environmentally friendly material is widely applicable also within these activities, including various combinations with other momentarily preferred materials (for details, see below, in sections **2.2** and **2.3**).

2.2. New types of carbon pastes and related materials

Besides common graphite powders, both paraffin and silicone oils can also be mixed with other carbonaceous materials, forming more or less specific carbon pastes. In the past decades, such investigations with newly proposed mixtures had always been of interest and the same was the case of numerous efforts appearing in the period of 2001-2008.

2.2.1. Carbon pastes made of alternate carbonaceous materials.

Shortly after the commencement of a new millennium, carbon pastes made of (i) glassy carbon powder (with spherical particles and specially pre-treated surface) came again to the fore [48,49] as the electrode material exhibiting excellent polarisation characteristics, electrocatalytic effect for some redox systems, or even significantly improved resistivity in media with a higher content of organic solvents (such as solutions containing up to 80-90% (v/v) MeOH [50]). More favourable reaction kinetics due to electrocatalysis have also been reported for carbon pastes prepared from (ii) acetylene black [51,52], (iii) template carbon or (vi) porous carbon foam [53]. A collection of reports [54-61] concerns the family of (v) diamond paste electrodes (DPEs), where the carbon moiety is replaced by natural or synthetic diamond. Reportedly, these mixtures exhibit remarkably high analytical currents due to which the respective DPEs are able to operate at extremely low concentrations (down to the picomolar level [56,60]). However, because both diamond and the binder in such pastes are electric insulators, the functioning of these electrodes remains rather mysterious. In last years, intensively popularized (vi) new forms of carbon complete the list with other pastes made of fullerenes ("C-60" [62,63]), carbon nanoparticles [64], or paste-like mixtures with carbon nanofibers [65], and various types of carbon nanotubes [66]; the latter representing a new phenomenon also within the electrochemistry with carbon pastes, deserving a special attention [2].

2.2.2. Carbon nanotube paste electrodes (CNTPEs or CNPEs, respectively).

This type of carbon pastes has already been the central subject of more than 30 original papers [67-97] and the respective research can now be regarded as a separate area in the field. Since the first reports by Palleschi's [67,68,73], Wang's [69] and Rivas's [66,70,71,75] groups, the CNTPEs have undergone a very diverse investigation, comprising the initial electrochemical characterisation of basic types of nanotubes and the respective CNTPEs (*e.g.* [67-70]), their comparison

with common CPEs [68,69,74], studies on specific electrocatalytic properties of CNTs [73,75,76], the respective reaction kinetics [73], specific ion transfer at liquid / liquid phase boundaries [92], or their capabilities to immobilise various substances into the electrode bulk (*e.g.*, redox mediators [67,73,77], enzymes [70,80] or even two enzymes together [87], and various catalysts from single metallic particles [80,96], *via* specially synthesised polymeric compounds – the so-called molecular wires [78]).

Numerous CNTPEs have already been successfully examined for the identification and quantification of numerous species of inorganic, organic, or biological origin. In inorganic analysis, CNTPEs were employed to determine Hg(II) in water samples [72], Cu(II) + Pb(II) in fish tissue [85] or Cu(II) alone in vascular tracts [94]; the latter being feasible with specially fluorinated CNTs. Among organic and biologically important compounds, of interest were: alcohols and phenols [70,77], thiolic amino acids (homocysteine [69]), flavonoid-antioxidants (quercetin and rutin [74,79]), glucose [80,87,88,96], dopamine [68,75,81], NAD(H) [70,73,77], DNA [90], as well as some pharmaceuticals (namely: *Isoniazid* [86], *Piroxicam* [89], *Urapidyl* [83], and antibacterial *Oxytetracycline* [93]) or environmental pollutants like herbicide *Amitrole* [71]. Furthermore, similarly to common types of CPEs, the CNTs-paste sensors have been shown to be versatile with respect to their combination with modern instrumentation such as highly selective amperometric detection [80,87,96], separation techniques like capillary zone electrophoresis (CZE [75]) or electrochemiluminesce detection (ECL-D [88]), including their mutual combination (CZE / ECL-D [91]).

In paste mixtures, carbon nanotubes – in both single-wall and multi-wall forms – are usually used as (i) substitute of graphite powder (see *e.g.* [67-71,74,81,86,89]), mixed directly with paraffin oil [67-70], silicone oil [84] or, alternatively, an ionic liquid (IL) [82]. In some cases, CNTs may represent (ii) additional component (modifier [90]), or a constituent in (iii) mixtures with another substances that further amplify the electrocatalytic effect of CNTs themselves [78,80,96].

2.2.3. Carbon Pastes Made from Atypical Binders.

Mixtures, where paraffin or silicone oils were replaced by alternate binder, have been of considerable interest mainly in the initial era of characterisation measurements with CPEs (see *e.g.* [37,40] and refs. therein), whereas reports on such carbon pastes from the recent years are quite rare. For instance, mixtures of this type have been employed in potentiometric indications, which is the case of carbon paste-based electrodes made of chemically active di-*iso*-nonyl phthalate (DINP [97]) or tricresyl phosphate (TCP [98]). The latter – when protonated in an acidic supporting electrode – is also applicable in electrochemical stripping analysis (ESA), acting as counter-ion for effective pre-concentration of some anions [99-101].

Common pasting liquids can also be alternated by some nearly solid binders like silicone grease (C/SG type, made from lubricant for fly-fishing floating lines [102]) or polypropylene (C/PP, [40]), forming very dense and difficult-to-handle mixtures. Occasionally, the so-called solid-like carbon paste electrodes are also reported, representing configurations where the binder is formed by solidified paraffin wax (s-CPEs or C/PWs, respectively [103-109]). In these cases, the PW moiety acts as a stabilising element, protecting the respective electrode material against the dissolution effect of organic solvents (*e.g.*, EtOH [104,105]), or may serve for immobilisation of modifiers applied as a mixture of reagents [108,109].

Finally, solid binder-based carbon pastes can also be represented by screen-printed electrodes (SPEs) prepared from thicker (paste-like) carbon inks [110,111]. Herein, the respective electrode material is classified as "carbon paste" by the authors themselves; maybe, due to a close relation of both CPEs and SPEs as typical representatives of carbon heterogeneous electrodes [32]. Otherwise, however, both types are being distinguished (see *e.g.* [112,113]).

2.2.4. Carbon Ionic-Liquid Electrodes (CILEs).

Similarly as carbon nanotubes, also room-temperature ionic liquids (RTILs or ILs, respectively) have recently come into the fore [114]. These substances are represented by molten salts with the melting point close to or below room temperature, consisting of two asymmetrical ions of opposite charges. Their excellent solvating properties, high conductivity, non-volatility, low toxicity, wide polarisation range, as well as good electrochemical stability make such ion-associates attractive for many applications, including their incorporation in various electrodes, (bio)sensors, and detection systems [114]. In the electrochemistry with carbon pastes, the corresponding boom is reflected in the rise of a new family of carbon paste-based electrodes – carbon ionic liquid electrodes (CILEs), reported, to date, in approx. 30 contributions [82,115-140].

Pioneering attempts with CILEs, initiated four years ago by Liu *et al.* [115] were soon followed by Opallo's group [116], together with especially active Maleki and Safavi plus co-workers [117-119,121,123]. Since then, other scientific teams had stepped into the field [82,120,122,124], and all the started investigations dealt again with a wide variety of experimental work – from the

fundamental characterisations and comparative studies with common CPEs (*e.g.* [115,117,119,126,127]), *via* studies on the specific ion / charge transfer in ILs [115-117,120] and their electrocatalytic effect [121,128,137], up to first analytical applications to the determination of various organic and biologically active compounds. Namely, of interest were the following substances: ClO_4^- and PF_6^- anions [116]; nitrite, NO_2^- [115,126,128]; hydrogen peroxide (in environmental samples [125]); hydrazine [133]; *n*-alkyl-amines [124]; phenol, amino-phenols, and catechol [123,130], nitro-phenols (*p*-nitrophenol and *Methylparathion* in waste-water [137]); hydroquinone (in cosmetic cream and waste-water [127,139]); glucose [138], calcium dobesilate (in capsule and urine [122]); *Paracetamol* (in pharmaceuticals and urine [136]); *Acetaminophen* [133]; ascorbic acid (AA, in model samples [117,133] or tablets of *Vitamin-C* [120]); dopamine (DO, in injection samples [117,129]), including simultaneous determination of AA, uric acid (UA), and DO in human blood and urine [118]; NAD(H) [117], and DNA [132,135].

In another analogy with CNTs, also (RT)ILs can be used as (i) mixtures with graphite, where the ionic liquid replaces ordinary binders (*e.g.* [115-117]); (ii) additional component (usually modifier [127]); or (iii) special medium for another reagent (*e.g.*, enzyme [138]). Regarding the individual types of (RT)ILs, the compounds of choice are heterocyclic structures of the [*n*-alkyl-pyridium]$^+A^-$ or [R,R'-imidazolium]$^+A^-$ type (where the respective anion is PF_6^-, Br^-, or *bis*(trifluoromethyl-sulfonyl)imide, NTF2 [115-120]). Regarding the techniques which are being coupled with CILEs, predominant are amperometric detections (*e.g.*, [125,133,138], feasible also as measurements in the FIA mode [124], followed by voltammetry [118,123,127], including a more effective detection with the rotated disc electrode (RDE) [82]. Some methods can be combined with potentiometric indication [119] or even electrochemiluminescence detection [124].

The commentary on new types of carbon pastes can be concluded by quoting (i) a mixture of carbon nanotubes with an ionic liquid [82] or (ii) CNTPEs immersed in ionic liquid-based supporting electrolytes [140]. In the first case, a combination of the two trendy materials has resulted in a unique paste of "new generation", in which both traditional components are replaced with alternate moieties, whereas the remaining two cases can be considered as a transient element between the CNTPEs and CILEs. Regarding the latter, such systems with specific electrochemical behaviour given by the presence of both CNTs and RTILs may offer yet some unique properties like long-term stability at high temperatures of about 60°C, reported for a CNTPE from ultra-long (aligned) nanotubes in connection with an ionic-liquid electrolyte [140].

2.2.5. Some innovations in the construction of carbon paste electrodes.

Practically since CPEs came to a wider use in electrochemistry, their usual arrangement is common macro-electrode operated in the stationary (batch) configuration (see *e.g.* [2] and [40] with the respective sections therein). Typical designs also reflect the fact that carbon pastes are a soft and non-compact material which has to be fixed in suitable electrode bodies, when various pre-filled tubes or piston-driven hollow shafts still prevail as the most popular constructions [2,40,141]. In flowing streams, properly designed detectors are then employed – often, as adaptations of commercial detection cells supplied by renowned producers of chemical instrumentation.

As throughout the publication activities within the 1960s-1990s, also the years after the Y2K have spawned some contributions, in which the CPE-design significantly differ from traditional constructions and configurations. One of such criteria can be the size of electrode and, in this respect, carbon paste ultramicroelectrodes (CP-UMEs) reported by Nyokong *et al.* [142] are certainly exceptional, when the respective ensembles were tested in two configurations: as (i) CP-disc-shaped electrode (with overall diameter $\varnothing_{CP}$ = 100-150 μm), and

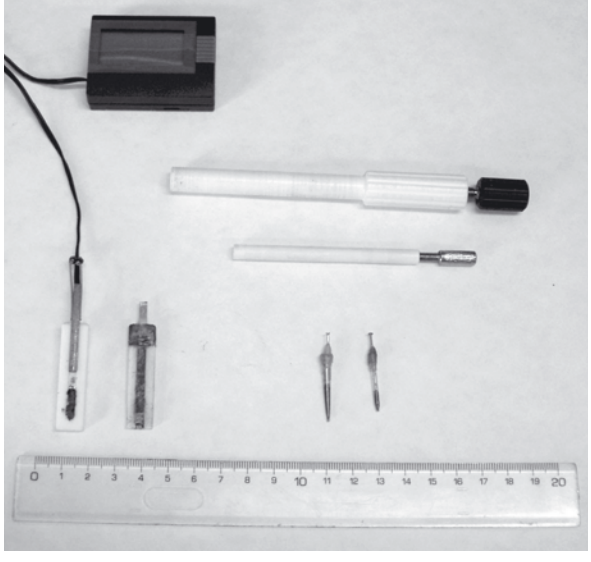

Figure 1. Some new construction types of electrode holders for carbon paste. Clockwise from right side: (i) piston-driven carbon paste holder for common use in the stationary (batch) configuration, with Teflon®-machined body and of ordinary size (authors' own construction); (ii) prototype of a small CPE as the exchangeable working electrode for wall-jet HPLC detector; (iii_{1+2}) two carbon paste mini-electrodes of slightly different surface size (via cut tip); (iv_{1+2}) two assembled carbon paste groove electrodes; set-up for a detection unit in FIA-mode (right) and the electrically heated variant (left) connected to a thermometer (above). (For further specification, see original reports [141,143-146].)

(ii) CP-band electrode; both exhibiting charac-teristic properties of microelectrodes, but suffering from a worse reproducibility (ca. ±20 %). A new type of carbon paste microelectrode (CP-μE; with diameter of *ca*. 5-50 μm) has been reported by Hočevar and Ogorevc [64]) and somewhat larger variant, carbon paste minielectrode (CP-mE, 0.10-0.15 mm in diameter) by Sotiropoulos *et al.* [143]. In the first case, the CPμE utilises a special piston-driven mechanism in a glass capillary, whereas CP-mE requires only a common plastic pipette tip whose vertical cutting (with a razor) provides the desired surface area. A simple construction of the latter is shown on Fig. 1, together with a prototype of small CPE-holder that has been designed recently to be used as exchangeable working electrode in a wall-jet detector for HPLC [144]. For comparison, the image illustrates a third piston-driven CP-holder [141], representing an older type of CPE with ordinary size.

Finally, the photo in Fig. 1 depicts also carbon paste groove electrode (CP-GrE [145]) as another atypical construction of a CPE, copying planar design of SPEs [114]. The CP-GrE assembly comprises a miniature plastic prismatic bar with horizontal channel for carbon paste filling, metal contact, and additional plastic insert(s) defining the electrode surface *via* its mechanical coverage / exposure. The whole construction has fulfilled the demands upon its use inside a detector for hydrodynamic measurements, when its satisfactory function in the FIA mode was demonstrated already on the first prototype [146] and confirmed again by a brand new study [147]. Momentarily, a more robust CP-GrE construction is being maintained into electrically heated carbon paste electrode (EH-CPE), when following the previous idea and construction by Flechsig and Gründler [148]. (It is expected that new EH-CPE would complete the hitherto-performed investigations on temperature-enhanced diffusion of electroactive species with similar assays on temperature-dependent non-faradic processes such as adsorption, extraction, or ion-pairing.)

The gallery of unusual CPE constructions can be ended by mentioning (i) magnet-incorporated carbon paste electrode (MI-CPE [149]), at which – reportedly – magnetically controlled fluxes are higher than those measured by the comparative non-magnetic carbon paste. Or, apparently unprecedented is recently described (ii) dual-electrode / dual-channel detection system for capillary electrophoresis [150], where two working CP-based electrodes and two amperometric detectors have enabled to determine simultaneously four different analytes.

2.3. Reflection of new technologies in the electrochemistry with carbon pastes

The years after 2000 are undoubtedly in the sign of widespread applicability of materials that have been developed with the aid of new technologies. In the electrochemistry with carbon pastes, they are represented mainly by various modifiers; namely, (i) complexants and (ii) redox electrocatalysts or mediators, when the latter can also be understood as synonym for catalysts in biochemical and biological processes. The group (i) comprises usually macromolecular variants of some reagents known from classical qualitative analysis [151] − *e.g.*, *Cuproin* and the Cu(I) counter-ion can be found in the structures of $[Cu_4$(1,3-bis(4-pyridyl) propane)$]_4$ [(2-methyl-acrylic acid)$_8(H_2O)_2$] × 2 H_2O, [78] and a [Cu^{I}-dipyridyl]$^+$ polymeric complex [152], or a new *Schiff base* inside *bis*-5-(4-nitrophenyl-azo) salisylaldimine]-1,8-diamino,3,6-dioxo-octan [153]).

The diversity of the group (ii) is much wider; nevertheless, also electrocatalysts can be sorted into several major subclasses, some of them having again origin in classical reagents and / or their products. For instance, this is the case of (a) *Dawson* compounds; *i.e.*, heteropoly-anions based on Si^{IV}, P^{V}, As^{V} / Mo^{VI}, W^{VI} and V^{V} hetero-atoms combined with voluminous organic cations, as well as neutral organic molecules [40]. In the new millennium, novel types of these substances, capable of catalysing the electrode transformations of both inorganic and organic analytes (*e.g.*, XO_3^-, where X is Cl, Br, and I; NO_2^- and NO_x, N_2H_4 and NH_2OH, H_2O_2, and O_2, or phenols, catechols, and aromatic amines; see *e.g.* [40,41] and tables therein) are regularly reported and, herein, one can present some selected examples: $H_3[P(Mo_{12}O_{40})]•nH_2O$ and 3-aminopropyl-triethoxysilane encapsulated in *MCM-41* (a mesoporous molecular sieve) [154]; $(C_{10}H_{18}N)_6[As_2(Mo_{18}O_{62})]$• •$6CH_2CN•8H_2O$ [155]; (H-2,4-bipyridine)$_4[Si(Mo_3O_{10})_4]$ [156]; $[C_3H_{12}N_2]_4[CdMo_{12}O_{24}(HPO_4)_6$ $(PO_4)_2(OH)_6]$ $[(Cd(H_2O)_2]•3H_2O$ [157]; $Cs_{14}Na_{22}\{[Sn(CH_3)_2$ $(H_2O)]_{24}[Sn(CH_3)_{212}\}[P^V/As^V(W_9O_{34})_{12}]•149H_2O$ [158]; *H*-2[Cd^{II} (1,10'-phenanthroline)$_3]_2\{[Cd(H_2O)$ (1,10'-phenanthroline)$_2](V_{16}O_{38}Cl)\}$•2.5H_2O [159]; [Ni^{II}/ Co^{II}_2(4,4'-bipyridine)$_3(H_2O)_2(C_2O_4)][P_2O_2(W_3O_{10})_6]_2$ (2-*H*-4,4'-bipyridine)•H_2O [160]. Attractive properties of such hybrid materials are given by their multifunctional nature, coupling in one the mechanical stability of the inorganic lattice, chemical reactivity of the organic moiety with its lipophilicity ensuring good adhesion to the hydrophobic carbon paste.

Another distinct group of electrocatalysts / mediators are (b) $Me^{II\,/\,III}$-porphyrin-based macro-structures like Fe^{III}-tetra(*o*-ureaphenyl)porphyrinosilica matrix [161] or Co^{II} / 4,4',4",4"'(21H-23H-porphine-5,10,15,20-tetra-yl)

tetrakis-benzoic acid immobilized onto grafted silica of the SiO_2 / Nb_2O_5 type [162]; (c) calixarenes (*e.g.*, Ni^{II}-5,11,17,23-tetra-tert-butyl-25,27-*bis*(di-ethylcarbamoyl-methoxy)calix[4]arene [163]; (d) Zr^{IV}-template based adducts (16*H*,18*H*-dibenzo[c,1]-7,9-dithia-16, 18-diazapentacene / Zr^{IV}-phosphate [164]; (e) *Doyle* catalyst: Rh^{II}_2 tetrakis[methyl-2-oxopyrrolidine-5(S)-carboxylate] (see [165]); or (f) radical-forming diimide derivatives (N,N'-bis(propyl)-3,4,9,10-perylenebis(dicarboximide), reported as highly organized *Langmuir-Blodgett* films [166]). New types of modifiers are often nanostructured – from single metal- or metal oxide nanoparticles (*e.g.*, gold- [167,168]), platinum- [169] and CuO [170]), *via* complex hybrid structures (octakis(cyano-propyl-dimethylsiloxy) octasil-sesquioxane / $Na_2[Fe(CN)_5NH_3]$ [171]), up to chemically functionalised core-shell Fe_3O_4≅Ag magnetic nanoparticles [172] or a film composite from sodium alginate + 1-butyl-3-methyl-imidazolium hexafluorophosphate (RIL) + SiO_2-nanoparticles + hemoglobin (Hb) [173]; both being biocompatible and applicable in the configuration of immunosensors. Also Dawson compounds can be prepared in nanoscale; *e.g.*, $[(C_4H_9)_4N]_4[Si(Mo_3O_{10})_4]$, $[(C_4H_9)_4N]_6[P_2O_2(Mo_3O_{10})_6]$•• $4H_2O$, and $[(C_2H_5)_4N]_4[P^VO_2(Mo_{11}O_{38})]$•$H_2O$ [174-176], multilayer films of both $(Mo\text{-}36)_n$ / $PAH)_m$ and $(P_2Mo_{18}$-pPy) [177,178] or chain structures of (Hb / 2,4-bipyridine)$_4[Si(Mo_{12}O_{40})]$ [179]; all representing the so-called three-dimensional ("3-D") modifiers.

Newly synthesised compounds are usually subjected to intimate analysis. Among the techniques of choice – often in combination –, one can find: scanning electron microscopy (SEM; see *e.g.* [171,176]), scanning tunneling microscopy and atomic force microscopy (STM, AFM [42,177]) microscopic elemental analysis (MEA [176]), thermogravimetry (TG [157,159]), UV/VIS- [177], IR-, FT/IR-, and Raman spectroscopy [155,171,180], XPS- and XRF-spectroscopy [159,177], XR-diffraction [155,159], or H^1-NMR, C^{13}-NMR, and Si^{29}-NMR [155,171]. With respect to electrochemical characte-risations, the most frequent is cyclic voltammetry (CV [158,160,176]), including configuration with the rotated disc electrode (RDE [159]), followed by voltammetry in the DPV or SWV mode [154,177], respectively, or occasionally by chronoamperometry (CA), coulometry (COU [158]), and potentiometry (POT [153]).

At the end of this brief journey across the realm of new electrochemical materials, one cannot avoid a critical note about nomenclature being used in this field. When going through the respective databases, a certain inflation of superlative and sometimes-duplicated terms can be noticed as demonstrated by the following examples. For instance, related heteropolyanionic structures are reported as (a) novel supramolecular compounds [155], (b) inorganic-organic hybrid polyoxometallate containing supramolecular helical chains [156] (c) new 3-D modifier with intersecting tunnels [157], and (d) ball-shaped heteropolytungstates with biomimetic properties [158]. Or, formerly described nanoparticle films [167] are newly classified as sandwiched polymers [168], novel nanoparticles as nanotubules [180], and a new type of carbon nanotubes is renamed to nanohorns [181]. Perhaps, the most typical example of this approach is the term "nano" itself. Whereas, in the mid 1990s, CPEs were modified with colloidal gold, the identical material has been described a few years later as gold nanoparticles (by the same authors; see [182] *vs.* [183]). Another authors' team has then reported on both terms within one year, including their combination in the only title (see [184] and [185]). Apart from the reasons, it is apparent that such a way of presentation complicates the orientation of further scientists interested in these otherwise valuable and inspiring research activities.

2.4. Recent achievements within special disciplines employing carbon pastes and carbon paste-based sensors

In the previous decades, research activities with carbon pastes had always included rather specialised investigations on the border of electrochemistry with other scientific fields [29,39,40]. Also the recent years saw the continuing efforts on such experiments, when falling predominantly into the areas that are highlighted in the following paragraphs.

2.4.1. Solid-State Electrochemistry.

Among such special areas, the widest applicability can be attributed to a coupling of voltammetric measurements with metallurgic, geological, or archaeological studies, when the respective experiments are performed with various minerals, ores, or raw materials in the solid state [186]. In the case of carbon pastes, the most typical configuration is a carbon paste electroactive electrode (CPEE [17]), whose function is accomplished by dissolution of such a solid substance in a strong electrolyte (concentrated solution of mineral acids or alkaline hydroxides) used, in small amount, as the binder.

In the new millennium, such activities have comprised a great variety of solids; namely: (i) metal oxides like Bi_2O_3 [187], $Mn^{II/IV}_xO_y$ [188], ferrites of the $Fe^{II/III}_xO_y$•nH_2O type, iron ores, and oolites [189,190], including mixtures with other oxides [191] or traces of toxic heavy metals [192]; (ii) metal- and metalloid

sulphides: ZnS [193-195], PbS [196,197], $CuFeS_2$ [198], α-HgS and β-HgS [199], As_2S_3, As_4S_4, and FeAsS [197,200], or As^{III}- and As^{V}-contaminated soils [201], including a study with a series of sulphides [202] focused on more theoretical aspects of dissolution processes, including the individual redox- and phase transformations. Finally, the CPEE configuration has been employed to investigate (iii) other materials such as ground ores sampled in a mine [203], dried green sea-weed (as bio-sorbent [204]), Na-nitroprusside (analytical reagent [205]), solid derivatives of 9, 10-anthraquinones [206], or non-toxic thiadiazoles, whose electro-inhibiting capabilities could be utilised in corrosion studies of ancient bronze patina [207].

2.4.2. In-vivo measurements.

Interesting applications of CPEs were always connected with voltammetric monitoring in living organisms with the aid of miniature sensors or integrated electrode-cells implanted into the vascular or central nerve system of anaesthesias-treated animals like a monkey, fishes, or laboratory rats (see [34,35] and refs. therein). Similar arrangements have also been described in some recent contributions [208-211], dealing with (i) the testing of a novel micro-dialysis pump for simultaneous determination of glucose, glutamate, and choline in free-moving rat [208]; (ii) *in-vivo* assay of Cd(II) ions in the fish's brain core and a plant tissue [209]; (iii) *in-vivo* determination of Cu(II) in a rat tail vascular system [210]; or (iv) monitoring of a pesticide by using a mini-CNTPE, implanted into the skin of an orange and an apple, or even interfaced to a fish brain tissue [211].

2.4.3. Development and testing of multichannel sensing assemblies: Electronic Tongues.

Another attractive link with carbon paste is the case of these highly sophisticated constructions based on measurement and proper evaluation of multiple signals, by means of which some specific properties / features can be identified, correlated, and thus distinguished. The recent years have spawned a series of configurations [212-216], in which the carbon paste electrode material have served for (i) qualitative analysis of potable waters, soft drinks, and beers [212]; (ii) recognition of five basic tastes (*i.e.*, sweet, bitter, salty, acidic, and umami [213]); (iii) classification of red wines *via* the release of specific compounds in consequence of ageing (in oak barrels whose different properties allows one to identify also the country of origin [214]); (iv) analysis of white wines in dependence of local climate and different quality of grapes [215]; or (v) evaluation of the overall bitterness of virgin olive oils [216].

2.4.4. Miscellaneous.

A short presentation of very special employments of carbon paste can be completed with: (i) a solar cell, employing a naturally occurring *Chlorophyll* analogue, molecular oxygen (dissolved in aqueous solution), and a CPE that yielded the measurable photo-current [217]; (ii) a photosynthetic system based on a cyanobacteria with a 1,4-benzoquinone-derived mediator that provides the steady-state current signal of photoelectrochemical oxidation of water [218]; (iii) construction of an electrostatic-quadrupole lens system with the aid of the carbon nanotube paste substrate acting as an emitter [219]; or (iv) multi-instrumental analysis of sunflower plant tissues exposed to the effect of Ag(I) ions in an effort to simulate a bio-indication of natural pollution ("environmental stress" [220]), which can then be evaluated *via* the growth depression, changes in colour, or a lack of root hairs; all being applicable in correlations with the cascade of natural processes connected with photosynthesis.

3. Inorganic analysis with carbon paste electrodes: typical trends and achievements in the new millennium

3.1. Intro: recent advances and selected topics of interest

In practical analysis, conservative users had for long time preferred mercury-based electrodes, which was the case of the hanging mercury drop electrode (HMDE) or mercury film electrodes (MFEs) obtainable from commercially available glassy carbon electrode (GCE) ([221] and refs. therein). Their reliability and feasibility to be employed for highly effective amalgam-formation based pre-concentrations in electrochemical stripping analysis (ESA) were appreciated in routine determinations of heavy metal ions, representing apparently the most popular area of inorganic electroanalysis at all.

Similarly, the GCE alone and its Pt-disc analogues were usually the electrodes of choice for the determination of noble metals, or anions and molecules that could not be determined with the HMDE or MFE, respectively [4]. Nevertheless, despite rather dominant position of these detection systems, various types of carbon paste-based electrodes were coming to the fore; mainly, thanks to their versatility, allowing one to employ them either as interesting alternative or even completely new possibility of how to determine some less-common inorganic analytes. In recent years, propagation of both CPEs and CMPEs in inorganic analysis has been further intensified [2]; mainly, in the framework of the

green-analytical-chemistry concept [47]. Some typical areas of these activities are overviewed in the following sections.

3.2. Zeolite- and silica-modified carbon paste electrodes

Intrinsic and sometimes unique properties of zeolites or silica-based materials in combination with electron transfer processes characterise a particular group of chemical modifiers whose use in the electrode configurations is of continuing interest, including the carbon paste-based variants [40,222-225].

Both natural and synthetic zeolites [222,225] are microporous crystalline alumino-silicates that exhibit ion-exchange capacity and molecular-sieve properties. Silicas [223,224] as special variants of SiO_2 then offer possibilities to be functionalized with a variety of organic groups, including preparation of inorganic / organic hybrids, combining – in a single solid – mechanical stability of the inorganic skeleton with reactivity of the organic moiety.

Typical properties of these two families may be synergistically merged in one unit, which is the case of some supramolecular assemblies obtainable by the sol-gel synthesis. The resultant products (called ordered mesoporous silicas [225]) are materials in which silica walls grew around the self-assembled template to form periodic mesoporous substrates that display a narrow, controlled pore-size distribution in well-organised structures. And when one consider specific features of carbon pastes, it can be understood why both zeolite- and silica-modified CPEs represent maybe the largest subclass of CMCPEs with widespread applicability to the determination of inorganic ions, complexes and molecules, including successful attempts in environmental speciation [40,222-224]. Also, the achievements within the last period have confirmed such prominent role of both zeolite-and silica-modified CPEs [225].

However, before the most typical electroanalytical arrangements are surveyed, it is useful to point out some particular features associated with the fabrication of zeolite- and silica-modified CPEs of new generation. Mainly, the respective studies and applications had to consider the main problem of working with zeolite and silicas – *i.e.*, the fact that most of them are electronic insulators and their effective connection with electrochemical sensing requires a proper confinement within / onto an electrode material [40]. It was confirmed that the preparation of mechanically stable and homogeneous deposits of zeolite / silica particles with their firm anchoring onto an electrode surface can advantageously be accomplished *via* organic polymers – typical products of latest technologies and the above-mentioned sol-gel processes. Some novel procedures for preparation of zeolite- and silica-modified CPEs have then been confronted with inevitable restrictions occurring in the course of fabrication, which was often the case of electrodes that had incorporated organic-inorganic hybrids with highly sophisticated functions and / or given mesostructures [225]. (These usually require strictly defined conditions for the proper synthesis which might not be adaptable with the formation of film structures of desired properties.) Due to this, intensive investigations in the recent years have resulted in establishment of a new routine for dispersion of zeolites, silica-based organic-inorganic hybrids or ordered mesoporous materials – in the form of dry powders admixed directly in the carbon paste matrix.

By summarising the most typical configurations with zeolite-modified CPEs, the individual contributions fall into four main categories:

(i) Electrochemical detection subsequent to open-circuit accumulation, where an electro-active cation of interest is accumulated by ion-exchange (*via* charge selectivity) or molecular sieving (size selectivity), prior to proper voltammetric quantification.

(ii) Direct and electrocatalysis-assisted amperometric / voltammetric detection, involving redox mediators encapsulated in the zeolite cages.

(iii) Indirect amperometric detection of non-electroactive species; representing maybe the most elegant application of zeolite-modified electrodes as it exploits both ion-exchange and size-selectivity properties. (In fact, it involves the use of a zeolite doped with a redox cation and the supporting electrolyte made of size-excluded cations, bigger than the zeolite pore aperture, so that solely redox probe can be exchanged, diffusing then towards the electrode surface in a moment when small and non-size-excluded cations are injected, thus giving rise to an indirect current response proportional to these non electroactive species.)

(iv) Incorporation in carbon paste-biosensors, for which the hydrophilic zeolites enable to expose enzyme(s) in more active form compared to its native species inside the hydrophobic carbon paste matrix; similar function *via* ion-exchange being also beneficial for redox mediators embedded in. Since electrochemical biosensing is a domain of organic and biological analysis, the corresponding methods are not discussed here and can be found elsewhere [40,41].

Regarding zeolite-modified CPEs, they exhibit one typical feature, which is more pronounced compared to related silica-modified variants. It is a tendency of solution impregnation in μm-thick region of the paste at the electrode and subsequent penetration of solution-phase species into the zeolite-carbon composite in contact with the aqueous solution for a longer time. In the case of common zeolites, the driving force for such solution penetration in the bulk of the electrode is again their hydrophilic character, counter-balancing of typically high-lipophilic (hydrophobic) carbon paste [29,39,40]. In order to prevent undesirable solution ingress into the electrode and thus possible memory effects of the sensor, some new approaches have been proposed. Either, they are based on (i) additional increase of the overall hydrophobicity of a CMCPE by using solid paraffin instead of ordinary mineral oil [226] or *via* (ii) confining ("jailing") the zeolite particles at the outermost surface layer, which can be attained with the aid of mechanical immobilization onto paraffin-impregnated electrodes [227].

An example of the resultant effectiveness of such approaches is then illustrated in Fig. 2, depicting the voltammetric detection of Cu(II) ions after open-circuit accumulation for a long time-period (30 min.) from a solution containing 10 mM Cu^{2+}. A rather high concentration of Cu(II) was chosen to simulate the conditions likely to induce severe memory effects in consequence of the above-described release / impregnation / penetration mechanism, which can be seen on faster and more effective chemical regeneration of the solid-like zeolite-modified CPE (a) in comparison with the traditional mineral oil-based variant (b).

Typical configurations of CMCPEs with silica-based materials, *i.e.*, (native) silica particles, organically-modified silicates, or functionalized mesoporous silica substrates, can also be divided into four main groups. Including the very first examples, presented by Walcarius *et al.* in the mid 1990s (see *e.g.* [40] and refs. therein). The respective methods are based on the following principles:

(i) Also herein, electroanalysis with a pre-concentration step is the most frequent concept, for which the silica-based organic / inorganic hybrids are synthesised enabling (i) selective recognition of target analytes by a fine tuning the nature of the organo-functional groups and (ii) high sensitivity *via* rapid mass transport toward the active centres controlled by the appropriate structure of a nano-material. The latter is illustrated in Fig. 3, making comparison between the efficiency of mesostructured mercapto-propyl-grafted silica and of non-ordered homologue silica-gel selected as modifiers in the respective CMCPEs tested for to the determination of Hg(II) ions.

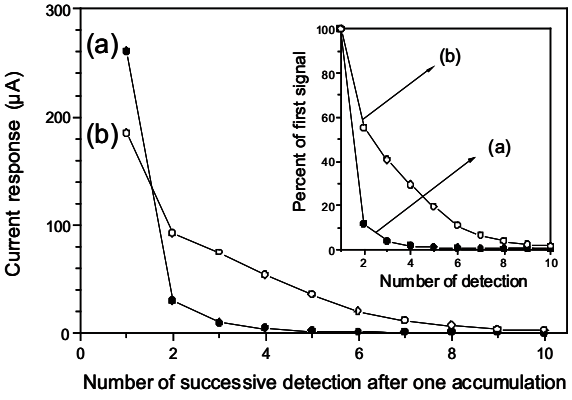

Figure 2. Voltammetric study on the release of Cu(II) ions from two different zeolite-modified carbon paste electrodes. (a) 10% (m/m) zeolite-modified solid-like carbon paste; (b) 10% zeolite-modified conventional carbon paste. Experimental conditions: carbon paste materials: (a) carbon powder with solidified paraffin wax, (b) carbon powder + paraffin oil mixture; measuring mode: differential pulse anodic stripping voltammetry with intermediate reduction; supporting electrolyte (s.e.): 0.1 M KNO_3 + 0.001 M $Cu(NO_3)_2$; open-circuit accumulation, t_{ACC} = 30 min.; reduction step, E_{RED} = −0.5 V vs. Ag/AgCl/3MKCl, t_{RED} = 60 s; potential range (stripping step), E_R: from −0.5 to +0.5 V; scan rate, v = 20 mV s^{-1}; relative normalized responses given in the inset. (Adapted from [226].)

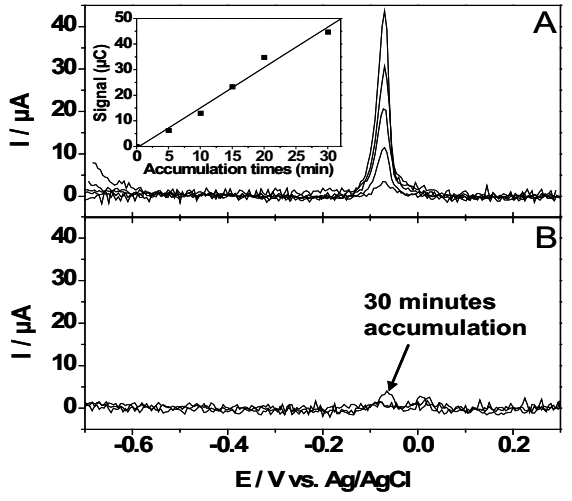

Figure 3. Effect of preconcentration time on the voltam-metric response of two carbon paste electrodes modified with different different silica-based materials. CPE modified with (A) mercaptopropyl-functionalised mesoporous silica, (B) mercapto-grafted amorphous silica-gel. Experimental conditions: carbon paste made of carbon powder (38%, m/m) + paraffin oil (20%) + modifier (20%). DPASV with intermediate reduction step; s.e. (i) 0.1 M HNO_3 + 5×10^{-7} M $Hg(NO_3)_2$ (medium for preconcentration step), (ii) 3 M HCl (stripping step, detection); E_{RED} = −0.7 V; other parameters as in Fig. 2; variation of the peak area with preconcetration time shown in the inset. (Hitherto unpublished results from authors' archives.

At first sight, both voltammograms document the better performance of a CMCPE with mesoporous silicas grafted with mercapto-propyl groups, for which the increase in sensitivity can be expressed by a factor of 50:1 compared to similarly grafted silica gels of the same average porosity [228,229].

Other examples are available for the detection of Cu(II) at CMCPEs with amine- [230], carnosine- [231], sulphonic acid- [232] or cyclam- [233] functionalized silicas, for the determination of Hg(II) with thiol-functionalized materials [234] or for the accumulation and quantification of Pb(II) ions, in this case using a CPE modified with a heterogeneous material represented by self-assembled monolayers of acetamide-phosphonic acid on mesoporous silica [235].

(ii) Direct detection *via* electrocatalytic effect, which can be accomplished by preparing special catalysts supported on silica-based materials. Having followed the pioneering work by Kubota, Gushikem *et al.* from the late 1990s, as well as of their continuators (see again [40] and refs. therein), who were using modifications of silica gels with metal oxides and / or metal phosphate layers for binding redox mediators of the Me^{II}-phthalocyanines type, some newer attempts of this kind are based on the immobilization of polyoxometalates in protonated amine-functionalized silica-mesostructures applicable as special charge-transfer co-factors for the amperometric detection of ClO_3^- / BrO_3^- [236]. As a hosting matrix for durable immobilization of such electron transfer co-factors, ordered mesoporous silicas are also quite promising, as shown recently on ferrocene-structure covalently attached to a *MCM-41* mesoporous molecular sieve [237].

(iii) In principle, indirect detection is also applicable to silica-modified carbon paste-based electrodes and sensors, but the search inside the recent bibliographic database has not revealed any particular method based on such a scheme.

(iv) Functionalised silicas can be mixed with carbon paste as a composite matrix for anchoring of some enzymes in amperometric biosensors; for example, silica gels coated with either TiO_2 / Ti-phosphate or ZrO_2 / Zr-phosphate skeletons; nevertheless, more typical bio-electroanalytical applications of the sol-gel-derived silica-based materials have involved polymeric thin-film configurations [225]. Again, due to the particular use in electrochemistry of organic pollutants, pharmaceuticals or drugs, and biologically active substances, the respective biosensors are described in more detail in other review articles [40,41].

Finally, some modifiers are based on combination of both novel zeolites / silicas with other new materials coming from latest research. In this respect, one can quote two examples utilising (i) newly synthesised zeolite with intercalated *Xylenol Orange*, *Morin*, or *Calmaigite* [238], when these dyes enable a highly selective chelating of Cu(II) ions. The second configuration has then consisted of either (ii) volcanic tuff as natural material or synthetic preparative ("X-type"); both chemically functionalised with *Methylene Green* and serving for sensitive sensing of H_2O_2 [239]. A similar connection of a novel silica with newly synthesised substances is then represented by a CMCPE incorporating the $[Ru(bpy)_3]^{2+}$ ion at sulphonate ion-exchanger functionalised *MCM-41* in the form of dispersion of such particles in an ionic liquid – *i.e.*, a CILE configuration [240]. The resultant device is characterized by a well-defined electro-chemiluminescence signal, which has been found to be more sensitive in the presence of ionic liquid than in paste with conventional silicone oil.

3.3. Metallic Film-Plated Carbon Pastes in Stripping Voltammetry

The 1970s saw the era of particular popularity of mercury film electrodes (MFEs) being better compatible with newly coming PC-controlled and miniaturised electrochemical instrumentation than rather robust and sensitive HMDE configurations (see *e.g.* [221] and refs. therein). Similarly, oxidation-suffering gold disc electrodes began to be replaced by easy regenerable gold-film variants (AuFEs). Throughout the 1980s until the mid-1990s, it had been believed that the best electrode substrate for electrolytic deposition of both mercury- and gold films was to be the GCE or similar supports. However, at that time, also carbon pastes were found to be suitable for this role and, since then, the first types of mercury- or gold-film plated carbon paste electrodes could be presented (see [241] and refs. therein).

The up-coming 2000s have spawned a series of reports, [113,242-247] in which both MF-CPEs and Au-CPEs were subjected to intimate examinations, including employment in practical analysis of real water samples (MF-CPE in [242] and AuF-CPE in [247]), showing that also hydrophobic carbon pastes may offer convenient conditions for being plated with metallic films. Moreover, a quick and easy-to-make carbon paste renewal, representing effective but absolute change at the surface of each CP-based substrate, was confirmed to have only minimal impact to the overall quality of both MF-CPEs and AuF-CPEs and their performance in ESA, including negligible changes in the sensitivity and reproducibility / repeatability of the respective signals.

Regarding the last advances in the field of metallic film-coated CPEs, the main boom is surely connected

with the development and applications of bismuth film-plated carbon paste electrodes (BiF-CPEs [42,243-245,248-262]) and other related configurations [254-256,258,260,263-265]. The respective activities started within our research group in the early 2000s [248] as an answer to the actual introduction of bismuth film-coated GCEs; again, within the challenges of green analytical chemistry (see [47,266-270] and refs. therein) as bismuth and its compounds represent environmentally friendly and less toxic element compared to mercury or mercury(II) salts. The BiF-CPE can be prepared either *in-situ* [249,250] or using external deposition of the film in a suitable plating solution [243,252]. In addition, a heterogeneous nature of carbon pastes allows one to modify this electrode material either at the outer surface by bismuth films, or *via* bismuth species added in the bulk. The latter has been utilised in designing two alternatives to the (i) firstly proposed BiF-CPE [248]; namely, (ii) bismuth oxide-carbon paste electrode (Bi_2O_3-CPE [263]) and (iii) bismuth-modified carbon paste electrode (Bi-CPE [264]); the latter containing bismuth powder at a ratio of about 20% (m/m) dispersed in the two main carbon paste components [256].

Worth of mentioning are also special microscopic studies focused on carbon pastes pre-plated with bismuth films [42,252,261]. As revealed by comparative observations, the electrolytic formation of bismuth microlayers proceeds in three subsequent steps, during which the overall morphology undergoes significant changes.

This is illustrated in Fig. 4, depicting the individual phases in an approximate appearance of the corresponding structures. Comparative experiments have then confirmed that there is a close relation between such microstructures and the resultant behaviour of a BiF-CPE– the best performance of an electrode has been attained with the initial arrangement of bismuth micro-particles ("phase 1") which, as such, resembles related structures of mercury films formed by consolidated layers of tiny droplets [221,241]). In other words, the more crystalline is the bismuth film (*i.e.*, in patterns 2 & 3), the poorer is the resultant electrochemical behaviour of a BiF-CPE ([261]).

Additional modifications of BiF-CPEs are also feasible and such approaches have recently been described in two reports [259,260]. In the first one, the originally two-component carbon paste was doped with the third substance – a synthetic zeolite [259], enabling to enhance the overall sensitivity towards the target ions. The second arrangement was then a BiF-CPE coated with fibrinogen [260], forming a protective barrier against interfering surfactants. The same effect can be aimed with *Nafion*® (a perfluorinated polymer widely usable in combination with MeFEs; see *e.g.* [221] and tables in), which has not been yet tested for BiF-CPEs, but in combination with a BiF-plated carbon film electrode [271], representing a configuration very similar to bismuth film-plated carbon pastes.

In the latest years, electroanalysis with bismuth electrodes has undergone a very dynamic progress (see *e.g.* [267] plus [270] and compare the reference lists inside). Such a boom was also the result of rapidly growing averse against mercury, evoking controversial moods among electrochemists and electroanalysts worldwide and dividing them into two major groups – propagators of new non-mercury electrodes against their defenders [272]. Somewhat different impulses were behind the discovery of further alternatives to BiF-CPEs – two new configurations of (i) antimony film-plated carbon paste electrode (SbF-CPE) and (ii) antimony powder-modified carbon paste electrode (Sb-CPE) [273]. Introduction of these electrodes has been inspired rather by chemical similarity of both antimony and bismuth, following also some previous (and nearly forgotten) results [274]. Similar motivations could also be the case of introducing a lead film-plated carbon paste electrode (PbF-CPE [275]), which is hitherto last member in the family of metallic film-plated CPEs. Although all these sensors offer excellent performance under properly adjusted experimental conditions, they mean a certain step back with respect to the already emphasised concept of green chemistry – both antimony and lead, together with their $Sb^{III/V}$ and $Pb^{II/IV}$ compounds, are highly harmful to the environment, as well as to humans.

Figure 4. Morphological transformation of bismuth film in three consecutive phases. A schematic view (Adapted from [252] and [261].)

In electrochemical measurements, the individual types of metal-modified CPEs are usually combined with anodic stripping voltammetric protocols. It means that the respective methods include a pre-concentration step utilising a potentiostatic electrolytic reduction of ion(s) of interest. In analogy to mercury-based electrodes, such accumulations involve an additional driving force – the formation of metal alloys [267-270] –, which apparently explains why these electrodes achieve so excellent function in the ASV regime. Regarding the proper voltammetric mode, the detection of accumulated species is preferably performed by stripping with a square-wave modulation which is generally less sensitive to undesirable effects from residual (background) signals than a differential pulse potential ramp [276]. The performance of voltammetric techniques can further be enhanced by appropriate choice of the quantitative method or by means of processing and evaluation of the respective current signals. As demonstrated with BiF-CPEs; *e.g.*computerised normalisation of originally distorted voltammograms may result in a significant improvement of the actual signal-to-noise characteristics [257,262].

A majority of hitherto proposed metal-modified CPEs have already been tested in analyses of real specimens, where both Cd(II) and Pb(II) ions were the main target analytes sought in the following samples: (i) tap, natural, and mineral waters [113,242,260,261, 263], (ii) tea extract [260], and (iii) certified reference material (soil [253]). Of interest were also some less typical specimens of (v) heavily polluted river water [247] or mineral acid-digested (vi) urine [263] and (vii) crude petroleum oil [244]; the last two demonstrating analyses of samples with extremely complex matrices. Other details on the respective methods can be found below – in four tables under the section **4**.

As seen, a majority of practical determinations illustrating the applicability of both Bi- and Sb-modified CPEs was carried out in various water samples. Fig. 5 depicts typical stripping voltammetric responses of both bismuth- and antimony-modified CPEs for Cd(II) and Pb(II) ions obtained by analysing a model water sample (when both sets of measurements had been optimised for determination with the antimony-modified variant). The figure gathers two sets of curves, showing also the response at a MF-CPE and a bismuth paste electrode (BiPE). The latter was found to be functioning – although not very satisfactorily – without any carbon powder in the electrode material, thus representing an example of "graphite-less" paste mixture [263]. Regardless of this curiosity, all the remaining electrodes have exhibited favourable electroanalytical performances for the determination of the two metal ions at the low ppb concentration level.

3.3.1. Carbon paste electrodes vs. screen-printed electrodes (SPEs).

The configuration of metal film-plated CPEs is a very good occasion to conclude the entire section with mutual relation between CPEs and SPEs, reflecting one of contemporary trends in the field. In certain respect, traditional carbon pastes can be classified as a transient

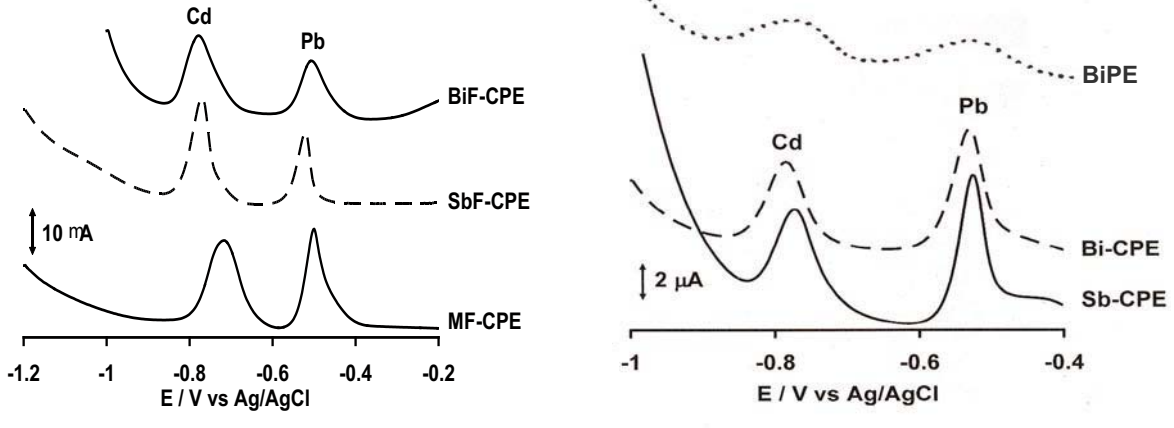

Figure 5. Square-wave anodic stripping voltammograms of Cd(II) + Pb(II) model mixtures at different types of metal film-plated and metal-modified carbon paste and paste electrodes. MeF-plated (A), Me-modified electrodes (B); the individual types as shown by inscriptions. Experimental conditions: silicone oil-based carbon paste [the same for all, except BiPE made of bismuth powder (50%, m/m) + silicone oil (SO); content of both metals in Bi-CPE and Sb-CPEs, 17% (m/m)]; SWASV; s.e.: 0.01 M HCl; c(Hg,Bi,Sb) = 1×10^{-5} mol L^{-1} (for A); c(Cd,Pb) = 50 ppb (for A), 25 ppb (for B); t_{ACC} = 120 s, E_{ACC} = −1.2 V; equilibrium time, t_{EQ}: 15 s, (A) and −1.0 V vs. Ag/AgCl/3MKCl; potential range, E_R, from −1.2 to −0.2 V; SWV parameters: potential increment, i_E = 4 mV; pulse amplitude, ΔE = 50 mV; SW-frequency, 25Hz. Note: vertical arrows (left) indicate the actual current range. (Adapted from [256], [264], and [273].)

element between solid carbon electrodes and printable carbon ink-based sensors. The initial considerations concerning this topic began already in the mid 1990s [32] – at the times of stormy development of first types of machine-produced SPEs. According to such approaches, there are some common characteristics of both CPEs and carbon-based SPEs: (a) the presence of carbon (or graphite, respectively) as the principal electrode material; (b) heterogenous character of both carbon pastes and carbon inks, (c) the choice and control of the carbon-to-binder ratio, (d) possibility of bulk-modification of these carbonaceous materials; (e) often similar or even identical employment.

On the other hand, there are also distinct differences: (A) presence of liquid phase (binder) in the carbon paste mixtures versus the solid state of carbon-ink binders (original liquid or paste-like dispersions are being solidified during / after printing); (B) incomparable geometry and size (whereas common CPEs are pencil-shaped electrodes in the disc configuration and for batch analysis, SPEs are usually designed as planar stripes (bars) of rather small dimensions employed mainly in various flow cells or miniaturised analysers; (C) long-time and permanent use of a CPE (limited just by stability of the actual carbon paste mixture) contra the generally-adopted concept of SPEs as disposable sensors; (D) existence in the only exemplar or in a set of few electrodes (for CPEs) compared to the mass production in large series (SPEs), and (E) manual and more-or-less individual preparation of carbon paste mixtures and of their filling into the electrode holder(s) versus commercial availability of ready-to-use carbon inks, together with automated and machine-controlled printing process.

Regarding the specific relation of both CPEs and SPEs, some implications are obvious if one combines the individual points in both surveys (a-e) and (A-E). A versatile character of carbon pastes enables that some differences listed under the latter can be minimised; for instance, by using small CP-GrEs [145-147] in planar configuration – see point (B). Or, oppositely, some antagonistic features can be advantageously utilised, which is the case of the following example: (i) a method is first developed and tested in laboratory, when using a CPE (or a set of CPEs) being prepared quickly and at minimal expenses; (ii) after the optimal procedure is being found, the same method can be examined with preliminarily made SPEs of analogical type (*e.g.*, pre-treated in the same way or containing identical modifier); (iii) in this phase, some conditions may be yet readjusted, best under regime which simulates the real experimental conditions; and (iv) when the ultimate version of a methodical procedure is obtained, the large series of SPEs can be produced and then used up during the proper analytical work – *e.g.*, in the field monitoring.

By keeping on such a strategy, our research group has elaborated a collection of electroanalytical procedures applicable to inorganic analysis that were tuned in accordance with the above-given example and, now, being available in combination with SPEs, although the original methods had been developed with CPEs and CMCPEs. A significant part of these procedures involved the use of MF- and BiF-plated CPEs, later adapted and re-optimised for MF- and BiF-SPEs (see [113,246,263] *vs.* [274,277,278]).

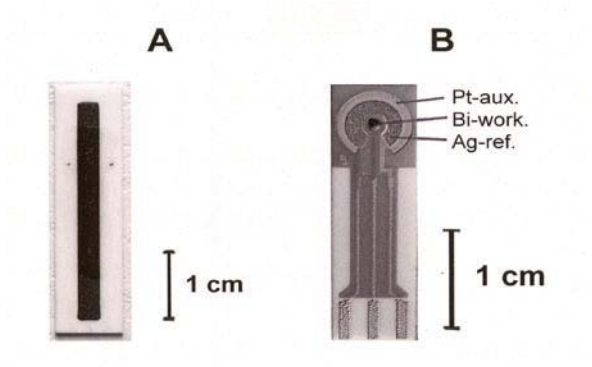

Figure 6. *Construction design of screen-printed electrodes of two generations, used in the metal film-plated configuration and tested together with related MeF-CPEs*. Ceramic substrate-based SPE (old type, A); integrated sensor with three-electrode cell (new type, B). (Adapted from [113] and [279].)

At present, our activities are focused on readapting of some previous procedures for use with screen-printed sensors of a new generation, represented by miniaturised integrated 2/3-electrode cells (see [279] and image "B" in Fig. 6). Finally, a very close concept of CPEs and SPEs can be documented on the fact that some recent reviews gather these electrodes into one group of the so-caled heterogeneous carbon electrodes and sensors [32,40,280].

3.4. Potentiometric measurements with carbon paste electrodes and sensors

3.4.1. Carbon paste-based ion-selective electrodes (CP-ISEs).

From the view of equilibrium potentiometry, the composition of carbon pastes makes possible to classify the CP-ISEs as ion-selective liquid membrane type electrodes. Pasting liquids exhibit usually good extraction ability against neutral electroactive species of the type of non-dissociated weak acids, neutral metal chelates or ion-associates. The potential of the

electrode containing such an organic solvent extract is predominantly governed by an ionic exchange at the interface between the organic phase of the electrode and the sample solution. It should be noted that the theoretical background of their function started by pioneer works of Růžička (*e.g.* see [281]) and actualized recently for CP-ISEs [282]. It should also be noted that virtually any ionic species can be detected and measured. In principle, rules for construction of CP-ISEs are analogous to those for liquid/polymeric membrane-based ISEs [283] − to build a paste responsive to ion X^-, for example, the salt Q^+X^- should be incorporated into a non-volatile solvent, and the Q^+ ion must be highly lipophilic. Similarly for an electrode responsive to cation Q^+, an oil-soluble salt Q^+X^- is used, where the X^- ion is lipophilic. Less frequently, insoluble inorganic precipitates are mixed to the paste [16]; in such cases, these CP-ISEs may be classified as solid-state type electrodes. Compared to analogous sensors equipped with liquid/polymeric membranes, carbon paste-based potentiometric sensors offer very low ohmic resistance ($R < 10\ \Omega$) and show rapid response [284].

As well known, measuring cells consisting of the CP-ISE and proper reference electrode can be used to determine the activity or concentration of the ion of interest. Empirical calibration graphs, in which the cell voltage is related to the activity or concentration of the desired ionic compound, are generally used. A typical form of the calibration curve is that given by Nikolskii's equation, and is usually linear in the range of 1 to 5 or 6 pX units, where the pX values are calculated as negative logarithms of the desired ion "*i*" activities or simplified, "*i*" concentrations. Often, procedures involving flow injection analysis (FIA) calibration are used. On the other hand, potentiometric titration technique is also applied; it offers the advantage of high accuracy and precision, though at the cost of increased time demands and a higher consumption of chemicals used as titrants. Nowadays, this question has successfully been solved by introducing modern automated titrators equipped with burettes of smaller volumes and allowing a computer-assisted end-point evaluation as well [285].

In the recent period, authors' attention has been paid to development of CP-ISEs applicable in determinations of both inorganic and organic species. Various modifications of carbon paste were applied in potentiometric sensors for copper [286-292], silver [97,153,293], mercury [94-296], lead [297], arsenic [97,298], antimony [299], bismuth [300], cobalt [301], osmium [302], aluminium [107], lithium [303], ammonium [304], halides and pseudo-halides [305-308], and sulphate ions [309]. Some of them [97,302] were applied to monitor titrations based on ion-pair formation principles described and discussed in detail previously [310].

Concerning recent applicability of CP-ISEs to the determination of organic and biological substances or pharmaceuticals, this topic is surveyed in more detail elsewhere [40,41]. Herein, it can be briefly stated that CP-ISE configurations dominate for the latter – for various drug compounds [311-318]. Their composition [311-315] usually follows traditional basic principles described in the previous reviews [319,320] and, analogously, they are often applied in both direct potentiometric measurements and potentiometric ion-pair formation-based titrations. Moreover, enantioselective potentiometric sensors based on carbon paste impregnated with various cyclodextrins were described [316-318,321]. CP-ISEs for ascorbic acid [322], acetylcholine [323], L-proline [321], cysteine [324,325], thioglycolic acid [326], or other organic thio-compounds [327] were also reported. Finally, one paper has dealt with a possibility to determine cetyltrimethylammonium ion [328], which is a popular *in-situ* modifier, including its combination with CPEs (again, see [40,41] and refs. therein).

In environmentally oriented studies, CPEs as potentiometric sensors were utilized in characterization of electro-chemical behaviour of Ni(II)- and Cd(II)-bearing ferrites obtained as by-products of wastewater purification [191,192]. As the substrate of choice, CPEs served also in a solid-state electronic tongue applied to beverage analysis [212].

3.4.2. Stripping (chrono)potentiometry.

As stripping potentiometry differs from stripping voltammetry by final step only, similar or analogous applications of CPEs can be expected (for examples, see review [329]). Nevertheless, introduction of more polar pasting liquids like tricresyl phosphate, dialkyl phthalates, *etc.* (often used as plasticizers in polymeric membranes of ion-selective electrodes) [330] offered some new possibilities for analyte accumulation, predominantly based on ion-pair formation [331,332].

This was shown already in the first years of a new millennium; *e.g.*, a former procedure elaborated for the determination of thallium [333] could be adapted for gold (as tetrachloroaurate [99,331]), or iodide [101,331], and the perspectives of stripping potentiometry with CPEs, focused on the role of pasting liquid, were thus outlined as quite promising; especially, for some determinations in samples with extremely complex matrices (*e.g.*, iodide in non-pretreated and solely diluted urine [334]). As already shown in the previous section **3.4.1.**, another recently frequent application of CPEs in stripping potentiometry is their use as the electrode support

for metallic films; the advantage of application being again that the electrode surface can easily be renewed compared to metallic film electrodes on solid supports [244,247,249,344-346]. Simultaneously, a series of methods was presented; namely, the determination of lead and cadmium [244,334] or copper [334] when using the MF-CPE configurations, copper and mercury [336] or arsenic [247] at AuF-CPEs, as well as lead and cadmium in parallel at either BiF-CPEs [244,249] or SbF-CPEs [273,337].

The latter approaches represent the starting point of stripping potentiometry in the already discussed and momentarily very popular area of non-mercury electrodes. In the PSA mode, original methods were employing MFEs and selected Hg(II) compounds (mostly $HgCl_2$, see *e.g.* [241] and refs in) served as the source for *in-situ* generated mercury film and as proper chemical oxidant [242]. In the same way, both bismuth [249] and antimony [337] may be applied in order (i) to form corresponding metallic film and (ii) to substitute mercury(II) in its role of an oxidant. Moreover, as shown in our theoretical considerations and their experimental verifications (see [249,337]), both Bi(III) and Sb(III) possess rather specific oxidation capabilities, differing from those known for Hg(II) species. And all these attributes open completely new possibilities for "mercury-free" procedures and their use for the determination of various heavy metals. Regarding computer-controlled stripping potentiometry and its potentialities in practical analysis, yet another feature can be mentioned here illustrated by an experiment with metallic film-plated CPEs [244]. It is shown in Fig. 7, making comparison between electroanalytical performance of stripping potentiometry and stripping voltammetry.

This confrontation of both related techniques was made with the same sample solution and identical working electrode – a bismuth film-plated CPE. As seen, both voltammograms (DPASV) exhibit distinct deformations of base-line, with a large maximum of unknown origin, and the signals of interest are poorly developed. Compared to this, the respective potentiograms (PSA) are much favourably drawn and easily evaluated.

This test is a textbook case of how the result of an analysis may rely on the technique chosen in the stripping step. Since voltammetric measurements are based on the detection of electric current whose origin may be quite diverse, including various non-Faradic phenomena or even electrical noise, the resultant signal may suffer – and usually does so – from numerous interferences. In contrast to this, potentiometric stripping regime registers the *E-t* dependence, where the equilibrium potential, E_i, represents a highly selective signal [242] independent of any current-releasing disturbance. As a result, the

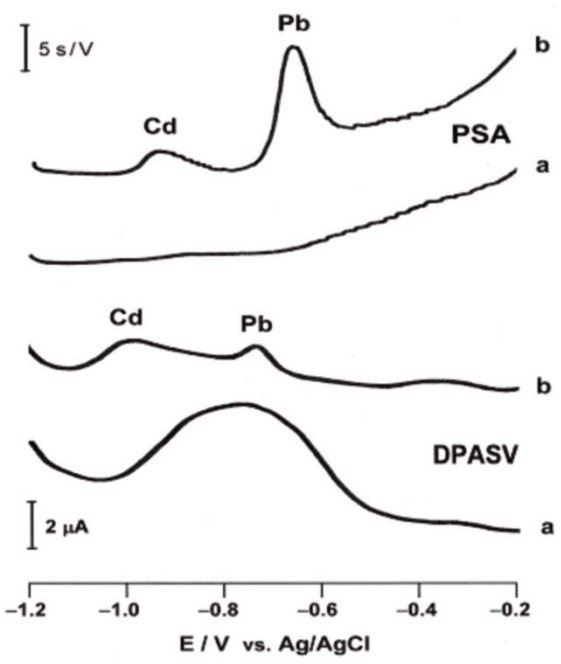

Figure 7. Stripping potentiograms and anodic stripping voltammograms of Pb(II) and Cd(II) obtained at bismuth film-plated carbon paste electrodes by analysing a model sample of mineral acid-digested petroleum oil. **PSA**: stripping potentiometric analysis (with chemical oxidation), **DPASV**: differential pulse anodic stripping voltammetry; sample base-lines (**a**), sample + 50 μL 1×10^{-4} M Pb^{II} + Cd^{II} (a spike corresponding to $c_{Me} = 2\times10^{-7}$ M) (**b**). Experimental conditions: silicone oil-based carbon paste; sample: digested crude oil in 0.9 M ammonia buffer + 1×10^{-5} M Bi^{III} (pH 4.3); t_{ACC} = 120 s, t_{EQ} = 15 s, E_R from −1.2 to −0.5 V *vs.* Ag/AgCl; PSA: sampling frequency: f_{PSA} = 90MHz, DPASV: v = 20 mV s^{-1}, ΔE = −50 mV. Note: Y-axis expressed as dt/dE [s/V] for PSA; and ΔI [μA] for DPASV. (After [244]).

interference effects under comparable conditions are severe for voltammetric measurements, but negligible in the PSA mode. And this "insensitivity" of PSA is also the main reason why methods employing this technique or its CCSA variant [247], respectively, are particularly convenient for analysis of highly polluted waters or, in general, samples with complex matrices.

4. Electroanalysis of inorganic ions, complexes, and molecules with carbon paste electrodes: survey of methods published within the years of 2001-2008

Applications of CPEs, CMCPEs, and other related configurations employed in inorganic analysis are surveyed in a quartet of tables gathering important data, together with some interesting details, of almost all

methods that have been published in the period of 2001-2008 and described in the respective contributions. Namely, Tables I-IV summarise the original papers referred herein from [351], up to [490] including numerous further references that have been cited in the previous paragraphs. Information material in the tables is accompanied by commentaries that highlight typical features and trends from the actual databases. Anyway, this approach follows the style chosen in our last reviews [39-41].

All hitherto reported methods of inorganic analysis with CPEs and related sensors concern 65 chemical elements that – either alone or in the form of various compounds – have already been analysed; a great majority of them being even determined [40]. At present, this large family can adopt other two elements, for which the respective reports [442,451] have been found newly during the final actualisation of this text. And when one adds further five elements whose compounds could be studied by SPV with CPEEs, there is a total of 72 chemical elements representing *ca*. 3/4 of naturally occurring species that have ever come into the contact with carbon paste. This is a number scarcely achieved with other electrode materials and hence, even such atypical criterion may document the versatility of CPEs, reflected in practically unlimited applicability in inorganic analysis.

Finally, the popularity of carbon paste-based electrodes can be illustrated in numerous reviews of very diverse focus, where the respective applications are regularly quoted. When selecting solely recent review articles [338-350], this is the case of generally focused compilations (*e.g.* [338]), including locally oriented reports [339,340], overviews devoted to particular techniques [341,342], group of analytes [343] and of samples [280,344-346], or some novel types of electrodes [221,267-270,347,348], modifiers and newly synthesised materials [225,349,350].

4.1. Noble Metals (Au, Ag, Hg, and Cu; see Table 1 plus refs.[72,94,97,99,104,153,231,288-296,298, 336, and 351-389]).

In the electrochemical order of metals, both gold and silver represent the noblest elements and their ionic forms, most frequently Ag(I) and $[AuCl_4]^-$, are reducible at the positive potentials. This makes the two metals nearly ideal analytes for the determination at solid electrodes, operating within such potential ranges, including various CPEs. This applies to the methods employing a direct electrolytic transformation $Me^N \rightarrow Me^0$ (*e.g.*, amperometry), as well as a deposition step with reduction and subsequent re-oxidation $Me^0 \rightarrow Me^N$. In the past, these favourable dispositions were often being exploited also in electroanalysis with CPEs and CMPEs and both Ag(I) and Au(III) had always belonged among prominent analytes [40]. However, in the period of 2001-2008, they did not uphold such a position and the respective methods were appearing only occasionally. Regarding gold, the ion-pairing affinity of the $[AuCl_4]^-$ anion was the principle of choice, whereas silver could be determined by selective accumulation *via* various complexes and the only method has utilised the above-mentioned electrolytic deposition.

In contrast, both mercury and copper were of permanent interest also in the recent years, which is also illustrated by their abundant appearance in the table. When one counts up the individual methods from the recent years with those published in the previous decades, these two metals – together with Pb and Cd – are the most popular inorganic analytes, being the central subject in about 50 reports for Hg and more than 60 devoted to Cu. (Herein, it should be noted that numerous authors sort copper into the group of toxic heavy metals.) The respective procedures for Hg(II) and Cu(II) typically involve the (i) accumulation under open-circuit conditions (by using adsorption, extraction, ion-exchange or even molecular sieving) according to the simplified scheme, $Me^N + m\ L \rightarrow [Me^NL_m]$, with (ii) intermediate reduction of the complex, $[Me^NL_m] \rightarrow ([Me^0L_m]) \rightarrow Me^0 + m\ L$, and (iii) subsequent re-oxidation, $Me^0 \rightarrow Me^{n+} + n\ e^-$, as the detection in the anodic regime. This seemingly complicated sequence, involving additional reduction step, hides one reasonable interpretation. CPEs, in general, are less convenient for cathodic reductions due to the presence of O_2, dissolved in the carbon paste bulk. If the intermediate step is incorporated into the protocol, the analyte of interest (usually atom Me^N) is reduced and can then be detected during re-oxidation, thus avoiding problematic cathodic detections of the $[Me^NL_m]$ complex, accompanied by unwanted signals from the parallel reduction of dioxygen. Finally, to determine both Hg(II) and Cu(II), their tendencies to form insoluble precipitates can also be exploited in proposals of new types of potentiometric CP-ISEs (see Table 1).

4.2. Heavy metals (Zn, Cd, Pb, Tl, In, Sn, Bi and Sb; Table 1l, refs. [51,60,103,113, 226,235,248,253,255,256,258,263, 297,299,300,333, and 390-422]).

Besides a widespread choice of the already existing methods with traditional mercury electrodes, also electroanalysis with CPEs may offer a number of interesting or even unique procedures for the determination of all title metal elements. And this statement can be underlined when screening research

activities in the recent years, where the use of both HMDE and MFE had to be partially suppressed due to the rapidly growing influence of the green-chemistry orientation.

Similarly as with Hg and Cu described in the previous paragraph, a predominant mechanism of the individual methods for zinc, cadmium, and lead was the formation of stable complexes of the $[Me^{N}L_{m}]$ type whose electroactive sites have enabled the identification and quantification in the properly selected voltammetric modulation ramp; at present, preferably by SWV. Again, most of procedures had involved the intermediate reduction step and many of them are also applicable to a simultaneous determination of either Cd(II) and Pb(II) or all three ions altogether.

The respective methods are usually fairly selective, but their detection capabilities rather limited compared to procedures utilising highly effective amalgamation onto mercury or related alloy formation at bismuth-based electrodes. Apart from the afore-mentioned green-chemistry dictate, this is the reason why BiF-CPEs and similar configurations come now to the fore, offering attractive methods for the determination of Zn, Cd, Pb, and other heavy metals (see Table 2).

When considering the remaining metals, *i.e.,* Tl, In, Sn, Sb, Bi, and their single ions or complexes, at least one method for each can be found in the table; for indium representing even a premiere appearance in conjunction with a CPE [40]. Typically, the respective procedures had paid a considerable attention to the interference effect from other heavy metals (Zn, Cd, Pb, and Cu) and therefore, the determination of Tl, In, Sn, Sb, or Bi could be performed at a remarkable concentration excess of all more common heavy metals.

4.3. Metalloids (As and Se; Table 2, refs. [98,248,298]).

From these elements, solely arsenic was of interest in a couple of methods published within 2001-2008 and, surprisingly, such a rare abundance among the methods with CPEs does not reflect the recent eminent interest in systematic monitoring of highly toxic arsenic compounds. It is a pity because *e.g.* the method employing an Au-CPE and based on detection in the CCSA mode permits differentiation of both As^{III} and As^{V} at a very low microgram level.

4.4 Metals of the iron, manganese, chromium, and vanadium groups (Fe, Co, Ni, Mn, Cr, Mo, V; Table 3, refs. [54,56,58, 105,244,275,302,423-427,430-436]).

This group comprises metal elements that are not very "friendly" from an electro-chemical point of view. They exist in numerous oxidation states with a tendency to be easily transformed from one valence to the other, or exhibit distinct inclinations to be converted into various complex forms, thus requiring rather sophisticated procedures to maintain these metals as the target analytes. Such characteristics are also more or less reflected in the respective procedures employing various types of CPES and CMCPEs, including methods reported in the years of 2001-2008. Among the title elements, the leading position is still held by the triad of iron, cobalt, and nickel. Regarding the first one, the corresponding methods have mostly been based on reversible transformation of the Fe(III) / Fe(II) pair; typically, in a complex form. In contrast to bivalent / trivalent iron, both Co^{II} and Ni^{II} atoms are reducible to the elemental state; however, the adhesion of their pure elemental forms at the electrode surface is very poor and analytically inapplicable. Thus, inevitable are combinations with complex formation *via* various Co^{II}-/Ni^{II}-precipitates, in which the central atoms can readily be reduced; in the electrochemistry of nickel, dimethylglyoxime and its derivatives still being preferred (Table 3). The determination of manganese does not require such complex intermediates for electrolytic transformations and the methods of choice have utilised rather the stability of this metal as either Mn(II) cation or MnO_4^- anion. Nearly the same applies to chromium, where a differentiation between Cr(III) and Cr(VI) is usually possible (see again Table 3). Finally, the last two elements, molybdenum and "metal chameleon" vanadium, can also be identified and quantified in variable oxidation states V/VI or IV/V, respectively; Mo(VI) being detected *via* an adduct with electrocatalytic properties.

4.5. Platinum metals and uranium (Pt Ir, Os, Ru, Rh, Pd, and U; Table 3, refs. [302,428,429, and 106]).

In electroanalysis with CPEs, platinum metals attracted one's attention mainly as effective electrocatalytic modifiers (see [40,343] and section 2.3 in this text). As target analytes, platinum metals were of less interest. This characterises also recent activities though some notable achievements can be found. For instance, a couple of years ago, there were the first successes to determine osmium (and less promises for rhodium

or ruthenium). The same method has then allowed to identify Pt, Ir, and Os at once; in all cases *via* anionic complexes of the $[MeX_6]^{2/3-}$ type. With respect to uranium, the only method utilised the detection carried out *via* UO_2^{2+} ion interacting with a modifier grafted onto mesoporous silica.

4.6. Metals of the fourth and third groups, light and heavy metals of rare earths (Zr, Ce, Al, Ga, Sc, Th, and $Me_{(light)}$ + $Me_{(heavy)}$; Table 3, refs. [106,107, and 437-452]).

Normally, these metals are also quite difficult to be detected electrochemically; however, thanks to their reactivity with some complexants (including classical analytical reagents like Morin, Alizarin Red, or Alizarin Complexon [151]), there is a relatively wide palette of methods available for their determination. Among the respective procedures, outstanding is the determination of twelve metal elements, comprising a majority from light and heavy rare earths (see Table 3). Also, the years of new millennium saw some methods, in which one can find the first reports on the determination of Ce, Ga, Sc, and Th at a carbon paste-based electrode.

4.7. Metals of alkaline earths and alkaline metals (Mg, Ca, Li, and Na; Table 3, refs. [226,303, and 453-457]).

From an electrochemical point of view, cationic forms of these metals represent totally indifferent species, reducible merely under extreme conditions. Their determination should thus be accomplished either indirectly or *via* non-electrolytic principles (see Table 3). The first approach facilitates the determination of magnesium, calcium, and sodium, whereas the second is behind the determination of lithium, where the intercalation effect at the ion-size level can be varied for both faradic and non-faradic measurements.

4.8. Non-metallic ions, complexes, and inorganic molecules (halides, pseudohalides, oxy-anions, hydrogen peroxide, dioxygen, nitrogen-containing ions and molecules; Table 4, refs. [55,100,101,109,236, 304-309,327, and 458-490]).

A wide diversity in physicochemical and electrochemical properties of species gathered in Table 4 corresponds to a variety of methodical approaches, modifiers used, or measuring techniques used. Nevertheless, typical principles concerning some recently analysed substances can be noticed and highlighted.

Among others, the table repeatedly quotes the (i) ion-pair formation for iodide, and mainly (ii) electrocatalysis-assisted oxidations, which is the case of a lengthy line of analytes: iodate, bromate and chlorate; sulphide and sulphite; nitrite and nitrous oxides; hydrogen peroxide, dioxygen; or hydroxylamine and hydrazine; mostly, when using newly synthesised materials as modifiers. Or, (iii) indirect detection can provide a way for determination of electrochemically inert anions such as sulphate and hydrogen phosphate.

When studying the data in Tables 1-4 in more detail, some less obvious facts can be revealed. In another context, they may then be interesting and motivating. For instance, (i) the performance of AuF-CPEs (see Tables 1 and 2), hitherto employed in simultaneous determination of Hg(II) and Cu(II), or differentiation of As(III) and As(V) could also be examined for Se(IV), for which an appropriate method with a CPE is still missing [2,40]. Or, Table 2 surveys (ii) selected voltammetric methods that could be maintained for stripping potentiometry (see section 3.4), thereby one would further improve the electroanalytical performance of some original procedures. Nearly the same can then be stated for (iii) still unexplored use of popular chemical modifiers, declared in Tables 2 and 3. Here, one can mention dimethylglyoxime for Ni(II), which would potentially be suitable also for Pd(II) or Fe(II); Zincon for Cu(II), likely applicable to Zn(II), or crown-ethers selectively encapsulating Pb(II), but possibly also Rb(I) and Cs(I) as ionic species with particularly large diameters. The tables themselves document clearly that certain modifying agents can be successfully employed for more inorganic ions – see Table 3 and the collection of methods with ARS or ARC for Zr(IV), Ce(III), Al(III), Ga(III), Sc(III), and Th(III). Finally, the first row of Table 4 includes valuable information on (iv) severe interference from fluoride. Maybe that the respective method and electrode – originally developed for both Br^- and Cl^- ions – could be adaptable also for the determination of fluoride, F^-. So far, this species occupies one permanent position within the group of naturally occurring chemical elements that have not been yet determined with carbon paste-based electrodes, sensors, or detectors [2,40].

5. Conclusions and future prospects

The electrochemistry and electroanalysis with carbon paste-based electrodes, sensors, and detectors have been reviewed as a retrospective of the last period – across the years of a new millennium. This narrowed focus has allowed the authors to present the field – profiting now from results of *ca*. 2000 scientific papers – in the mirror of latest achievements and trends.

Based on the above-presented documentation, two principal conclusions can be made herein. Firstly, it is

Table 1. Determination of noble metals at carbon paste electrodes and sensors. Survey of methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
Au^{III} ($AuCl_4^-$)	C/PO (SWy-2)	DPCSV	- accum. via ion-exchange / adsorption; cathodic redn.	(8×10^{-7} M;--)	pharms., blood serum	- SWy-2: Na-montmorillonite; s.e.: NaCl + HCl; study on pH-effect	351
Au^{III} ($AuCl_4^-$)	C/TCP (binder as modif.)	SP (CCSA)	- accum. via ion-pairing; - redn. with I_{CONST}	(1×10^{-7} M; 5 min)	soils ctng. gold	- interfs. of Fe^{III} suppressed. by F^-; - samples mineralised by MWD	99
Ag^+	C/PO (S_2O_8-podant)	DPCSV	- accum. via donor podant; - electrocatalysis-assisted cathodic redn.	5×10^{-7}- 6×10^{-6} M (2×10^{-7} M; 10 min)	model solns.	- $S_2O_8^{2-}$: added in-situ; no interfs. from common ions (except Pb^{2+})	352
Ag^+	C/PO (EDTA)	ASV	- accum.(electrolytic redn.); - anodic reoxidn.	2×10^{-9}- 1×10^{-6} M (1×10^{-9}M; 10 min)	model solns.	- EDTA used as modif. agent elim. interfs from other ions	353
Ag^+	C/PO (DPO)	DPASV	- o.c.accum. via compl./ redn.; anodic reoxidn.	5×10^{-9}- 1×10^{-7} M (0.7 nM; 10 min)	model solns.	- DPO: N,N'-diphenyl oxamide - no interfs from common ions	354
Ag^+ Pb^{2+}	C/PO (SWy-2)	DPASV	- accum. via ion-pairing; - redn.+ anodic reoxidn.	8×10^{-9}- 1×10^{-7} M (0.1 nM; 4 min)	model solns.	- SWy-2: Na-montmorillonite (clay); in presence of CTAB; simult. detn. of Pb^{2+} investigated	355
Ag^+	C/PO (Alizarin violet)	DPASV	- accum. via complexation; - el. redn./ MEx / reoxidn.	3×10^{-10}- 1×10^{-7} M (0.1 nM; 3 min)	waste water, zinc alloy	- s.e.: a) 0.1 M AcB (pH 5.2), b) 0.1 M H_2SO_4 + 1×10^{-4} M KBr; - no interfs from Me^I and Me^{II}	356
Ag^+	C/DINP (Ag-Thimerosal)	POT, FIA (dir.,titr.)	- chemical equilibrium and steady-state potential for: $Ag^+ \leftrightarrow Ag^I$-compl.	1×10^{-8}- 5×10^{-7} M (3×10^{-7} M)	cosmetics, pharms.; radiology films	DINP: di-iso-nonyl phthalate der.; pharms: Thiopental, Thimerosal (both by potentiometric titration)	97
Ag^+	C/PO + memb. (BNSAO)	POT (dir.,titr.)	- chemical equilibrium and steady-state potential for: $Ag^+ \leftrightarrow Ag^I$-compl.	9×10^{-7}- 0.03 M (4×10^{-7} M)	cosmetics, radiology films	BNSAO: bis 5-(4-nitrophenyl-azo) salisylaldimine (Schiff base); CPE compared with similar CWE	153
Ag^+	C/PO. (DPSG)	POT (dir.)	- chemical equilibrium and steady-state potential for: $Ag^+ \leftrightarrow Ag^I$-compl.	5×10^{-7}- 0.1 M (1×10^{-7} M)	waste water	DPSG: dipyridyl-functionalized silica gel; s.s.: AcB (pH 5.5); - CPE long stable (>6 months)	293
Ag^+	C/PO (AMQ)	DPASV	- accum. via ion-pairing; - redn.+ anodic reoxidn.	1-300 $\mu g\ L^{-1}$ (0.4 $\mu g\ L^{-1}$; 12 min)	natural waters, photographic films	AMQ: 3-amino-2-mercapto quina-zolin-4(3H)-one; detn. compared with GF-AAS	357

Continued **Table 1.** Determination of noble metals at carbon paste electrodes and sensors. Survey of methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
Ag^{+}	C/PO ($AgCrTiS_4$)	LSV	- accum. via complexation; - el. redn.+ reoxidn.	3×10^{-10}- 1×10^{-7} M (3×10^{-6} M; 5 min)	model solns.	- modif. characterised by X-RF in powdered form; interfs. studies	358
Hg^{2+}	C/PO (SWy-2 clay)	DPASV	- ion-exchange + adsorption - redn.+ anodic reoxidn.	1×10^{-9} - 5×10^{-7} M (1×10^{-10} M; 6 min)	water samples	- SWy-2: sodium montmorillonite	359
Hg_2^{2+}	C/PO (PA-NO)	ASV	- specific interact. with Hg^{I} - anodic reoxidn.	3×10^{-8} - 1×10^{-6} M	human urine	- PA-NO: picolinic acid N-oxide; - analysed as Hg^{I} + Hg^{II} mixtures	360
Hg^{II}, HgI_3^{-}	C/PO (TZ^{+};$[HgI_3]^{-}$)	POT (dir.)	- chemical equilibrium: Hg^{2+} ↔ Hg^{II}-compl.	6×10^{-6} - 0.001 M (4×10^{-6} M)	waste water, alloy, dental amalgam	- TZ: tetrazolium (quaternary) ion; - incl. studies on select. coeff.	294
Hg^{2+}	C/SO, C/PO (+AuF, ex situ)	SP (CCSA)	- accum. by electrolytic redn. - reoxidn. with I_{CONST}	(2 ppb; 10 min)	model solns.	- AuF plated in situ or preplated; - simult. detn. of Hg2++ Cu2+	336
Hg^{II} (var. sp.)	C/PO (SH-, NH_2-PSXL)	LSV, DPCSV	- specific sorption processes - o.c. accum + cathodic redn.	-- (not specified)	soils, water samples	- species studied: $HgCl_4^{2-}$, $HgCl_3^{-}$, $HgCl_2$, $Hg(OH)_2$ (speciation st.) - PSXL: polysiloxane ligand	361
Hg^{2+}, Hg^{II} (HgX_n^{m-})	C/PO (BbTSC)	CV, SWV	- specific complexation; - anodic reoxidn.	10-50 ppb (8 ppb; 15 min)	river water samples	BbTSC: benzyl-bis-thiosemicarba-zone;- speciation of Hg^{2+}, $HgCl_3^{-}$, and $HgCl_4^{2-}$ via ligand competion.	362
Hg^{2+}	C/PO (DTTD-SG)	CV, DPCSV	- sorption + ion-exchange; - accum./ cathodic redn.	3×10^{-8} - 1×10^{-8} M (1×10^{-8} M; 3 min)	polluted water	- DTTD-SG: 2,5-dithio-1,3,4-thia-diazole functionalised silicagel - CMCPE regenerated chemically	363
Hg^{2+}	C/PO (APSC, MPSC)	DPASV	- o.c. accum (ion-exchange) - anodic reoxidn.	1×10^{-8} - 7×10^{-8} M (8×10^{-8} M; 5 min)	model solns.	- A(M)PSC: amino(mercapto) phyl-lo silicate clay (synth. by grafting)	364
Hg^{2+}	CNT-PE (unm.)	CV, SWASV	- electrocatalysis-assisted electrolysis; reoxidn.	1-25+40-200 $\mu g\ L^{-1}$ (0.4 $\mu g\ L^{-1}$; 12 min)	water samples	- CNT-PE: carbon nanotube paste electrode; s.e.: AcB (pH 4.0)	72
Hg^{2+}	C/PO (TZT-HDTA-C)	CV, DPASV	- selective sorption + redn.; - anodic reoxidn.	--	model solns.	- TZT-HDTA-C: 2-thiazoline-2-thiol-hexadecyl-trimethylammonium-clay; no interfs of Pb, Cd, Cu, Zn	365

Continued **Table 1.** Determination of noble metals at carbon paste electrodes and sensors. Survey of methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
Hg^{2+}	C/PO (EBHMP)	POT (dir.)	- chemical equilibrium and steady-state potential for: $Hg^{2+} \leftrightarrow Hg^{II}$-compl.	3×10^{-7}- 0.01 M (1×10^{-7} M)	waste water (spiked); amalgam	- EBHMP: ethyl-2-(benzoylamino)- 3-(2-hydroxy-4-methoxyphenyl)-2-propenoate; pH 1-4, t_{EQ} < 5s	295
Hg^{2+}	C/PO (SIAMT)	CV, DPASV	- accum. via sorption and complex.; redn.+ reoxidn.	1-20 μg L^{-1} (0.1 μg L^{-1}; 15 min)	waste water (spiked); amalgam	SIAMT: silica gel functionalised with 2-aminothiazole; var. s.e.	366, 367
Hg^{2+}	C/PO (SWy-12 / MATD)	LSV, EC-LC	- accum. via sorption and complexation; redn.	(10 μg L^{-1};--)	model solns.	SWy-12 / MATD: Na-montmorillo- nite + 2-mercapto-5-amino-1,3,4-thiadiazol; clay of natural origin	368
Hg^{2+}	C/PO (DTSA)	POT (dir.)	- chemical equilibrium and steady-state potential for: Hg^{II}-HA $\leftrightarrow$ Hg^{II}-compl.	1×10^{-7}- 3×10^{-4} M (2×10^{-8} M)	model solns.	DTSA: dithiosalicylic acid; HA: humic acid (competitive ligand); - evaluation of stability constants	296
Hg^{2+}	C/PO (chitosan, Ch)	CV, DPASV	- accum. via sorption and complex.; redn.+ reoxidn.	1×10^{-6} - 4×10^{-5} M (6×10^{-7} M; 4 min)	water (spiked)	- CP-composition: 60%(m/m) C + 20% PO (Nujol)+ 20%(m/m) Ch; - s.e.: 0.2 M KNO_3 (pH 6.2)	369
Hg^{2+}	C/PO (Cryptofix)	ASV	- accum. via complexation; - el. redn./ anodic reoxidn.	-- (0.1 μg L^{-1})	model solns.	- Cryptofix: commercial reagent (with ion-exchange capabilities)	370
Hg^{2+}	C/PO (Cadion A)	CV, LSV	- accum. via complexation; - el. redn./ anodic reoxidn.	0.1-20 μg L^{-1} (0.1 μg L^{-1}; 1 min)	polluted waters	- Cadion A: 4-nitrophenyldiazo- amino-azobenzene; s.e.: 0.2 M NaAc (pH 7); o.c. accum.	371
Hg^{2+}, Cu^{2+}+ Pb^{2+}	C/PO (AMT / plex-μS)	SWASV	- accum. via complexation; - el. redn.+ reoxidn.	15-75 μg L^{-1} (5 min) (5 μg L^{-1}; 15 min)	tap (spiked); waste water	AMT / plex-μS: 2-aminothiazole / plexi-polymer made microsphere; - simult. detn. with Cu^{2+}, Pb^{2+}	372
Hg^{2+}, Cu^{2+}+ Pb^{2+}	C/PO (SBA-15)	CV, DPASV	- accum. via sorption and complex.; redn.+ reoxidn.	2×10^{-6} - 1×10^{-5} M (5×10^{-7} M; 4 min)	natural water; sugar –cane alcohol drink	SBA-15: nanostructured silica functionalised with 2-benzothiazo- lethiol; simult. detn with Cu^{2+},Pb^{2+}	373
Cu^{2+}	C/PO (AP-GS)	CV, SWV	- o.c.-accum. via compl. - MEx; redn.+ reoxidn.	5×10^{-8} - 2×10^{-7} M (3×10^{-9} M, 10 min)	tap water	- AP-GS: aminopropyl-functionali- lised grafted silica; studies on accum. mechanism; interfs. st..	230

Continued **Table 1.** Determination of noble metals at carbon paste electrodes and sensors. Survey of methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
Cu^{2+}	C/PO (TH)	CV, LSV	- o.c.-accum. via compl.+ redn./ cathodic reoxidn.	(0.5 μg L^{-1}, 10 min)	river water	- TH: macrocyclic thiohydrazone - incl. studies on interfs.	374
Cu^{2+}	C/PO (DTPT)	POT (dir.)	- chemical equilibrium and steady-state potential for: $Cu^{2+} \leftrightarrow Cu^{II}$-DTPT	1×10^{-6} - 0.08 M (7×10^{-7} M)	electronics (waste solns.)	- DTPT:(3,4-dihydro-4,4,6-tri-methyl-2(1H) pyrimidine thione	375
Cu^{2+}	C/PO (TPP)	DPASV	- o.c.-accum. by compl. - MEx / redn.+ reoxidn.	9×10^{-8} - 5×10^{-5} M (2×10^{-9} M, 12 min)	minerals	- s.e.: BR-buffer (pH 6) - sample extracted prior to detn.	376
Cu^{2+}	C/PO (CAR-SG)	DPASV	- o.c. accum. by compl. - redn.; anodic reoxidn.	5×10^{-8} - 1×10^{-6} M (4×10^{-9} M)	model solns.	- CAR-SG: Carnosine immobilised onto silica (solid phase extractant)	231
Cu^{2+}	C/SO, C/PO (+ AuF)	SP (CCSA)	- accum. by electrolytic redn.; reoxidn. by I_{CONST}	(5 ppb; 10 min)	model solns.	- Au-film plated in situ or preplated - simultaneos detn. of Cu^{2+} + Hg^{2+}	336
Cu^{2+}	C/PO (humic acid)	CV, DPV	- o.c. compl.+ redn. - anodic reoxidn.	3×10^{-8} - 1×10^{-5} M	model and real samples	- study on accum. mechanism and possible speciation	377
Cu^{2+}	C/PO (MDPT)	ASV	- o.c. accum. by compl.+ redn.; anodic reoxidn.	1×10^{-7} - 1×10^{-4} M (1×10^{-7} M, 6 min)	coal ash	- MDPT: 4-methoxy-2,6bis(3,5-di-methylpyrazoyl)-1,3,5 triazine - s.e.: tartrate buffer (pH 4)	378
Cu^{2+}	C/PO (MBTZ-SG)	LSV, ASV	- o.c. accum. via compl.+ sorption / MEx / el. redn.; - anodic reoxidn.	1-10$\times10^{-7}$ & 1×10^{-5} - 0.01 M (0.1 μM)	model solns.	- MBTZ-SG: 2-mercaptobenzothia-zole functionalised silica gel; two linear ranges for calibration	379
Cu^{2+}	C/PO (salicylaldoxime)	CV, ASV	- o.c. accum. via compl.; - el. redn./ anodic reoxidn.	0.1-10 ppm (0.1 ppm; 3 min)	waste water, wine	- s.e.: diluted HNO_3; intermediate reduction for 100 s.	380
Cu^{2+}	C/PO (Z)	DPCSV	- o.c. accum. via sorption; - MEx / cathodic redn.	5×10^{-8} - 5×10^{-6} M (2×10^{-8} M, 3 min)	model and real samples	- Z: natural zeolite (modif.); accum. / regeneration scheme during anal.	381
Cu^{2+}	C/PO (ARS / $S_2O_8^{2-}$)	CtAdSV, 2nd DLSV	- o.c. accum. via compl.+ adsorption / el. redn./ el. catalyst-assisted reoxidn.	8×10^{-10} -3×10^{-8} M (2×10^{-10} M, 3 min)	natural water, soil samples	- s.e.: BRB (pH 4.6); modif. in situ; no regeneration required	382
Cu^{2+}	C/PO [calix[4]arene]	DPASV	- o.c. accum. via intercalation - el. redn./ anodic reoxidn.	(0.1 μgl^{-1}; 10 min)	tap water	- s.e.: buffer (pH 6.5-7.5); analysis compared to the reference (AAS).	383

Continued **Table 1.** Determination of noble metals at carbon paste electrodes and sensors. Survey of methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
$Cu^{2+/+}$	C/PO (nano-Pt)	CV, ASV	- el. acc. $Cu^{II} \rightarrow Cu^{I} \rightarrow Cu^{0}$ with intemediate catalysis; - anodic reoxidn.	4×10^{-8} - 2×10^{-6} M (4×10^{-9} M, 10 min)	model solns.	- Pt-particles, 20 nm characterised by SEM and XRF; LOD lowered by the effect of some surfactants	384
Cu^{2+}	C/PW(s) (AMTZ-SG)	CV, DPASV	- o.c. accum. via complex.; - el. redn./ anodic reoxidn.	8×10^{-8} - 3×10^{-6} M (3×10^{-8} M, 20 min)	commercial ethanol fuel	- electrode of the C/PW type stable in EtOH; AMTZ-SG: 2-amino- thiazole functionalized silica	104
Cu^{2+}	C/PO (DPN-SG)	POT (dir.)	- chemical equilibrium and steady-state potential for: $Cu^{2+} \leftrightarrow Cu^{II}$–DPN	1×10^{-7} – 0.01 M (8×10^{-8} M, 50s)	waste water	- DPN-SG: dipyridyl group-functio- nalized nanoporous silica gel ; - slope: Nenstian, ca 28.5 mV/dec.	288
Cu^{2+}	C/PO (Cu-SALHMN)	POT (dir.,titr.)	- chemical equilibrium and steady-state potential for: $Cu^{2+} \leftrightarrow Cu^{II}$–SALHMN	4×10^{-7} – 0.01 M (6×10^{-8} M, 12s)	tap water, multivitamin tablets	- SALHMN: N,N'-disalicylic-lene-hexameythylenediaminate; s.s.: buffer (pH 4-6.5); interfs. study	289
Cu^{2+}	C/PO (chitosan)	ASV	- o.c. accum. via adsorption + el. redn.; anodic reoxidn.	2×10^{-7} - 7×10^{-6} M (8×10^{-8} M, 4.5 min)	waste water samples	- modif. content in CP: 25%(m/m); s.e.: 0.1 M KNO_3 (pH 6.5).	385
Cu^{2+}	C/PO (Zincon)	DPASV	- o.c. accum. via compl.+ sorption / anodic reoxidn.	2-220 μg L^{-1} (1 μg L^{-1}; 5 min)	natural waters, human hair	- modif.: 2-carboxy-2'-hydroxy-5' sulfo-formazyl benzene; s.e.: PhB (pH 6.4)	386
Cu^{2+}	C/PO (s.a. n-Au + 3 diff. modifs)	POT (dir.)	- chemical equilibrium and steady-state potential for: $Cu^{2+} \leftrightarrow Cu^{II}$-SA-nAu / M	8×10^{-9} – 0.001 M ($3\text{-}4\times10^{-8}$ M; 5s)	water sample, human hair	- s.a.: self-assembled n-Au-parts.; - modifs.: MMN-IT, MNFT, MNTT (SH–heterocyclic derivatives)	292
Cu^{2+}	CNT-PE, CNT(F)PE	CV, SWV	- o.c. accum. via compl.+ sorption / anodic reoxidn.	0.01-0.10 μg L^{-1} (0.005 μg L^{-1};--)	tap water, rat tail (blood)	- CNT(F): fluorinated carbon nano- tubes; electrode life-time for appl. in-vivo, t_L > 1 month	94
Cu^{2+}	C/PO (TMTDS)	POT (dir.,FIA)	- chemical equilibrium and steady-state potential for: $Cu^{2+} \leftrightarrow Cu^{II}$–TMTDS	(5×10^{-8} M for stac.; 2×10^{-7} M for FIA)	model and real samples	- TMTDS: tetramethyl-thiuram di- sulfide; optimisation studies for both stac. and FIA modes.	290
Cu^{2+}	C/PO (SAL / PSX)	POT (dir., titr.)	- chemical equilibrium and steady-state potential for: $Cu^{2+} \leftrightarrow Cu^{II}$-SAL	2×10^{-7} – 0.001 M (3×10^{-8} M; 8s)	water samples, urine	- SAL / PSX: salicylidine-functiona- lised polysiloxane; opt.: pH 2-5.5; titr. performed with EDTA	387

Continued **Table 1.** Determination of noble metals at carbon paste electrodes and sensors. Survey of methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
Cu^{2+}	C/PO (naphthazarin)	AdSV, POT (dir.,FIA)	- chemical equilibrium and steady-state potential for: $Cu^{2+} \leftrightarrow Cu^{II}$–TMTDS	(2×10^{-6} M for stac.; (3×10^{-5} M for FIA) (t_R < 50s)	metal alloys with Cu-traces	- modif.: 5,8-dihydroxy-1,4-naphto-quinone; s.s.: 0.1 M AmB/AcB; life-time, t > 60 days	291
Cu^{2+}	C/PO (microalgae)	DPCSV	- o.c. accum via bio-sorption; - cathodic redn.	5×10^{-8} - 1×10^{-6} M (5×10^{-10} M,--)	model and real samples	- microalgae sp.: Tetraselmis Chuii; added in content of 3-20%(m/m)	388
Cu^{2+}	C/PO (H-BDBTU)	POT (dir.)	- chemical equilibrium and steady-state potential for: $Cu^{2+} \leftrightarrow Cu^{II}$-BTU	1×10^{-5} – 0.001 M (1×10^{-5} M; 10s)	model solns.	- H-BDBTU: N-benzoyl-N',N'-di-n- butyl-thiourea; studies on the mechanism and eq. conditions	389

For other abbreviations and symbols, see the respective list at the end of the article

Table 2. Determination of heavy metals at carbon paste electrodes and sensors. Survey of Methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
Zn^{2+}, Cd^{2+} + Pb^{2+}	C/SO [HgO, Bi_2O_3 (s)]	DPASV	- accum. (electrolytic redn.) at in-nascenti formed MF or BiF; anodic. reoxidn.	50-1000 ppb Zn^{II} 1-50 ppb Cd^{II},Pb^{II} (1-2 ppb; 10 min)	tap and natural waters	- HgO, Bi_2O_3 added in CP (5%); tests on reproducibility ($R_{\pm}$ < 5 %); compared with MF- and BiF-SPE	113
Zn^{2+}; Cd^{2+} + Pb^{2+}	C/SO + BiF, (--, Bi_2O_3)	DPASV	- accum. via electrolytic redn.+ alloy formation; - anodic reoxidn.	50-200 μg L^{-1} Zn^{II} (20 μg L^{-1}; 5 min)	model solns.	- way of plating: (i) in-situ, (ii) ext., (iii) in-nascenti (via Bi_2O_3 redn.); detn. of Zn with high background	248
Zn^{2+}; Cd^{2+} Pb^{2+} + Cu^{2+}	C/PW(s) ($Hg_2C_2O_4$)	DPASV	- accum. via ion-exchange; - redn.; anodic reoxidn.	--	medicinal plants, pharms.	- simultanneous detn., compared with ref. analyses by AAS - pharm.: ayurvedic tablets	103
Cd^{2+}	C/PO (BTT + am. SiO_2)	DPASV	- adsor. accum. via compl. - redn.; anodic reoxidn.	6×10^{-7} - 4×10^{-5} M (1×10^{-7} M; 2 min)	natural water (spiked)	- BTT: benzothiazole-thiol - s.e.: phosphate buffer (pH 7.5)	390
Cd^{2+}	C/PO (ZrP_2O_7-SG)	DPASV	- o.c. accum (ion-exchange) - el. redn. / anodic reoxidn.	3-1400 ng L^{-1} (3 ng L^{-1}; 2 min)	waste water	- SG: functionalised silica gel; - incl. optimalisation studies	391
Cd^{2+}	C/PO (BTZT / SBA-15)	DPASV	- accum. via complex and sorption); redn. / reoxidn.	1-10 × 10^{-6} M (5×10^{-7} M; 2 min)	natural water	- BTZT: 2-benzothiazolethiol, SBA- 15 nanostructured silica; s.e.: PhB	392
Cd^{2+}	C/PO (MNT / n-Au)	POT (dir.)	- chemical equilibrium and steady-state potential for: $Cd^{2+} \leftrightarrow Cu^{II}$–MNT / nAu	3×10^{-8} – 3×10^{-4} M (2×10^{-8} M; 6 s)	water, human hair	- MNT: 2-mercapto-5-3-nitrophenyl 1,3,4-thiadiazole; slope: Nenstian, ca 29.5 mV/dec; s.s.: pH 2-4	393

Continued **Table 2.** Determination of heavy metals at carbon paste electrodes and sensors. Survey of Methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
Cd^{2+}	C/PO (PTD, in-situ)	2nd DLSV	- el. accum. enhanced by sorption; anodic reoxidn.	6×10^{-9} - 2×10^{-7} M (3×10^{-10} M; 10 min)	water	- PTD: 1,10-phenanthroline-dione; - s..e.: 0.05 M AcB (pH 4.7); interfs.	394
Cd^{2+} + Pb^{2+}	C/PO (CCHA)	DPASV	- accum. by compl.; MEx - redn.; anodic reoxidn.	4×10^{-8} - 3×10^{-6} M (1×10^{-9} M; 2 min)	municipal, mineral waters	- CCHA: N-p-chlorophenylcinnamo-hydroxamic acid; CP: anodic regnt.	395
Cd^{2+} + Pb^{2+}	C/PO (Bi_2O_3 , in nasc.)	DPASV	- accum. via electrolytic redn - anodic reoxidn.	(5 μg L^{-1}; 6 min)	tap, mineral waters, urine	- BiF generated from oxide in nasc.; s.e.: 0.1 M acetate buffer (pH 4.5) - simult.detn. of Pb^{II} possible	263
Cd^{2+} + Pb^{2+}, Cu^{2+}	C/PO (CPA + ms.SiO_2)	SWV	- accum. via compl. / adsorp. - redn. / anodic reoxidn.	10-200 ppb (0.5 ppb; 20 min)	model solns.	- CPA: carbamoyl-phosphonic acid - simult.detn. of Pb^{II} + Cu^{II} possible	396
Pb^{2+} + Cu^{2+}	CNT-PE (+ DNA)	CV, SWASV	- accum. via el. enhanced by sorption; anodic reoxidn.	(2×10^{-12} M for Pb, 7×10^{-12} M for Cu; 2.5 min for both)	fish tissue	- DNA coating serves for specific enhancement of the accum. step; s.e.: PhB (pH 10.0)	397
Cd^{2+}, Pb^{2+}	C/PO (+BiF / Fbg)	SWASV (BIA)	- accum. via electrolytic redn. + alloy formation; reoxidn.	(0.2 mg L^{-1} for Cd, 0.1 μg L^{-1} for Pb)	tap water tea samples	- Fbg: Fibrinogen (protective layer against surfactants) ; BIA-mode: batch injection analysis, m-volume	226
Pb^{2+} + Cd^{2+}	C/SO + ZD (+ BiF)	DPASV	- accum. via electrolytic redn.+ alloy formation; - anodic reoxidn.	(0.10 mg L^{-1} for Pb, 0.08 mg L^{-1} for Cd; 2 min for both)	real samples	- ZD: natural zeolite doped in CP (serving for more effective plating with BiF); s.e.: AcB (pH 4.5)	398
Pb^{2+}, Cd^{2+}	C/PO (DMG)	DPCSV	- accum. (compl. + adsort.) - cathodic redn.	1×10^{-7}- 2×10^{-5} M Pb 3×10^{-7}- 3×10^{-5} M Pb	waters	- DMG: dimethyl glyoxime - interfs. from Ni^{II} and Hg^{II}	399
Pb^{2+}, Cd^{2+}	C/PO (α-CD, β-CD)	ASV	- accum. by ion-inclusion effect; cathodic redn.	(6×10^{-7} M Pb, (2×10^{-5} M Cd)	model solns.	- CDs: cyclodextrins; incl. studies on diff. prfm. of α-CD and β-CD	400
Pb^{2+}	C/PO (crown ethers)	DPASV	- accum. via compl. - redn.; anodic reoxidn.	20-100 ppb (1 ppb; 30 s)	alcoholic beverages	- s.e.: aqueous solns.+ 40% MeOH - simult. detn. of Cu^{II} also tested	401
Pb^{2+}	C/PO (SH−ms.SiO_2)	SWV	- accum. via compl. - redn.; anodic reoxidn.	10-1500 ppb Pb 20-1600 ppb Hg	model solns.	- SH-ms.SiO_2: thiol-ctng. mesopo- rous silica; simult. detn. of Hg^{II}	402
Pb^{2+}	C/PO (plant tissue)	DPASV	- bioaccum. (ion-exchange) - redn.; anodic reoxidn.	(0.01 ppb)	natural waters	- modif.: grass weed (Pennisetum) - s.e.: acetate buffer (pH 5)	403
Pb^{2+}	C/PO (1,8-DAN)	DPASV	- accum. via compl.; redn. - anodic reoxidn.	50-2000 ppb (30 ppb; 10 min)	model solns.	- DAN: diamminonaphthalene + CP acts as conducting polymer	404
Pb^{2+}	C/PO [(OH-AQ-Me)$_2$S]	DPASV	- accum. via complexation; - e. redn. / anodic reoxidn.	6×10^{-10} - 6×10^{-6} M (4×10^{-10} M; 11 min)	waste water	- modif.: bis[1-hydroxy-9,10-anthra- quinone-methyl]sulfide; no interfs from various metal ions, Me^{2+}	405

Continued **Table 2.** Determination of heavy metals at carbon paste electrodes and sensors. Survey of Methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
Pb^{2+}	D/PO (DPEs, 3 types)	DPASV	- accum. via electrolytic redn; anodic reoxidn.	1×10^{-10} - 1×10^{-6} M, depending on DPE; (10-100 pM; --)	natural water, tea samples	- D: natural or synthetic diamond (particle size: 1 or 50 μm); DPE: diamond paste electrode	60
Pb^{2+}	C/PO (o-, m-, p-PD/E)	DPASV	- accum. via complexation; - e. redn. / anodic reoxidn.	5×10^{-8} - 1×10^{-5} M (1×10^{-9} M; 10 min)	model solns.	- PD/E: phenylendiamine (three isomers) admixed in CP / electro-polymerised; interfs. of Me^{2+}.	406
Pb^{2+}	C/PO (APA-MMS)	AD, FIA / WJD	- Pb^{II}-vs- APA affinity; - el. redn. by E_{CONST};	1-25 ppb Pb (RSD < ± 2.5%)	model solns.	- APA-MMS: acetamid-phosphonic acid functionalised mezoporous SiO_2; WJD: wall-jet detector	235
Pb^{2+}	C/PO (ZrP_2O_7-SG)	DPASV	- o.c. acc. (ion-exchange); - el. redn. / anodic reoxidn.	3×10^{-9} - 5×10^{-6} M (4×10^{-10} M; 2 min)	waste water	- SG: functionalised silica gel; - interfs. study with Zn, Cd, Sn, Tl	407
Pb^{2+}	AB/PO (I^-, in-situ)	SWASV	- accum. via spec. sorption; - el. redn. / anodic reoxidn.	2×10^{-8} - 4×10^{-6} M (6×10^{-9} M; 10min)	water samples	- AB: acetylene black (replacing graphite powder); addition of I^- further enhances the sensitivity	51
Pb^{2+}	C/PO (OF-S)	DPASV	- accum. by adsorption to S; - el. redn. / anodic reoxidn.	5-1000 ng L^{-1} (5 ng L^{-1}; 1 min)	hair sample (spiked)	- OF-S: organo-functionalised silica (not specified); t_L > 4 months	408
Pb^{2+}	C/PO (Dithizone)	DPASV, FIA	- o.c. accum. via complex.; - redn / anodic reoxidn.	8×10^{-8} - 1×10^{-5} M ($5\text{-}8\times10^{-8}$ M; 8 min)	soil samples	- interfs. study with Zn, Cd, Cu, Hg; - samples collected at metallurgic plant; analyses compared to AAS	409
Pb^{2+}	C/PO (fruit tissue)	DPCSV	- o.c. accum via biosorption; MEx / cathodic redn.	1-10 mg L^{-1} (5 ng mL^{-1}; 1 min)	water (spiked), laboratory waste	- fruit: dried / pulverised pineapple; - interfs. study with 15 Me^{n+} ions; Bio-CPE regeneration by EDTA	410
Pb^{2+}	C/POs (+ DTBA / MBA)	POT (dir., titr.)	- chemical equilibrium and steady-state potential for: $Cu^{2+} \leftrightarrow Cu^{II}$–TMTDS	5×10^{-8} M for CPE-1 4×10^{-8} M for CPE-2	humate extracts	- two modifs: dithiodibenzoic acid, mercaptobenzoic acid (added in: 25%, m/m); evaluation of $\beta_{Pb\text{-}TBA}$	297
Pb^{2+}	C/PO (SiO_2 / Al_2O_3)	CV, DPASV	- o.c. accum. via sorption; - el. redn. / anodic reoxidn.	2×10^{-9} - 5×10^{-5} M (1×10^{-9} M; 5 min)	real samples (--)	- modif.: mixed oxide, studied with TG, XRF, FTIR; added as 5% (m)	411
Pb^{2+}	C/PO (Ca^{II}-MMT)	CV, DPASV	- o.c. accum. via ion-exch.; - el. redn. / anodic reoxidn.	-- (6×10^{-9} M, --)	water samples	- MMT: montmorillonite; s.e.: 0.01 M HCl; comparison with bare CPE	412
Pb^{2+}	C/PO (NFR, in-situ)	DPV, AdCSV	- accum. via adsorption of complex; cathodic redn.	0.5-200 ng mL^{-1} (0.2 ng mL^{-1}; 1 min)	lake, mineral waters, drinks (powdered)	- NFR : Nuclear fast red; s.e.: buffer (pH 3) + 5×10^{-5} M modif.; intefs.s.	413
Pb^{2+}	C/SO (QPu-TU)	CV, SWASV	- o.c. accum. via chelating ; - el. redn. / anodic reoxidn.	0.005-5(0) mg L^{-1} (0.2 mg L^{-1}; 10 min)	water samples (tap, lake, and waste w.)	- QPu-TU: thiourea-functionalised macroporous resin QuadraPure; 30% (m) in CP; s.e.: 0.1 M AcB;	414
Pb^{2+}	C/SO (chitosan)	DPCSV	- o.c. accum via biosorption; - cathodic redn.	10-110 ng mL^{-1} (2 ng mL^{-1}; --)	water, pharm., human blood and urine	- s.e.: 0.5 M HCl; no interfs. from Cd, Tl, Sn, Cu (10-fold excess)	415

Continued **Table 2.** Determination of heavy metals at carbon paste electrodes and sensors. Survey of Methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
Tl^{+} + Cd^{2+}+Pb^{2+}	C/SO (+BiF, in-situ)	DPASV	- accum. via complexation, el. redn.+ alloy formation; - anodic reoxidn.	50-500 μg L^{-1} Tl^{I} --	model solns.	- s.e.: 0.1-1.0 M NaOH (pH > 12); studies on Tl-deposition at BiFE plated from $Bi(OH)_4^-$	256
Tl^{+} + Cd^{2+}+Pb^{2+}	C/SO (+Bi-powder)	DPASV, SWASV	- accum. via complexation, el. redn.+ alloy formation; - anodic reoxidn.	25-500 μg L^{-1} Tl^{I} --	model solns.	- s.e.: 0.1 M AmB (pH 9.5); study on behaviour of Tl+Pb+Cd mixt. in atypical supporting media	258
$Tl^{I,III}$ ($TlCl_4^-$)	C/TCP (unm.)	SP (CCSA)	- accum. via ion-pairing as {H-TCP$^+$; $TlCl_4^-$}; redn. with I_{CONST} in SP-regime	(1×10^{-7} M; 3 min)	model solns.	- TCP: tricresyl phosphate (binder); s.e.: 0.1 M HCl + 2 M KCl; study on differentiation of Tl^{I} and Tl^{III}	333, 416
In^{3+} + Cd^{2+}+Pb^{2+}	C/SO (+BiF, in-situ)	SWASV	- accum. via electrolytic redn.+ alloy formation; - anodic reoxidn.	25-250 μg L^{-1} In^{III} (10 μg L^{-1}; 5 min)	water (spiked) CRM (soil)	- s.e.: 0.1 M AcB + 0.2 M KBr; studies on simultaneous detn. of In+Cd+Pb and detn. of In^{III} alone	253
Sn^{2+}	C/SO (BiF in-situ) C/SO (Bi-powder)	SWASV	- accum. via electrolytic redn.+ alloy formation; - anodic reoxidn.	0.2-1 mg L^{-1} (0.1 mg L^{-1}; 5 min)	model solns.	- s.e.: 0.2-1.0 M HCl (pH < 2) + 0.005 M $N_2H_5^+$ (stabilising agent); studies on detn. of tin as Sn^{II}	255
Sn^{IV} (SnO^{2+})	C/PO (Alizarin violet)	ASV	- o.c.-accum. via complex; MEx / redn. / an. reoxidn.	8×10^{-9} - 1×10^{-6} M (4×10^{-9} M; 2 min)	canned food sample	- s.e.: AcB (pH 4.5); studies on adsorpt. mechanism of accum.	417
$Sn^{II,IV}$	C/PO (BPR)	DPASV	- o.c. accum. via complex.; - el. redn. ($Sn^{II} \rightarrow Sn^{O}$) - MEx / anodic reoxidn.	0.1-50 μg L^{-1} (0.1 μg L^{-1}; 2 min)	waste water, canned food	- BPR: bromo-pyrogallol red; s.e.: (a) 0.1 M AcB, (b) 4 M HCl; pre-redn. $Sn^{IV} \rightarrow Sn^{II}$ by chem. agent	418
Bi^{3+}	C/PO (SWy-2)	DPASV	- o.c. accum. via ion-exch. ; - el. redn. / anodic reoxidn.	4×10^{-9} - 1×10^{-6} M (1×10^{-10} M; 5 min)	water sample, nickel alloy	- SWy-2: Na-montmorillonite; ion-exchange with adsorption of Bi^{III}	419
Bi^{3+}	C/PO (BPR)	DPASV	- o.c. accum. via chelating ; - el. redn. / anodic reoxidn.	1×10^{-9} - 5×10^{-7} M (5×10^{-10} M; 3 min)	water sample, human hair	- BPR: bromo-pyrogallol red; s.e.: 0.3 M HCl + 2×10^{-5} M BPR; incl.. interfs. studies with various Me^{n+}	420
Bi^{3+}	C/PO [2 types] (BiI_4^-+ POE/OPE + $Fe(phen)_3$)	POT (dir.)	- chemical equilibrium and steady-state potential for: $Bi^{3+} \leftrightarrow (POE/OPE)^+BiI_4^-$	(4×10^{-6} M ... type 1) (2×10^{-6} M ... type 2) t_R = 20-40s)	suppositories, ointment	-POE: polyoxyethylene, OPE: octyl-phenyl ether, "phen": 1,10-phenan-throline); s.s.: buffers (pH 3-9)	300
Sb^{3+}	C/PO (BPR)	DPASV	- o.c. accum. via chelating ; - el. redn. / anodic reoxidn.	2×10^{-9} - 5×10^{-7} M (1×10^{-9} M; 2.5 min)	water sample, human hair	- BPR: bromo-pyrogallol red; s.e.: 0.1 M HCl + 3×10^{-5} M BPR; incl.. interfs. studies with various Me^{n+}	421
Sb^{3+} + Cu^{2+}	C/PO	DPASV with RDE	- accum. via electrolytic redn; anodic reoxidn.	10-50 ng mL^{-1} Sb^{III} (5 ng mL^{-1}; 5 min)	CRMs (iron and steel)	- RDE: rotated disc electrode; s.e.: HCl + KI + ascorbic acid (sep. of Sb- and Cu-peaks)	422
Sb^{3+}	C/PO [2 types] (SbI_4^-+ CPy/ TPhT)	POT (dir.)	- chemical equilibrium and steady-state potential for: $Sb^{3+} \leftrightarrow$ (CPy/ TPhT)$^+SbI_4^-$	(4×10^{-6} M ... type 1) (5×10^{-6} M ... type 2) t_R = 20-30 s)	waste water, antibilharzial comp.	- CPy: cetyl pyridinium, TPhT: tri-phenyl tetrazolium, s.m.: pH 4-10; little interfs. from Cd^{2+}, Hg^{2+}, Bi^{3+}.	299

Continued **Table 2.** Determination of heavy metals at carbon paste electrodes and sensors. Survey of Methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
As^{III} + As^{V}	C/SO (+ AuF, ex situ)	SP (CCSA)	- accum. by electrolytic redn. - oxidn. with I_{CONST}	As^{III}: 3 ppb (15 s.) As^{V}: <1 ppb (5 min)	river water (polluted)	- interf. from Cu^{II} (Cu:As >5:1) - with diffn. of As^{III} vs As^{V}	247
As^{V} ($HAsO_4^{2-}$)	C/TCP (unm.)	POT (titr.)	- chemical equilibrium with ion-pairing: $HAsO_4^{2-} \leftrightarrow CPyB^{+}H_2[As(Mo_3O_{10})_4]^{-}$	(0.2 mg L^{-1} As^{V})	mineral water, org. compds.	- TCP: tricresyl phosphate (binder) - CPyB: cetylpyridinium bromide - dry ashing of solid samples	98
As^{V} ($HAsO_4^{2-}$)	C/PO (Fe^{II}-clinoptite)	POT (dir.)	- ion-pairing equilibrium, steady-state potential for: $HAsO_4^{2-} \leftrightarrow (ZE)_2$-$HAsO_4^{2-}$	2×10^{-8} – 0.001 M (3×10^{-8} M; 5-10 s)	natural water, waste water	- modif.: natural zeolite; pH 4-10; t_L for CP-ISE > 2 months; incl. evaluation of $k^{POT}i$	298

For other abbreviations and symbols, see the respective list at the end of the article

Table 3. Determination of the remaining metals at carbon paste electrodes and sensors: Survey of methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
Fe^{2+}	D/PO (DPEs, 3 types)	DPASV	- accum. (electrolytic redn) anodic reoxidn.	1×10^{-8} - 1×10^{-4} M, depending on DPE; ($1\text{-}10\times10^{-10}$ M)	pharms.	- D: natural or synthetic diamond (particle size: 1 or 50 μm); DPE: diamond paste electrode	54
$Fe^{2+/3+}$	C/PO + Nf (1,10-phen)	SWASV, AD	- accum. (electrolytic redn) - anodic reoxidn.	6×10^{-6} - 2×10^{-5} M (2×10^{-6} M; 5 min)	fuel ethanol samples	- Nf: Nafion® (stabiliser of carbon paste in EtOH; results of analysis compared to reference AAS	423
Co^{2+}	C/PO (Cyclam)	POT (dir., titr.)	- chemical equilibrium and steady-state potential for: $Co^{2+} \leftrightarrow Co^{II}$–Cyclam	6×10^{-6} – 0.1 M (3×10^{-6} M; --)	waste water (electroplating baths)	- Cyclam: agent entraping Co^{2+} via its ion-diameter; solns. cntg. 25% EtOH; Nerstian slope: 28.4 mV/dec.	424
Co^{2+}	C/SO (+ PbF, in-situ)	CtAdSV	- accum. via compl.; electro-catalysis assisted el. redn. (nioxime / NO_2^- system)	1×10^{-9} - 5×10^{-7} M (4×10^{-10} M; 2 min)	model solns.	- s.e.: 0.1 M AmB+5×10^{-4M} nioxime + 0.25 M KNO_2; detn. of Co^{II} in presence of Ni + Zn at high excess	275
Co^{2+}	C/PO (ZEs: 3 types)	ASV	- accum. via ion-exchange + sorption / el. redn.; - anodic reoxidn.	-- (3 ppm; 15 min)	model solns.	- ZEs: zeolites; characterisation by XRF + particle size-analysis	425
Ni^{2+}	C/PO (Dowex 50W)	AdSV	- oc. accum by ion-pairing - redn. + reoxidn.	1-6000 μg L^{-1} (5 ng L^{-1}; 12 min)	tap, mineral waters	- s.e.: 0.005 M HCl (pH 3) - interfs. from Hg^{II} and Ag^{I}	426
Ni^{2+}	C/SO + MF (DMG, in situ)	DPCSV, CCSA	- ads. accum. by chelating - redn. (cathodic or I_{CONST})	(5×10^{-7} M; 60s)	crude oil (digested)	- coupled with MWD and buffering samples with NH_3 (to pH 9) and spiked with Ni^{2+} ions	244
Ni^{2+}	C/PO (DMG)	DPCSV, AD / HA	- accum. via chelating + adsoption; cathodic redn.	5×10^{-9} - 5×10^{-7} M (3×10^{-9} M; 25 min)	fuel ethanol samples	- DMG: dimethyl glyoxime; detn. compared with GF-AAS	427
Ni^{2+}	C/PW(s) / AMTS (+ DMG, in-situ)	DPCSV	- accum. via adsoption (as Ni^{II}-AMT) / MEx + DMG; deposition / cathodic redn.	8×10^{-9} - 1×10^{-6} M (2×10^{-9} M; 20 min)	fuel ethanol samples	- solid-like CPE (sTable 1n EtOH-solns.); AMTS: aminothiazole der. silica; intermediate transfer	105
Pt^{IV}, Ir^{III}, Os^{IV}	C/SO (CTAB, Septonex; applied in-situ)	DPCSV, POT (titr.)	- accum. via ion-pairing as $CTA(Sept)^+$; $MeCl_6^{3(4)-}$ / extraction; cathodic redn.	$1\text{-}10\times10^{-6}$ for Pt,Ir; $1\text{-}50\times10^{-8}$ for Os; (5×10^{-9} M Os; 60s)	waste water (spiked)	- Septonex: 1-(ethoxycarbonyl)-penta-decyltrimethyl-ammonium bromide; s.e.: 0.1 M HCl	302, 428, 429

Continued **Table 3.** Determination of the remaining metals at carbon paste electrodes and sensors: Survey of methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
Ru^{III}, Rh^{III}, Pd^{II}	C/SO (CPyB; in-situ)	DPCSV	- accum. via ion-pairing as CPy^+; $MeCl_6^{3(4)-}$ / sorpt.; - cathodic redn.	5-10×10^{-7} M Ru,Rh 1×10^{-6} M M Pd; (--; 1 min)	model solns.	- CPyB: cetylpyridinium bromide; initial study on detn. of $Me^{III(II)}$	428
Al^{3+}	C/PW (s) (α-CD clp + ARS)	POT (dir.)	- accum. via inclusion and compl.; chem. equilibrium	1×10^{-4} - 0.1 M (8×10^{-5} M; --)	pharms.	- modif.: α-cyclodextrin cross-linked polymer mixed with Alizarin Red S	107
Ga^{3+}	C/PO (ALC / ARS)	2nd DLSV	- accum. via adsorption / complex.; cathodic redn. of the ligand (in modif.)	5-20×10^{-10}- 1-8×10^{-7} M (3×10^{-10} M, 4 min)	food samples	- modif.: Alizarine Complexon; high scan-rate (200 mV/s); s.e.: AcB + phthalate (pH 4.5); no Al^{III}-interfs.	445, 446
Sc^{3+}	C/PO (ARS, in situ)	2nd DLSV	- adsort. accum. as compl. - cathodic redn. of ligand	1×10^{-9} - 4×10^{-7} M (6×10^{-10} M; 3 min)	minerals, CRM (ore sp.)	- ARS: Alizarin Red 'S'; s.e.: mixed acetate / phthalate buffer (pH 4-6)	447, 448
Th^{4+}	C/PO (ALC, in situ)	AdSV	- accum. via adsorption / compl. of Th^{IV}O-ALC; - cathodic redn.of ligand	3×10^{-9} - 8×10^{-7} M (5×10^{-10} M; 3 min)	clays, CRMs (ore sps.)	- ALC: Alizarin complexon reagent incl. interfs studies (10 Me-ions)	449, 450
U^{VI} (UO_2^{2+})	C/PW (s) (CPHA-MS)	AdSV (SWV)	- accum. via adsorption of the complex UO_2^{2+}-CPH; - cathodic redn.: $U^{VI} \rightarrow U^{IV}$	5-50 ppb (1 ppb; 20 min)	model solns.	- CPHA-MS: carbamoyl-phosphonic acid in self-assembled mesoporous silica; no interfs. from Me-anions	106
Eu^{3+}	C/PO (montmorillonite)	SWCSV	- accum. via adsorption to modif.; cathodic redn.:	1×10^{-7} - 2×10^{-5} M (4×10^{-8} M; --)	stream sediments	- modif.: natural zeolite; high selectivity over other rare-earth ions	451
$Me_{(l)}^{3+}$, $Me_{(h)}^{3+}$ *)	C/PO (ALC, in situ)	AdSV	- adsort. accum. by compl. - anodic reoxidn.	ca. 1×10^{-7} M $Me_{(l)}$ ca. 5×10^{-8} M $Me_{(h)}$	CRM (nodular cast iron)	- ALC: Alizarin Complexon (soln.) - rare earths quantified as a sum of both $Me_{(l)}$ and $Me_{(h)}$; individual ions not identified; AcB / phthalate	452
*) $Me_{(l)}$ ..... Y, Sc, Sm, Eu, Gd, Tb (light rare earths); $Me_{(h)}$ ... Dy, Ho, Er, Tm, Yb, Lu (heavy rare earths).							
Mg^{2+}	C/PO (+ MeF) (TP; in-situ)	AdSV (SWV)	- accum. via adsoprtion of the $Mg(OH)_2$–TP adduct; cathodic redn. of ligand	6×10^{-9} - 9×10^{-8} M (5×10^{-9} M; 1 min)	tap water, human urine	- TP: thiopenton; s.e.: PhB (pH 11); no interfs. of Al, Ca, Fe, Zn, Pb; indirect detn. (compared to AAS)	453
Ca^{2+}	C/PO (ARS, in situ)	2nd DLSV	- accum. via adsorption of Ca^{II}-ARS; redn. of ligand	3×10^{-8} - 2×10^{-6} M (9×10^{-9} M; 1.5 min)	tap water; milk, human serum	- ARS: Alizarin Red 'S'; s.e.: 0.02 M KOH; regeneration in 0.2 M HCl	454
Li^+	C/PO [λ-MnO_2 (spinel)]	CV, DPV, POT (dir.), FIA	- accum: redn. $Mn^{IV} \rightarrow Mn^{III}$ followed by intercalation (insertion) of Li^+ into the spinel structure; re-oxidn.	3×10^{-6}- 0.002 M (SV) 8×10^{-5} - 0.01 M (POT) (6×10^{-7} M; 30 / 5 s)	natural waters, pharms (tabs.)	- modif.: 25% λ-MnO_2 (m/m) in CP; - s.e.: borate buffer / Tris (pH 7-10) - no interfences by Me^+ / Me^{2+} ions; POT: Nerstian slope, 79 mV/dec.	303, 455-457
Na^+	C/PW (s) (natural zeolite)	AD, FIA	- accum. via ion-exchange equivalent to Na^+-conc.	1-50 ppm Na^+	model solns.	- modif. dispersed in electrode bulk; - indirect detn. (via another analyte)	226

For other abbreviations and symbols, see the respective list at the end of the article

Table 4. Determination of non-metal ions, complexes, and molecules at carbon paste electrodes and sensors. Survey of Methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
Cl^-, Br^-	C/PO (Fec-CXP)	SWV	- functioning via modif. as redox receptor; binding X^- anion and its oxidn.	10-100 μM Cl^-	model solns.	- Fec-CXP: Ferrocene functionalised calix[4]pyrrole; interfs. by fluoride (as the single F^- ion)	458
Br^-	C/PO (Hg^{II}-Py / PTC)	POT (titr.)	- PTC as carrier for Br^- ion; - chem. equilibria between $H^+ \leftrightarrow$ PTC-HBr	1×10^{-5} - 0.03 M (4×10^{-6} M; --)	tap water	- Py: pyridine, PTC: proton-transfer compound (not specified); opt. pH 4.0-8.3; Nerstian slope: 61 mV/pH	308

Continued **Table 4.** Determination of non-metal ions, complexes, and molecules at carbon paste electrodes and sensors. Survey of Methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
I^-, I_n^- (n = 3, 5)	C/TCP (binder as modif.)	DPCSV	- accum. via ion-pairing / extr. (after el. oxidn. $I^- \rightarrow I_2$) - cathodic redn. ($I_2 \rightarrow I^-$)	5×10^{-7} - 5×10^{-5} M (3×10^{-7} M; 5 min)	KI-ctng. tablets	- KI-tbs: distributed to people that live nearby nuclear power-plants; - incl. study on interfs. from $S_2O_3^{2-}$	100
I^-, (IO_3^-)	C/TCP (binder as modif.)	SP (CCSA)	- accum. via ion-pairing / extr. (after electrode oxidn.); redn. by I_{CONST}	3×10^{-7} - 5×10^{-5} M (1×10^{-7} M; 5 min)	mineral water, table salts	- s.e.: 0.5 M NaCl + 0.1 M HCl - IO_3^- chem. pre-red. with $N_2H_5^+$ - high selectivity ($Cl^- : I^- = 10^{5.1}$)	101
I^-	C/PO (LDH)	DPASV	- accum. via ion-pairing / MEx; anodic oxidn.	50 μM - 1 mM (0.05 μM; --)	ground, sea waters	- LDH: layer double hydroxide; - s.e.: chloride-based medium	459
I^-	C/PO (CTAB, in situ)	LSSV	- accum. via ion-pairing; - oxidn and extraction; cathodic redn.	8×10^{-9} - 5×10^{-6} M (2×10^{-9} M; 3 min)	table salts	- CTAB: cetyltrimethylammonium bromide; s.e.: 0.1 M NaCl ; - incl. interf. studies of X^- and Y^-	460
I^-, $Q^+I_3^-$	C/PO (CTAI)	POT (dir.)	- ion-pairing of membr. type, - chemical equilibrium for: I^- / I_3^- ↔ {CTA^+; I^-/ I_3^- }	5×10^{-5} - 0.1 M (4×10^{-5} M, 30 s)	pharms. (relaxant)	- Q^+: org. cation (ion-pair moiety) - CTAI: cetyltrimethyl ammonium iodide; Nerstian s.: −55 mV/dec.	305
I^-	D/PO (DPEs, 3 types)	DPASV	- accum. via electrolytic redn; anodic reoxidn	(1×10^{-7} M; --)	vitamins, table salts	- D: natural or synthetic diamond, DPE: diamond paste electrode; no intefs. by Cl^- and Br^- ions	55
I^-	CP-composite ($\tilde{\mu}$Ag / n-Ag)	CV, HV AD / IC	- interaction Ag and I^-; redox behaviour of I^- / I_2 - el. oxidn. at E_{CONST}	0.64-64 μg L^{-1} (0.47 μg L^{-1} = 4 nM)	milk powder, CRM	- μAg / nAg: micro- / nano-silver powder; org. iodide-compounds also studied; μ−volume: 20 μL	109
IO_3^-	C/PO (SGAm+PW_{12})	CV, AD, FIA	- electrocatalytic redn. with renewable modif.	5×10^{-6}– 0.001 M (3×10^{-6} M; --)	model solns. (in stream)	- SGAm-PW_{12}: phospho-wolframo- functionalised silicagel derivatised with amino-group (3-D modif.)	461
ClO_3^-, BrO_3^-	C/PO (MMS+PMo_{12})	CV, DPV	- elchem. activity of modif. + catalytic effect	(1 μM XO_3^-)	model solns.	- PMo_{12}: $H_3[P(Mo_3O_{10})_4 \bullet nH_2O$ - MMS: mesoporous molecular sieve	236
CN^-, I^-	C/PO (+ membr.) (AgI / Ag_2S mixt.)	POT (dir.)	- ion-pairing (at membrane); - chemical equilibrium for: X^- ↔ AgX^-; eq. potential	pX = 2.6-4.7 CN^-, pX = 2.0-6.5 I^- (t_R = ca 30 s)	model solns.	- Nernstian slopes: 69 (for CN^-) & 58 mV/dec (I^-); indication of CN^- requires regeneration of CP	306
CN^-	C/PO (Co^{II}-TPPA)	POT (dir.)	- chemical equilibrium for: CN^- ↔ CoTTPA-CN adduct	2×10^{-5} - 0.01 M (9×10^{-6} M; 5 s)	mineral water	- TPPA: 3,4-tetra pyridino-porphira- zinate; no interfs of Cl^-,Br, I^-, and SCN^-; Nernstian s.: 60 mV / dec.	307
S^{2-}	C/PO (FePC)	CV, POT (dir.)	- catalytic effect + oxidn. - equilibrium potential	1×10^{-6} - 0.005 M (--)	model solns.	- FePC: Fe^{II}-phthalocyanine; detn. of S^{-II}-org. compds. also studied	327
$S_2O_8^{2-}$	C/PO ($Ru^{II}(phen)_3$ Cl_2)	ECL-D	- ECL-effect by strongly oxidative intermediate	1×10^{-5} - 0.001 M (--)	model solns.	- phen: phenanthroline; s.e.: pH 4-6	462
SO_4^{2-}	C/PO (Cr^{III}-SBC)	POT (dir.,titr.)	- chemical equilibrium for: SO_4^{2-} ↔ Cr-SB-SO_4 adduct;	2×10^{-6} - 0.05 M (9×10^{-7} M; 10 s)	mineral water	- SBC: Schiff base complex (N,N'-ethylene-bis(5-hydroxy-salicylidene-iminate; pH 4-9	309
SO_3^{2-}	C/PO (BFEFM)	CV, CA DPV	- electrocatalysis-assisted oxidn. of SO_3^{2-} anion	4×10^{-6} - 0.01 M (2×10^{-7} M, DPV)	real sample	- BFEFM: bis (ferrocenyl-ethyl)-fluorenone; kinetic parameters evaluated; opt. pH 8.0	463
SO_3^{2-}	C/PO (Fec-EPhE)	CV, DPV	- electrocatalysis-assisted oxidn. of SO_3^{2-} anion	4×10^{-6} - 1×10^{-4} M (2×10^{-7} M, DPV)	model solns.	- Fec-EPhE: 1-[4-(ferrocenyl-ethy-nyl) phenyl]-ethanone; kinetic parameters evaluated; pH 8.0	464
SO_3^{2-}	C/PW (s) [Ni^{II}-Fe(aq) $(CN)_5$]	CV, CA LSV, FIA	- electrocatalysis-assisted oxidn. of SO_3^{2-} anion	3×10^{-6} - 0.003 M (9×10^{-7} M, LSV)	real samples	- modif. characterised by XRD,UV s.e.: PhB (pH 8-10); long t_L	465

Continued **Table 4.** Determination of non-metal ions, complexes, and molecules at carbon paste electrodes and sensors. Survey of Methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
HPO_4^{2-}	C/PO (μE-conf.) $[P(Mo_3O_{10})_4]^{3-}$	CV, BIA, FIA	- precipitation via complex; indirect detn. via its redn.	1-20 μM (0.3 μM; --)	sea water, bacterial bio-films	- intefs. from SiO_4^{4-} suppressed by HNO_3 + MoO_4^{2-}; bio-films collected in Roman catacombs	466
HPO_4^{2-}	C/PO + BE $P(Mo_3O_{10})_4$ / BUR	CV, ECL-D	- ECL-signal (BUR oxidn); - indirect detn. of HPO_4^{2-}	2×10^{-10} - 1×10^{-8} M (8×10^{-11} M ; ECL)	water samples	- BE: benzene; BUR: Butyl-Rhodamine 'B'; ECL: electrochemiluminescence; opt. s.e.: pH >10	467
H_2O_2	C/PO (Rh-Blue)	CV, AD, FIA	- electrocatalytic effect - amperometric oxidn.	5×10^{-5} - 9×10^{-4} M (3×10^{-5} μM--)	model solns.	- Rh-Blue: $Rh^{III}_4[Ru^{II}(CN)_6]_3$ - modif. deposited electrolytically	468
H_2O_2	C/PO (Ni-calix[4] arene)	CV, DPV	- electrocatalytic effect - anodic oxidn.	2×10^{-6} - 1×10^{-4} M (1×10^{-6} M; --)	rain water	- L: 5,11,17,23-tetra-tert-butyl-25, 2,7-bis(diethylcarbamoylmethoxy); 0.05 M $NaClO_4$ + 0.001 M NaOH	469
H_2O_2	C/PO (n-CM / Mn-ox.)	CV, AD	- electrocatalysis-assisted oxidn. of H_2O_2 (E_{CONST})	1×10^{-5} - 7×10^{-4} M (2×10^{-6} M; 10 s)	model solns.	- n-CM / Mn-oxides: nanostructured manganese(II,IV) oxides of Crypto- melane type, 5 % (m/m) in CPE	470
O_2	C/PO (MPP-si-Sb_2O_3)	CA, LSV	- electrocatalytic reduction of O_2 via modif. effect	1-13 mg L^{-1} (< 1 mg L^{-1})	water solns (with dissolved O_2)	- MPP: tetrakis(1-methyl-4-pyridyl) 21H,23H-porphine immobilised by sol-gel method; 4-el. oxidn.	471
O_2	C/PO (CTAB; in-situ)	CV, LSV	- electrocatalytic reduction of O_2 via effect of modif. (charged as $CTAB^+$)	1-10 mM	water solns.	- CTAB: cetyltrimethylammonium bromide; modif. attached using hydrophobic adsorption	472
O_2	C/PO (SiO_2 / Nb_2O_5)	CV, CA, LSV	- electrocatalytic reduction of O_2 via effect of modif.	1-14 mg L^{-1} (< 1 mg L^{-1}; 5 s)	model solns.	- immobilised by sol-gel method; 2-el. process; s.e.: 1 M KCl	473
NO_2^-	C/PO (Ru^{II}-BPD)	CV, FIA	- electrocatalytic effect - cathodic redn.	(1×10^{-5} M; --)	model solns.	- modif.: $[Ru(bipy)_2dppz]^{2+}$ polymer - s.e.: HCl-based medium	474
NO_2^-	C/PO (Mb+colloid-Au)	CV	- electrocatalytic effect - cathodic redn.	10-110 μM	model solns.	- Mb: myoglobin - s.e.: 0.1 m BR-buffer (pH 7)	475
NO_2^-	C/PO (+ membr.)	LSV	- electrolytic oxidn. within the LSV-scan	14 ppb (3 ppm)	cured meat (preserved by NO_2^-)	- cellulose-acetate membrane; stabilisation soln.: AA + m-PhA + EDTA; compared with UV-VIS	476
NO_2^-	C/PO (MPP-si-SnO_2)	CA, LSV (with RDE)	- electrocatalytic reduction of O_2 via modif. effect	(50 μM; --)	model solns.	- MPP: tetrakis(1-methyl-4-pyridyl) 21H, 23H-porphine ion; studies on mechanism and rc. kinetics	477
NO_2^-	C/PO (DAN)	DPV, FIA	- formation of triazole der. and its electrolytic oxidn.	(0.2 mM; --)	real samples	- DAN: 2,3-diammino-naphthalene; in FIA-mode: up to 150 detns./ h.	478
NO_2^-	C/PO $Fe(CN)_6^{3-}$; in-situ	CV, CA	- electrocatalytic reduction of NO_2^- via modif. effect.	5×10^{-5}–0.001 M (3×10^{-5} M, --)	model solns.	- overpotential lowered for 700 mV; reaction at higher pH; mechanism, kinetic, and activity coeffs. ($y_\pm$)	479
NO_2^-	C/PO (poly-o-TO)	CV, CA	- electrocatalytic reduction of NO_2^- via modif. effect.	5×10^{-4}–0.02 M (3×10^{-4} M, --)	real samples	- poly-o-TO: poly(ortho-toluidine); redn requires highly acidic solns	480
NO_2^-	C/PO (PW-12)	CV, CA	- electrocatalytic redn. of NO_2^- by modif. (mediator)	3×10^{-5}–0.001 M (3×10^{-5} M, 2 s)	water samples	- PW-12: $H_3[P(Mo_3O_{10})_4]$; H_2SO_4; electrocatalysis evaluated via reaction kinetics	481
NO_2^-	C/PO ($V^{IV}O$-SBC)	CV, LSV	- electrocatalytic reduction of NO_2^- via modif. effect.	4×10^{-6}–0.004 M (6×10^{-7} M, --)	model solns.	- SBC: Schiff base complex; mechanism, diffusivity, kinetics and electrocatalysis studied.	482
NO_x	C/PO (Ni-DFTAA)	CV, FIA	- electrocatalytic oxidn. / redn. via modif. effect	(down to 1 μM)	aqueous solns.	- modif.: 6,17-diferrocenyldibenzo- 5,9,14,18-tetraaza[14]annulen-Ni^{II}	483

Continued **Table 4.** Determination of non-metal ions, complexes, and molecules at carbon paste electrodes and sensors. Survey of Methods

Ion, sp. (form)	Type of CPE (modifier)	Technique (mode)	Measuring principles (method sequences)	Linearity range (LOD; t_{ACC} / t_R)	Sample(s) analysed	Other specification (remarks)	Refs.
NH_4^+	C/PO (NH_4HPO_4 + si-SnO_2)	POT (dir.,titr.)	- chemical equilibrium for: NH_4^+(soln.) ↔ NH_4^+(E-bulk)	8×10^{-7}–0.04 M (2×10^{-7} M, 60 s)	natural waters	- modif.: prepared by the sol.-gel method; k^{POT}_i coeffs evaluated; sub-Nerstian response for ISE	304
NH_2OH, N_2H_4	C/PO (coumestan)	CV, BA DPV	- electrocatalytic oxidation of $N^{-II/-I}$ via modif. effect	0.2-15 mM NH_2OH (--)	model solns.	- mechanism, reaction kinetics + catalytic activity being studied	484
N_2H_4	C/PO (Nb^V-si+H_2TCPP)	CV, FIA	- electrocatytic effect - anodic oxidn.	1×10^{-5} - 5×10^{-4} M	aqueous solns. (pH 7)	- modif.: meso-tetracarboxyphenyl- porphyrin + grafted silica / Nb_2O_5	485
N_2H_4	C/PO (+ SX-pol.) (Fe-tSPhP / SiAl)	CV, CA	- electrocatalytic oxidation of N_2H_4 via modif. effect	5×10^{-5} - 6×10^{-4} M (3×10^{-5} M, --)	model solns.	- tSPhP: tetrakis-(2,6-difluoro-3-sulfo-natophenyl)porphyrinate on SiO_2/Al_2O_3 / siloxan polymer	486
N_2H_4	C/PO (Co^{II}-Pc)	CV, AD / CZE	- electrocatalytic oxidation of N_2H_4 via modif. effect	20-200 μM N_2H_4 (10 μM i n PhB)	model solns, water samples	- Pc: Phthalocyanine; method for "on-chip" separation and usable for org. R– / Ar–hydrazines	487
N_2H_4	C/PO (Cu^{II}/Co^{II}-HCF)	CV, CA, CCP	- electrocatalytic oxidation of N_2H_4 via modif. effect	0.1-12 mM N_2H_4 (--)	model solns.	HCF: hexacyanoferrate; s.e.: PhB (pH 7); mechanism, react. kinetics and diffusion processes studied	488
N_2H_4	C/PO (Q / HQ)	CV, CA, DPV	- electrocatalytic oxidation of N_2H_4 via modif. effect	7×10^{-6} - 8×10^{-4} M (5×10^{-6} M, for DPV)	waste waters	- s.e.: buffer (pH 10); overpotential lowered for >500 mV; water was sampled at wood-&-paper factory	489
N_2H_4	C/PO (Co^{II}-Pc)	CV, LSV	- electrocatalytic oxidation of N_2H_4 via modif. effect	1×10^{-4} - 1×10^{-5} M (7×10^{-5} M, --)	industrial boiler feed water	- Pc: Phthalocyanine; redn. in highly alkaline solns. (pH 13); no interfs. from common ions	490

For other abbreviations and symbols, see the respective list at the end of the article

the fact that carbon paste still represents one of the most popular electrode materials with almost unlimited applicability in basic research, highly specialised investigations, as well as in practically oriented electroanalysis as documented in Tables 1-4. Secondly, the recent turbulences in the area of CPEs, CMCPEs, CP-biosensors, and CP- detectors have shown that carbon paste is also one of the most flexible substrates. This can be illustrated by the fact that the respective activities with carbon pastes have already absorbed innumerable outputs coming from progressive and new technologies. Starting with developments of novel types of electrodes, including various innovations of these configurations, continuing *via* a massive testing of new modifiers and mediators, up to the introduction of completely new carbon paste mixtures, in which both graphite and binder moieties are replaced by alternate materials.

Finally, a deeper analysis of the recent databases, together with older archives, allows us to speculate on some up-coming trends and future prospects, when the following directions and trends can be outlined:

(**i**) Development of new methods and procedures that obey criteria of the green-chemistry concept; especially, in the area of environmental inorganic analysis with metal-modified electrodes that would alternate or – more likely replace – the mercury-based analogues.

(**ii**) Further adaptations of the already existing methods in terms of improved performance, combination with other techniques, compatibility with analysers of new generation, or even acceptability given by actual economic and ecologic demands. In this respect, a majority of carbon pastes have great promise as a cheap, easy-to-prepare, and – in the native form – also almost non-toxic material.

(**iii**) Regarding future trends in practical analysis with CPEs, one can get a rough estimate by comparing the abundance of the individual methods for particular analytes or groups of analytes. For inorganic ion and molecules, this is feasible by means of Tables I-IV presented above, whereas for organic, pharmaceutical and biological compounds that have not been surveyed here, it can be seen in the actual reviews [40,41] or,

eventually, *via* some original papers reporting on analyses of typical substances of interest (see *e.g.* [491-500]).

(**iv**) A growing role of carbon pastes as a laboratory platform during the development, testing, and later mass production of new types of screen-printed electrodes, sensors, and integrated cells based on carbonaceous materials.

(**v**) More intensive efforts in the use of new carbon paste-like formulations *versus* the traditional carbon paste mixtures, when one or even both main components will be substituted by alternate substances. This approach is already feasible at present, as shown with some mixtures containing new forms of carbon and / or ionic liquids.

And it is possible that such a mixture of so-far unknown type would be someday applicable as a fluid to the dropping carbon electrode (DCE) – a non-mercury variant of the DME and hitherto unrealised Adams' vision which had once led to the discovery of the carbon pastes themselves [2-5].

Acknowledgements:

Financial grants from the Ministry of Education, Youth, and Sports of the Czech Republic (project ***MSM0021627502*** *and Research Centrum,* ***LC 06035****) are gratefully acknowledged.*

This article has been compiled on the occasion of the 50th Anniversary of Awarding the Nobel Prize for Chemistry to Professor Jaroslav Heyrovský.

Abbreviation & symbols used

A) a: stoichiometric coefficient; AAS: atomic absorption spectrometry; acc(um).: accumulation (pre-concentration); AcB: acetate buffer; AD: amperometric (potentiostatic) detection; AdSV: adsorptive stripping voltammetry; AFM: atomic force microscopy; am.: amorphous; AmAc: ammonium acetate; AmB: ammonia buffer; (aq): aqua (H_2O); ASV: anodic stripping voltammetry; AuF: gold film; AuF-CPE: gold film-plated carbon paste electrode.

B) b: stoichiometric coefficient; BIA: batch injection analysis; Bi-CPE: bismuth powder- modified carbon paste electrode; Bi_2O_3-CPE: bismuth oxide-modified carbon paste electrode; BiF: bismuth film; BiF-CPE: bismuth film-plated carbon paste electrode; Bi-PE: bismuth paste electrode; BRB: *Britton-Robinson* buffer.

C) C: carbon (graphite); CA: chronoamperometry; CCP: classical (stripping) chrono-potentiometry; CCSA: constant current stripping analysis; CD: cyclodextrine; chem.: chemical; CILE(s): carbon ionic-liquid electrode(s); CMCPE(s), chemically modified carbon paste electrode(s); coeff.: coefficient; compl.: complexation, complexed; conc.: cencentration, concentrated; CNTs: carbon nanotubes; CN(T)PE(s): carbon nanotube paste electrode(s); CP: carbon paste; CPE(s): carbon paste electrode(s); CPEE: carbon paste electroactive electrode; CP-ISE(s): carbon paste ion-selective electrode(s); C/PO: carbon paste, paraffin oil-based mixture; CP-UMEs: carbon paste ultramicro-electrodes; C/SO: carbon paste, silicone oil-based mixture; CRM(s): certified reference material(s); CtAdSV: (electro)catalysis-assisted adsorptive stripping voltammetry; CTAB: cetyl-trimethyl-ammonium bromide; ctng.: containing; CV: cyclic voltammetry; COU: coulometry; CZE: capillary zone electrophoresis.

D) D: diamond; DCE, dropping carbon electrode; dec.: decade; der.: derivative; detn.: determination, determined; dir.: direct; 2nd-DLSV: second order-differential linear-scan voltammetry; DME, dropping mercury electrode; DNA, deoxyribonucleic acid; DPE: diamond paste electrode; DPV: differential pulse voltammetry; DPA(C)SV: differential pulse anodic(cathodic) stripping voltammetry.

E) E_{CONST} : constant potential (potentiostatic mode); ECL-D: electrochemiluminescence (signal) detection; EDTA: ethylene-diamminotetraacetic acid; EIS: electrochemical impedance spectroscopy; EH-CPE: electrically heated carbon paste electrode; el./elec.: electron / electrolysis, electrolytic; eq.: equilibrium; ESA: electrochemical stripping analysis; EtOH: ethanol.

F) Fc: ferrocene; FIA: flow injection analysis; Fig(s): figure(s); FT-IR: Fourier transform infrared (spectroscopy).

G) g: gram; GF: graphite furnace; GrE: groove electrode.

H) Hb: hemoglobin; HA(V): hydrodynamic amperometry (voltammetry); HPLC: high performance liquid chromatography.

I a **J**) i: stoichiometric coefficient; I_{CONST}: constant current; IL(s): ionic liquid(s); interfs.: interferences (interference effects); incl.: including; IC: ion-chromatography; IR: infrared (spectroscopy); ISE: ion-selective electrode; j: stoichiometric coefficient.

K) k^{POT}_{i} : (potentiometric) selectivity coefficient.

L) L: liter; L: ligand; LSV: linear scan (sweep) voltammetry.; LOD: limit of detection; LOQ: limit of quantification (determination).

M) m: milli; M: molar concentration [mol L^{-1}]; *m*-: meta; MCM-41: (commercial) molecular sieve; mE: mini-electrode; MF: mercury film; MeF: metallic film; memb.:

membrane; MeOH: methanol; MEx: medium exchange; MI-CPE: magnet-incorporated carbon paste electrode; min.: minute; mixt.: mixture; m/m: mass ratio; modif.: modifier, modified; ms.: mesoporous; MWD: microwave-assisted digestion (decomposition).

N) n: counting coefficient; n-: nano; NAD(H): nicotinamide dinucleotide; NMR: nuclear magnetic resonance.

O) *o*- ortho; o.c.: open-circuit; opt.: optimum, optimal; org.: organic; ox: oxide; oxidn.: oxidation.

P) *p*-: para; PbF: lead film; PbF-CPE: lead film-plated carbon paste electrode; Pc: phthalocyanine; PhB: phosphate buffer; pharm(s): pharmaceutical(s); ph / Ph: phenol, phenyl; pH: acidity /alkality unit; pharm(s): pharmaceutical formulation(s); phen: phenanthroline; PO: paraffin oil (binder); POT: potentiometry; ppm: part-per-million (concentration unit); ppb: part-per-billion (conc. unit); PSA: potentiometric stripping analysis (with chemical oxidation); PW: paraffin wax; pX: −log [X]; py / Py: pyridine.

Q) Q / HQ: quinone / hydroquinone; QPu: quadra-pure.

R) R: (electric) ohmic resistance; RDE: rotated disc electrode; red.: reduced; redn.: reduction; regnt.: regeneration, regenerated; reoxidn.: reoxidation; RSD: relative standard deviation [%]; RTIL(s): room-temperature ionic liquid(s).

S) s: second; (s): solid state; Sb-CPE: antimony powder-modified carbon paste electrode; Sb_2O_3-CPE: antimony oxide-modified carbon paste electrode; SbF: antimony film; SbF-CPE: antimony film-plated carbon paste electrode; s-CPE: solid-like carbon paste electrode; sep.: separation / separated; s.e.: supporting electrolyte; s.s.: sample solution; *sp*.: species; sp(s): specimen(s); SEC: spectroelectro-chemistry; SECM: scanning electrochemical mictroscopy; SEM: scanning electron mictroscopy; simult.: simultaneous; SO: silicone oil; SX: siloxane; SP: stripping potentiometry; SPE(s): screen-printed electrode(s); soln(s): solution(s); sorpt.: (ad)sorption; stac.: stacionary; STM: scanning tunneling microscopy; SV: stripping voltammetry; SWV: square-wave voltammetry; SWA(C)SV: square-wave anodic(cathodic) stripping voltammetry.

T) t_{ACC} : accumulation time (period); tab.: table; tb(s): tablet(s); TCP: tricresyl phoshate; t_L: life-time; $t_{R/EQ}$: response / equilibrium time; TCP: tricresyl phosphate; TG: thermogravimetry; titr.: titration, titrated; TRIS: buffer (commercial formulation); t_{EQ}: equlibrium time.

U) unm.: unmodified (bare, pure); UV/VIS: ultraviolet / visible spectrometry.

V) V: volt (electrical unit); var.: various; v/v: volume ratio.

W) W: wax.

X) XPS: X-ray (roentgen) probe spectroscopy; XRF: X-ray fluorescence.

Y) y± : activity coefficient.

Z) ZE: zeolite.

• *Other symbols*: -- ... not specified, not found; 3-D: three dimensional; *β*: stability (complexity) constant; μ: micro; $^{I,II\ ...\ N}$: valence (oxidation state); $^{n,m+/-}$: ion charge.

References

Thanks to willingness of the Editorial board of the CEJC, the authors were allowed to prepare their list of references in atypical form – as the full-text versions, presenting also the respective title for each article. It is believed that such exceptional approach, offering a lot of additional information, will be appreciated mainly by the readers themselves.

List of Full-Text Citations

[1] P. Zuman, Electrolysis with a dropping mercury electrode: J. Heyrovský's contribution to electrochemistry. Critical Reviews in Analytical Chemistry, 31 (2001): 281-289.

[2] I. Švancara, K. Vytřas, K. Kalcher, A. Walcarius, and J. Wang, Carbon paste electrodes in facts, numbers, and notes: A review on the occasion of the 50-years jubilee of carbon paste in electrochemistry and electroanalysis. Electroanalysis, 21 (2009): 7-28.

[3] R. N. Adams, Carbon paste electrodes. Analytical Chemistry, 30 (1958): 1576-1576.

[4] R. N. Adams, Electrochemistry at Solid Electrodes (New York: M. Dekker, 1969).

[5] R. N. Adams, Carbon paste electrodes: A Review. Review of Polarography (Kyoto, Japan), 11 (1963): 71-78.

[6] M. Březina, Estimation of electrochemical activity of carbon using a paste electrode. Nature, 212 (1966): 283-283.

[7] J. Heyrovský, "Elektrolysa se rtuťovou kapkovou kathodou" (in English: Electrolysis with the mercury drop cathode). Chemické Listy XVI (1922): 258-264.

[8] C. Olson and R. N. Adams, Carbon paste electrodes. Application to anodic voltam-metry. Analytica Chimica Acta, 22 (1960): 582-589, plus C. Olson and R. N. Adams, Carbon paste

electrodes application to cathodic reductions and anodic stripping voltammetry. Analytica Chimica Acta, 29 (1963): 358-363.

[9] T. Kuwana and W. G. French, Carbon paste electrodes containing some electroactive compounds. Analytical Chemistry, 36 (1964): 241-242.

[10] L. S. Marcoux, K. G. Prater, B. G. Prater, and R. N. Adams, Nonaqueous carbon paste electrode. Analytical Chemistry, 37 (1965): 1446-1447.

[11] D.G. Davis and M.E. Everhart, Chronopotentiometry of the bromide-bromine couple at platinum and carbon paste electrodes. Analytical Chemistry, 36 (1965): 38-40.

[12] A. L. Beilby and B.R. Mather, Resistance effects of two types of carbon paste electrodes. Analytical Chemistry, 37 (1965): 766-768.

[13] C. A. H. Chambers and J. K. Lee, Studies of the extraction of organic molecules into the carbon-paste electrode. Journal of Electroanalytical Chemistry, 15 (1967): 309-314.

[14] Gy. Farsang, Voltammetric properties and analytical uses of carbon paste electrodes prepared with silicone oil. Acta Chimica Academiae Scientiarum Hungaricae, 45 (1965): 163-176.

[15] H. Monien, H. Specker, and K. Zinke, Application of various carbon electrodes for inverse voltammetric determination of silver. Fresenius Zeitschrift fuer Analytische Chemie, 225 (1967): 342-351.

[16] Š. Mesarić and E. M. F. Dahmen, Ion-selective carbon-paste electrodes for halides and silver(I) ions. Analytica Chimica Acta, 64 (1973): 431-438.

[17] D. Bauer and M. P. Gaillochet, Etude du comportement de la pate de carbone a compose electroactif incorpore. Electrochimica Acta, 19 (1974): 597-606.

[18] J. Lindquist, A Study of seven different carbon paste electrodes. Journal of Electroanalytical Chemistry, 52 (1974): 37-46.

[19] P. Söderhjelm, A Comparison of the analytical utility of three different potential ramp techniques in voltammetry, using a carbon-paste electrode. Journal of Electroanalytical Chemistry, 71 (1976): 109-115.

[20] R. N. Adams, Probing brain chemistry with electroanalytical techniques. Analytical Chemistry, 48 (1976): 1126A-1138A.

[21] T. Yao and S. Musha, Electrochemical enzymic determinations of ethanol and L-lactic acid with a carbon paste electrode modified chemically with nicotinamide adenine dinucleotide. Analytica Chimica Acta, 110 (1979): 203-209.

[22] K. Ravichandran and R. P. Baldwin, Chemically modified carbon paste electrodes. Journal of Electroanalytical Chemistry & Interfacial Electrochemistry, 126 (1981): 293-300.

[23] M. E. Rice Z. Galus, and R. N. Adams, Graphite paste electrodes: Effects of paste composition and surface states on electron-transfer rates. Journal of Electroanalytical Chemistry, 143 (1983): 89-102.

[24] F. N. Albahadily and H. A. Mottola, Improved response of carbon-paste electrodes for electrochemical detection in flow systems by pretreatment with surfactants. Analytical Chemistry, 59 (1987): 958-962.

[25] W. Matuszewski and M. Trojanovicz, Graphite paste-based enzymatic glucose electrode for flow-injection analysis. Analyst (UK), 113 (1988): 735-738.

[26] K. Kalcher, Chemically modified carbon paste electrodes in voltammetric analysis. Electroanalysis, 2 (1990): 419-433.

[27] I. Švancara, K. Vytřas, F. Renger, and M.R. Smyth, Application of carbon paste electrodes in electroanalysis. A Review. Sborník Vědeckých Prací, Vysoká Škola Chemicko-technologická; Pardubice, 56 (1992/93): 21-57.

[28] N. A. Ulakhovich, E. P Medyantseva, and G.K. Budnikov, Carbon-paste electrodes as chemical sensors in voltammetry. Journal of Analytical Chemistry, 48 (1993): 980-998.

[29] K. Kalcher, J. M. Kauffmann, J. Wang, I. Švancara, K. Vytřas, C. Neuhold, and Z. Yang, Sensors based on carbon paste in electrochemical analysis: A Review with particular emphasis on the period of 1990-1993. Electroanalysis, 7 (1995): 5-22.

[30] L. Gorton, Carbon paste electrodes modified with enzymes, tissues, and cells (A Review). Electroanalysis, 7 (1995): 23-45.

[31] K. Kalcher, X. H. Cai, G. Koelbl, I. Švancara, and K. Vytřas, New trends in voltam-metric analysis: modified carbon paste electrodes. Sborník Vědeckých Prací, Vysoká Škola Chemicko-technologická; Pardubice, 57 (1994): 5-27.

[32] K. Kalcher, K. Schachl, I. Švancara, K. Vytřas, and H. Alemu, Recent progress in the development of electrochemical carbon paste sensors. Scientific Papers of the University of Pardubice, Series A; 3 (1997): 57-85.

[33] Z.-Q. Zhang, H. Liu, and Z.-F. Li, New developments of carbon paste electrode

(Review). Fenxi Kexue Xuebao (Journal of Analytical Science), 14 (1998): 80-86 ; Chemical Abstracts, 125 (1998): 175403x.

[34] R. D. O'Neill, Sensor–tissue interactions in neurochemical analysis with carbon paste electrodes in vivo. Analyst (UK), 118 (1993): 433-438.

[35] C. D. Blaha, Evaluation of stearate-graphite paste electrodes for chronic measurement of extracellular dopamine concentrations in mammalian brain. Pharmacology, Biochemistry and Behavior, 55 (1996): 351-364.

[36] I. Švancara, J. Zima, and K. Schachl, The testing of carbon paste electrodes: an example on the characterization of a carbon paste electrode prepared from newly used graphite powder. Scientific Papers of the University of Pardubice, Series A; 4 (1998): 49-63.

[37] I. Švancara and K. Schachl, Testing of unmodified carbon paste electrodes. Chemické Listy, 93 (199): 490-499.

[38] I. Švancara and K. Vytřas, Physico-chemical processes in analytical electrochemistry with carbon paste electrodes. An overview. Chemija (Vilnius),11 (2000): 18-27.

[39] I. Švancara, K. Vytřas, J. Barek, and J. Zima, Carbon paste electrodes in modern electroanalysis. Critical Reviews in Analytical Chemistry, 31 (2001): 311-345.

[40] K. Kalcher, I. Švancara, R. Metelka, K. Vytřas, and A. Walcarius, Heterogeneous Electrochemical Carbon Sensors, in The Encyclopedia of Sensors, Vol. 4; eds. C. A. Grimes, E. C. Dickey, and M. V. Pishko (Stevenson Ranch: American Scientific Publishers, 2006), ch. 4, pp. 283-429.

[41] J. Zima, I. Švancara, J. Barek, and K. Vytřas, Recent Advances in Electroanalysis of Organic and Biological Compounds at Carbon Paste Electrodes. Critical Reviews in Analytical Chemistry, 39 (2009): 204-227.

[42] G. U. Flechsig, M. Kienbaum, and P. Gruendler, Ex situ atomic force microscopy of bismuth film deposition at carbon paste electrodes. Electrochemistry Communations, 7 (2005) 1091-1097.

[43] F. D. Munteanu, M. Mosbach, A. Schulte, W. Schuhmann, and L. Gorton, Fast-scan cyclic voltammetry and scanning electrochemical microscopy studies of the pH-dependent dissolution of 2-electron mediators immobilized on zirconium phosphate containing carbon pastes. Electroanalysis, 14 (2002): 1479-1487.

[44] T. Mikysek, A. Ion, I. Švancara, K. Vytřas, and F. G. Banica, Carbonaceous Materials for Single-Use Metal Ion Sensors. Quality Assesment by Electrochemical Impedance Spectrometry; in Sensing in Electroanalysis, eds. K. Vytřas and K. Kalcher (Pardubice: University of Pardubice, 2005), pp. 19-27.

[45] J.-M. Zen, A. S. Kumar and H.-W. Chen, Electrochemical behavior of stable cinder/prussian blue analogue and its mediated nitrite oxidation. Electroanalysis, 13 (2001): 1171-1178.

[46] T. Mikysek, I. Švancara, M. Bartoš, K. Kalcher, K. Vytřas, J. Ludvík: "New Approaches to the Characterization of Carbon Paste Electrodes Based on Ohmic Resistance and Qualitative Carbon Paste Indexes". Analytical Chemistry, 81 (2009): 6327-6333.

[47] J. Wang, Real-Time Electrochemical Monitoring: Toward Green Analytical Chemistry. Accounts of Chemical Research, 35 (2002): 811-816.

[48] J. Wang, Ü. A. Kirgöz, J.-W. Mo, J. Lu, A.N. Kawde, and A. Muck, Glassy carbon paste electrodes. Electrochem. Commun., 3 (2001): 203-208.

[49] S. Varma, C. K. Mitra, Low frequency impedance studies on covalently modified glassy carbon paste. Electroanalysis, 14 (2002): 1587-1596.

[50] J. Zima, J. Barek, and A. Muck, Monitoring of environmentally and biologically important substances at carbon paste electrodes. Revista de Chimie (Bucharest), 55 (2005): 657-662.

[51] G. Li, Z.-M. Ji, and K.-B. Wu, Square wave anodic stripping voltammetric determination of Pb2+ using acetylene black paste electrode based on the inducing adsorption ability of I(−). Analytica Chimica Acta, 577 (2006): 178-182.

[52] G. Li, C.-D. Wan, Z.-M. Ji, and K.-B. Wu, An electrochemical sensor for Cd2+ based on the inducing adsorption ability of I(−). Sensors & Actuators B, Chemical; 124 (2007): 1-5.

[53] A. J. G. Zarbin, (Nano)materials chemistry. Quimica Nova, 30 (2007): 1469-1479.

[54] R. I. Stefan and S. G. Bairu, Monocrystalline diamond paste-based electrodes and their applications for the determination of Fe(II) in vitamins. Analytical Chemistry., 75 (2003): 5394-5398.

[55] R. I. Stefan, S. G. Bairu, and J. F. van Staden, Diamond Paste Based Electrodes for determination of iodide in vitamins and table salt. Analytical Letters, 36 (2003): 1493-1500.

[56] R. I. Stefan, S. G. Bairu, and J. F. van Staden, Diamond paste-based electrodes for determination of Cr(III) in pharmaceutical compounds. Analytical and Bioanalytical Chemistry, 376 (2003): 844-847.

[57] R. I. Stefan and R. G. Bokretsion, Determination of creatine and creatinine using a diamond paste based electrode. Instrumentation Science Technology, 31 (2003): 183-188.

[58] R. I. Stefan and S. G. Bairu, Diamond paste based electrodes for the determination of chromium(VI) at trace levels. Instrumentation Science Technology, 31 (2003): 261-267.

[59] R. I. Stefan and R. G. Bokretsion, Diamond paste based immunosensor for the determination of azidothymidine. Journal of Immunoassay and Immunochemistry, 24 (2003): 319-324.

[60] R. I. Stefan and S. G. Bairu, Diamond paste based electrodes for the determination of Pb(II) at trace concentration levels. Talanta, 63 (2004): 605-608.

[61] R. I. Stefan, R. M. Nejem, J. F. van Staden, and H. Y. Aboul Enein, New ampero-metric biosensors based on diamond paste for the assay of L- and D-pipecolic acids in serum samples. Preparative Biochemistry and Biotechnology, 34 (2004): 135-143.

[62] A. Miranda Hernández, M. E. Rincón, and I. González, Characterization of carbon–fullerene–silicone oil composite paste electrodes. Carbon, 43 (2005): 1961-1967.

[63] S.V. Lokesh, B. S. Sherigara, A.T. Jayadev, H.M. Mahesh, and R.J. Mascarenhas, Electrochemical reactivity of C(60) modified carbon paste electrode by physical vapor deposition method. International Journal of Electrochemical Science, 3 (2008):578-587.

[64] S. B. Hočevar and B. Ogorevc, Preparation and characterization of carbon paste micro-electrode based on carbon nano-particles. Talanta, 74 (2007): 405-411.

[65] G. Shul, M. A. Murphy, G. D. Wilcox, F. Marken, M. Opallo, Effects of carbon nanofiber composites on electrode processes involving liquid vertical bar liquid ion transfer. Journal of Solid State Electrochemistry, 9 (2005): 874-881.

[66] G. A. Rivas, M. D. Rubianes, M. L. Pedano, N. F. Ferreyra, G. L. Luque, M. C. Rodriguez, and S. A. Miscoria, Carbon nanotubes paste electrodes: A New alternative for the development of electrochemical sensors. Electroanalysis, 19 (2007): 823-831.

[67] F. Ricci, A. Amine, D. Moscone, and G. Palleschi, Prussian blue modified carbon nanotube paste electrodes: A Comparative study and a biochemical application. Analytical Letters, 36 (2003): 1921-1938.

[68] R. Antiochia, I. Lavagnini, F. Magno, F. Valentini, and G. Palleschi, Single-wall carbon nanotube paste electrodes: A comparison with carbon paste, platinum and glassy carbon electrodes via cyclic voltammetric data. Electroanalysis, 16 (2004): 1451-1458.

[69] N. S. Lawrence, R. P. Deo, and J. Wang, Detection of homocysteine at carbon nanotube paste electrodes. Talanta, 63 (2004): 443-449.

[70] M. D. Rubianes and G. A. Rivas, Enzymatic biosensors based on carbon nanotubes paste electrodes. Electroanalysis, 17 (2005): 73-78.

[71] M. Chicharro, E. Bermejo, M. Moreno, A. Sanchez, A. Zapardiel, and G. A. Rivas, Adsorptive stripping voltammetric determination of amitrole at a multi-wall carbon nanotubes paste electrode. Electroanalysis, 17 (2005): 476-482.

[72] S.-Y. Ly, S.-K. Kim, T.-H. Kim, Y.-S. Jung, and S.-M. Lee, Measuring mercury ion concentration with a carbon nano tube paste electrode using the cyclic voltam-metry method. Journal of Applied Electrochemistry, 35 (2005): 567-571.

[73] R. Antiochia, I. Lavagnini, and F. Magno, Electrocatalytic oxidation of NADH at single-wall carbon-nanotube-paste electrodes: kinetic considerations for use of redox mediator in solution and dissolved in the paste. Anal. Bioanal. Chem., 381 (2005): 1355-1361.

[74] J.-B. He, X.-Q. Lin, and J. Pan, Multi-wall carbon nanotube paste electrode for adsorptive stripping determination of quercetin: A comparison with graphite paste electrode via voltammetry and chronopotentiometry. Electroanalysis, 17 (2005): 1681-1686.

[75] M. Chicharro, A. Sanchez, E. Bermejo, A. Zapardiel, M. D. Rubianes, and G. A. Rivas, Carbon nanotubes paste electrodes as new detectors for capillary electrophoresis. Analytica Chimica Acta, 543 (2005): 84-91.

[76] F. Kurusu, S. Koide, I. Karube, and M. Gotoh, Electrocatalytic activity of bamboo-structured carbon nanotubes paste electrode toward hydrogen peroxide. Analytical Letters, 39 (2006): 903-911.

[77] R. Antiochia and I. Lavagnini, Alcohol biosensor based on the immobilization of meldola mlue and alcohol dehydrogenase into a carbon nanotube paste electrode. Analytical Letters, 39 (2006): 1643-1655.

[78] X.-J. Tian, J.-F. Song, X.-J. Luan, Y.-Y. Wang, and Q. Z. Shi, Selective detection of dopamine in the presence of ascorbic acid by use of glassy-carbon electrodes modified with both polyaniline film and multi-walled carbon nanotubes with

incorporated β-cyclodextrin. Analytical and Bioanalytical Chemistry, 386 (2006): 2081-2094.

[79] X.-Q. Lin, J.-B. He, and Z. G. Zha, Simultaneous determination of quercetin and rutin at a multi-wall carbon-nanotube paste electrodes by reversing differential pulse voltammetry. Sensors & Actuators B, Chemical; 119 (2006): 608-614.

[80] G. L. Luque, N. F. Ferreyra, and G. A. Rivas, Glucose biosensor based on the use of a carbon nanotube paste electrode modified with metallic particles. Microchimica Acta, 152 (2006): 277-283.

[81] S.-Y. Ly, Detection of dopamine in the pharmacy with a carbon nanotube paste electrode using voltammetry. Bioelectrochemistry, 68 (2006): 227-231.

[82] R. T. Kachoosangi, G. G. Wildgoose, and R. G. Compton, Room temperature ionic liquid carbon nanotube paste electrodes: Overcoming large capacitive currents using rotating disk electrodes. Electroanalysis, 19 (2007): 1483-1489.

[83] L. Zheng and J. F. Song, Voltammetric behavior of urapidil and its determination at multi-wall carbon nanotube paste electrode. Talanta, 73 (2007): 943-947.

[84] J.-Y. Qu, X.-Q. Zou, B.-F. Liu, and S.-J. Dong, Assembly of polyoxometalates on carbon nanotubes paste electrode and its catalytic behaviors. Analytical Chimica Acta, 599 (2007): 51-57.

[85] S.-Y. Ly, Y.-S. Jung, S.-K. Kim, and H.-K. Lee, Trace analysis of lead and copper ions in fish tissue using paste electrodes. Analytical Letters, 40 (2007): 2683-2692.

[86] S. Shahrokhian and M. Amiri, Multi-walled carbon nanotube paste electrode for selective voltammetric detection of isoniazid. Microchimica Acta, 157 (2007): 149-158.

[87] R. Antiochia and L. Gorton, Development of a carbon nanotube paste electrode osmium polymer-mediated biosensor for determination of glucose in alcoholic beverages. Biosensors & Bioelectronics, 22 (2007): 2611-2617.

[88] J.-H. Chen, Z.-Y. Lin, and G.-N. Chen, An electrochemiluminescent sensor for glucose employing a modified carbon nanotube paste electrode. Analytical and Bioanalytical Chemistry, 388 (2007): 399-407.

[89] A. Abbaspour and R. Mirzajani, Electrochemical monitoring of piroxicam in different pharmaceutical forms with multi-walled carbon nanotubes paste electrode. Journal of Pharmaceutical and Biomedical Analysis, 44 (2007): 41-48.

[90] L.-B. Nie, H.-S. Gu, Q.-G. He, J.-R. Chen, and Y.-Q. Miao, Enhanced electrochemical detection of DNA hybridization with carbon nanotube modified paste electrode. Journal of Nanoscience and Nanotechnology, 7 (2007): 560-564.

[91] Y.-T. Chen, Z.-N. Lin, J.-H. Chen, J.-J. Sun, L. Zhang, and G.-N. Chen, New capillary electrophoresis–electrochemiluminescence detection system equipped with an electrically heated Ru(bpy)3(2+)/multi-wall-carbon-nanotube paste electrode. Journal of Chromatography A, 1172 (2007): 84-91.

[92] R. T. Kachoosangi, L. Xiao, G. G. Wildgoose, F. Marken, P. C. B. Page, and R. G. Compton, A new method of studying ion transfer at liquid|liquid phase boundaries using a carbon nanotube paste electrode with a redox active binder. Journal of Physical Chemistry C, 111 (2007): 18353-18360.

[93] S.-Y. Ly, C.-H. Lee, and Y.-S. Jung, Measuring oxytetracycline using a simple prepared DNA immobilized on a carbon nanotube paste electrode in fish tissue Journal of the Korean Chemical Society, 51 (2007): 412-417.

[94] S.-Y. Ly, Diagnosis of copper ions in vascular tracts using a fluorine-doped carbon nanotube sensor. Talanta, 74 (2008): 1635-1641.

[95] S. Shahrokhian, Z. Kamalzadeh, A. Bezaatpour, and D. M. Boghaei, Differential pulse voltammetric determination of N-acetylcysteine by the electrocatalytic oxidation at the surface of carbon nanotube-paste electrode modified with cobalt salophen complexes. Sensors & Actuators B, Chemical; 133 (2008): 599-606.

[96] J.-N. Xie, S.-Y. Wang, L. Aryasomayajula, and V.-K. Varadan, Effect of nano-materials in platinum-decorated carbon nanotube paste-based electrodes for amperometric glucose detection. Journal of Material Research, 23 (2008): 1457-1465.

[97] H. Ibrahim, Carbon paste electrode modified with silver thimerosal for the potentiometric flow injection analysis of silver(I) ion. Analytica Chimica Acta, 545 (2005): 158-165.

[98] R. Metelka, S. Slavíková, K. Vytřas, Determination of arsenate and organic arsenic via potentiometric titration of its heteropoly-anions. Talanta, 58 (2002): 147-151.

[99] J. Konvalina, K. Vytřas, Reductive Determination of gold at carbon paste electrode using constant-current stripping analysis. Chemické Listy, 95 (2001): 505-508.

[100] I. Švancara, K. Vytřas, Determination of iodide in potassium iodide dosage tablets using cathodic stripping voltammetry with a carbon paste electrode. Scientific Papers of the University of Pardubice, Series A; 7 (2001): 5-15.

[101] I. Švancara, B. Ogorevc, M. Novič, and K. Vytřas, Simple and rapid determination of iodide in table salts containing anticaking agents using stripping potentio-metry with selective sensing at a carbon paste electrode. Analytical and Bioanalytical Chemistry, 372 (2002): 795-800.

[102] I. Švancara, K. Vytřas, and K. Kalcher, Half-decade of carbon paste electrodes in fact and interesting glosses. Atypical reminiscence of an electrochemical and electroanalytical jubilee (in Czech); in Modern Electrochemical Methods – XXVIII, Book of Abstracts. eds. J. Barek and T. Navrátil. (Prague: Czech Chemical Society, 2008), pp. 114-115.

[103] R. J. Mascarenhas, A. K. Satpati, S. Yellappa, B. S. Sherigara, and A. K. Bopiah, Wax-impregnated carbon paste electrode modified with mercuric oxalate for the simultaneous determination of heavy metal ions in medicinal plants and ayurvedic tablets. Analytical Sciences (Japan), 22 (2006): 871-875.

[104] R. M. Takeuchi, A. L. Santos, P. M. Padilha, and N. R. Stradiotto, Copper determination in ethanol fuel by differential pulse anodic stripping voltammetry at a solid paraffin-based carbon paste electrode modified with 2-aminothiazole organo-functionalized silica. Talanta, 71 (2007): 771-777.

[105] R. M. Takeuchi, , A. L. Santos, P. M. Padilha, and N. R. Stradiotto, A solid paraffin-based carbon paste electrode modified with 2-aminothiazole organofunctionalized silica for differential pulse adsorptive stripping analysis of nickel(II) in ethanol fuel. Analytica Chimica Acta, 584 (2007): 295-301.

[106] W. Yantasee, Y.-H. Lin, G. E. Fryxell, and Z.-M. Wang, Carbon paste electrode modified with carbamoylphosphonic acid functionalized mesoporous silica: A new mercury-free sensor for uranium detection. Electroanalysis, 16 (2004) 870-873.

[107] H.-L. Liu, Chemically modified carbon paste sensor for aluminium(III) and its application. Fenxi Huaxue (Chinese Journal of Analytical Chemistry), 31 (2003): 1511-1513.

[108] B. Blankert, O. Domínguez, W. El Ayyas, J. Arcos, and J.-M. Kauffmann, Horseradish peroxidase electrode for the analysis of clozapine. Analytical Letters, 37 (2004): 903-913.

[109] T. K. Malongo, S. Patris, P. Macours, F. Cotton, J. Nsangu, and J.-M. Kauffmann, Highly sensitive determination of iodide by ion chromatography with ampero-metric detection at a silver-based carbon paste electrode. Talanta, 76 (2008): 540-547.

[110] K. Grennan, A. J. Killard, and M. R. Smyth, Physical characterizations of a screen-printed electrode for use in an amperometric biosensor system. Electroanalysis, 13 (2001): 745-750.

[111] G. Cui, J.-H. Yoo, B.-W. Woo, S.-S. Kim, G.-S. Cha, and H. Nam, Disposable amperometric glucose sensor electrode with enzyme-immobilized nitrocellulose strip. Talanta, 54 (2001): 1105-1111.

[112] P. Fanjul Bolado, D. Hernández Santos, P. J. Lamas Ardisana, A. Martin Pernia, A. Costa García, Electro-chemical characterization of screen-printed and conventional carbon paste electrodes. Electrochimica Acta, 53 (2008): 3635-3642.

[113] I. Švancara, R. Metelka, M. Stibůrková, J. Seidlová, G. Jansová, K. Vytřas, and B. Pihlar, Carbon paste electrodes and screen-printed sensors plated with mercury- and bismuth films in stripping voltammetry of heavy metals. Scientific Papers of the University of Pardubice, Series A; 8 (2002) 19-33.

[114] D. Wei and A. Ivaska, Applications of ionic liquids in electrochemical sensors. A Review. Analytica Chimica Acta, 607 (2008): 126-135.

[115] H.-T. Liu, P. He, Z.-Y. Li, C.-N. Sun, L.-H. Shi, Y. Liu, G.-Y. Zhu, and J.-H. Li, An ionic liquid-type carbon paste electrode and its polyoxometalate-modified properties. Electrochemistry Communations, 7 (2005): 1357-1363.

[116] G. Shul, J. Sirieix Plenet, L. Gaillon, and M. Opallo, Ion transfer at carbon paste electrode based on ionic liquid. Electrochemistry Communications, 8 (2006): 1111-1114.

[117] N. Maleki, A. Safavi, and F. Tajabadi, High-performance carbon composite electrode based on an ionic liquid as a binder. Analytical Chemistry, 78 (2006): 3820-3826.

[118] A. Safavi, N. Maleki, O. Moradlou, and F. Tajabadi, Simultaneous determination of dopamine, ascorbic acid, and uric acid using carbon ionic liquid electrode. Analytical Biochemistry, 359 (2006): 224-229.

[119] A. Safavi, N. Maleki, F. Honarasa, F. Tajabadi, and F. Sedaghatpour, Ionic liquids modify the performance of carbon based potentiometric sensors. Electroanalysis, 19 (2007): 582-586.
[120] W. Sun, M.-X. Yang, R.-F. Gao, and K. Jiao, Electrochemical determination of ascorbic acid in room temperature ionic liquid BPPF6 modified carbon paste electrode. Electroanalysis, 19 (2007): 1597-1602.
[121] N. Maleki, A. Safavi, and F. Tajabadi, Investigation of the role of ionic liquids in imparting electrocatalytic behavior to carbon paste electrode. Electroanalysis, 19 (2007): 2247-2250.
[122] J.-B. Zheng, Y. Zhang, and P.-P. Yang, An ionic liquid-type carbon paste electrode for electrochemical investi-gation and determination of calcium dobesilate. Talanta, 73 (2007): 920-925.
[123] A. Safavi, N. Maleki, and F. Tajabadi, Highly stable electrochemical oxidation of phenols at carbon ionic liquid electrode. Analyst (UK), 132 (2007): 54-58.
[124] J. Li, M.-H. Huang, X.-Q. Liu, H. Wei, Y.-H. Xu, G.-B. Xu, and E.-K. Wang, Enhanced electrochemiluminescence sensor from tris(2,2'-bipyridyl)Ru(II) incorporated into MCM-41 and ionic liquid-based carbon paste electrode. Analyst (UK), 132 (2007): 687-691.
[125] S.-F. Wang, H.-Y. Xiong, and Q.-X. Zeng, Design of carbon paste biosensors based on the mixture of ionic liquid and paraffin oil as a binder for high performance and stabilization. Electrochemistry Communications, 9 (2007): 807-812.
[126] W. Sun, D.-D. Wang, R.-F. Gao, and K. Jiao, Direct electrochemistry and electro-catalysis of hemoglobin in sodium alginate film on a BMIMPF6 modified carbon paste electrode. Electrochemistry Communications, 9 (2007): 1159-1164.
[127] Y. Zhang, J.-B. Zheng, Comparative investigation on electrochemical behavior of hydroquinone at carbon ionic liquid electrode, ionic-liquid modified-, and the bare carbon paste electrode. Electrochimica Acta, 52 (2007): 7210-7216.
[128] W. Sun, R.-F. Gao, and K. Jiao, Electrochemistry and electrocatalysis of hemoglobin in nafion/nano-CaCO3 film on a new ionic liquid BPPF6 Modified Carbon Paste Electrode. Journal of Physical Chemistry B, 111 (2007): 4560-4567.
[129] W. Sun, M.-X. Yang, and K. Jiao, Electrocatalytic oxidation of dopamine at an ionic liquid modified carbon paste electrode and its analytical application. Analytical and Bioanalytical Chemistry, 389 (2007): 1283-1291.
[130] Y. Zhang and J.-B. Zheng, An ionic liquid bulk-modified carbon paste electrode and its electrocatalytic activity toward p-aminophenol. Chinese Journal of Chemistry (Shanghai), 25 (2007): 1652-1657.
[131] W. Sun, R.-F. Gao, D.-D. Wang, and K. Jiao, Direct electrochemistry of hemoglobin at room temperature ionic liquid [BMIM]PF6 modified carbon paste electrode. Wuli Huaxue Xuebao (Chinese Acta Physica Chimica), 23 (2007): 1247-1251.
[132] X.-Z. Zhang, K. Jiao, and X.-L. Wang, Paste electrode based on short single-walled carbon nanotubes and room temperature ionic liquid: preparation, characterization and application in DNA detection. Electroanalysis, 20 (2008): 1361-1366.
[133] M. Musameh and J. Wang, Sensitive and stable amperometric measurements at ionic liquid-carbon paste microelectrodes. Anal. Chim. Acta, 606 (2008): 45-49.
[134] M. M. Musameh, R. T. Kachoosangi, and R. G. Compton, Enhanced stability and sensitivity of ionic liquid-carbon paste electrodes at elevated temperatures. Analyst (UK), 133 (2008): 133-138.
[135] W. Sun, Y.-Z. Li, M.-X. Yang, S.-F. Liu, and K. Jiao, Direct electrochemistry of single-stranded DNA on an ionic liquid modified carbon paste electrode. Electrochemistry Communications, 10 (2008): 298-301.
[136] G. Shang, D. Xiao, H.-F. Zhang, and J.-B. Zheng, Electrochemical behavior and differential pulse voltammetric determination of Paracetamol at a carbon ionic liquid electrode. Analytical and Bioanalytical Chemistry, 391 (2008): 1049-1055.
[137] S.-S. Fan, F. Xiao, L. Liu, F.-Q. Zhao, and B.-Z. Zeng, Sensitive voltammetric response of methylparathion on single-walled carbon nanotube paste coated electrodes using ionic liquid as binder. Sensors & Actuators B, Chemical; 132 (2008): 34-39.
[138] M. M. Musameh, R. T. Kachoosangi, L. Xiao, A. Russell, and R. G. Compton, Ionic liquid-carbon composite glucose biosensor. Biosensors & Bioelectronics, 24 (2008): 87-92.
[139] W. Sun, Q. Jiang, M.-X. Yang, and K. Jiao, Electrochemical behaviors of hydro-quinone on a carbon paste electrode with ionic liquid as binder. Bulletin of the Korean Chemical Society, 29 (2008): 915-920.

[140] H. Zhang, G.-P. Cao, Y.-S. Yang, and Z.-N. Gu, The capacitive performance of an ultralong (aligned) carbon nanotube electrode in an ionic liquid at 60oC. Carbon, 46 (2008): 30-34.

[141] I. Švancara, R. Metelka, and K. Vytřas, K., Piston-driven carbon paste electrode holders for electrochemical measurements; in Sensing in Electroanalysis. eds. K. Vytřas and K. Kalcher. (Pardubice: University of Pardubice, 2005), pp. 7-18.

[142] J. Oni, P. Westbroek, and T. Nyokong, Construction and characterization of carbon paste ultramicro-electrodes. Electrochemistry Communications, 3 (2001): 524-528.

[143] L. Baldrianová, I. Švancara, and S. Sotiropoulos, Anodic stripping voltammetry at a new type of disposable bismuth-plated carbon paste mini-electrodes. Analytica Chimica Acta, 599 (2007): 249-255.

[144] J. Zima, H. Dejmková, and J. Barek, HPLC determination of naphthalene amino derivatives using electrochemical detection at carbon paste electrodes. Electroanalysis, 19 (2007): 185-190.

[145] I. Švancara, P. Kotzian, M. Bartoš, and K. Vytřas, Groove electrodes: A new alternative of using carbon paste in electroanalysis. Electrochemistry Communications, 7 (2005): 657-662.

[146] I. Švancara, P. Kotzian, R. Metelka, M. Bartoš, P. Foret, and K. Vytřas, Plastic bars with carbon paste: A new type of the working electrode in electroanalysis (in Czech); in Monitoring of Environmental Pollutants – IV, eds. K. Vytřas, J. Kellner, and J. Fischer. (Pardubice: University of Pardubice, 2002), pp. 145-158.

[147] R. Metelka, M. Žeravík, and K. Vytřas, Groove electrodes filled with carbon paste in flow injection analysis (in Czech); in Monitoring of Environmental Pollutants – X, eds. K.Vytřas, J. Kellner, and J. Fischer. (Pardubice: University Pardubice, 2008), pp. 153-158.

[148] G. U. Flechsig, O. Korbout, S. B. Hočevar, S. Thongngamdee, B. Ogorevc, P. Gründler, and J. Wang, Electrically heated bismuth-film electrode for voltammetric stripping measurements of trace metals. Electroanalysis, 14 (2002): 192-196.

[149] D .C. Dunwoody, M. Unlu, A. K. H.. Wolf, W. L. Gellett, and J. Leddy, Magnet incorporated carbon electrodes: Methods for construction and demonstration of increased electrochemical flux. Electroanalysis, 17 (2005): 1487-1494.

[150] B.-Y. Yang, J.-Y. Mo, and R. Lai, Determination of environmental nitrophenols by dual-electrode and dual-channel electrochemical detection in capillary electrophoresis with a carbon paste electrode. Gaodeng Xuexiao Huaxue Xuebao (Chemical Journal of Chinese Universities), 26 (2005): 227-230.

[151] Gy. Svehla: Vogel's Qualitative Inorganic Analysis, 7th Ed., revised and extended. (Singapore: Longman Publi-shing, 1996).

[152] Y.-N. Zeng, N. Zheng, P. G. Osborne, Y.-Z. Li, W.-B. W.-B. Chang, and Z.-M. Wang, Preparation and cyclic voltammetry characterization of Cu(I)-dipyridyl imprinted polymer. Chinese Chemistry Letters, 13 (2002): 317-320.

[153] M. H. Mashhadizadeh, A. Mostafavi, H. Allah Abadi, and I. Sheikh-shoai, New Schiff base modified carbon paste and coated wire PVC membrane for silver ion. Sensors & Actuators B, Chemical; 113 (2006): 930-936.

[154] L.-D. Li, W.-J. Li, C.-Q. Sun, and L.-S. Li, Fabrication of carbon paste electrode containing 1:12 phospho-molybdic anions encapsulated in modified mesoporous molecular sieve MCM-41 and its electrochemistry. Electroanalysis, 14 (2002): 368-375.

[155] S.-X. Liu, C.-M. Wang, D.-H. Li, Z.-M. Su, E.-B. Wang, N.-H. Hu, and H.-Q. Jia, Synthesis, structure and properties of a novel supramolecular compound. Acta Chimica Sinica (Shanghai), 62 (2004): 1305-1310.

[156] Z.-G. Han, Y.-L. Zhao, J. Peng, Q. Liu, and E.-B. Wang, Inorganic-organic hybrid polyoxo-metalate containing supramolecular helical chains: Preparation, characterization and application in chemically bulk-modified electrode. Electrochimica Acta, 51 (2005): 218-224.

[157] L.-Y. Duan, F.-C. Liu, X.-L. Wang, E.-B. Wang, C. Qin, Y.-G. Li, X.-L. Wang, and C.-W. Hu, A new 3-D cadmium molybdenum phosphate with intersecting tunnels: hydro-thermal synthesis, structure and electrochemical properties of the [C3H12N2]4[CdMo12O24(HPO4)6(PO4)2(OH)6][(Cd(H2O)2]x3H2O compound. Journal of Molecular Structure, 705 (2004):15-20.

[158] B. Keita, P. de Oliveira, L. Nadjo, and U. Kortz, The ball-shaped heteropolytungstates [{Sn(CH3)(2)(H2O)} (24){Sn(CH3)(2)}(12)-(A-XW9O34)(12)](36-) (X = P, As): Stability, redox and catalytic properties in aqueous media. Chemistry – A European Journal (Wiley), 13 (2007): 5480-5491.

[159] B.-X. Dong, J. Peng, A.-X. Tian, J.-Q. Sha, L. Li, and H.-S. Liu, Two new inorganic-organic hybrid

single pendant hexadecavanadate derivatives with bifunctional electrocatalytic activities. Electrochimica Acta, 52 (2007): 3804-3812.

[160] X.-Y. Zhao, D.-D. Liang, S.-X. Liu, C.-Y. Sun, R.-G. Cao, C.-Y. Gao, Y.-H. Ren, and Z.-M. Su, Two Dawson-templated 3-D metal-organic frameworks based on oxalate-bridged binuclear Co(II)/Ni(II) SBUs and bpy-linkers. Inorganic Chemistry, 47 (2008): 133-138.

[161] E. S. Ribeiro, Y. Gushikem, J. C. Biazzotto, and O. A. Serra, Electrochemical properties and dissolved oxygen reduction study on Fe^{III}-tetra(o-ureaphenyl)porphyrinosilica matrix surface, Journal of Porphyrins & Phthalocyanines, 6 (2002): 527-532.

[162] C. A. Pessoa, Y. Gushikem, and S. Nakagaki, Cobalt porphyrin immobilized on a niobium(V) oxide grafted-silica gel surface: Study of the catalytic oxidation of hydrazine. Electroanalysis, 14 (2002): 1072-1076.

[163] C.-Y. Li, Y. Chen, C.-F. Wang, H.-B. Li, and Y.-Y.Chen, Electrocatalytic oxidation of H_2O_2 at a carbon paste electrode modified with a Ni(II)-calix[4]arene complex and its application. Wuhan University, Journal of Natural Sciences; 8 (2003): 857-860.

[164] D. Munteanu, D. Dicu, I. C. Popescu, and L. Gorton, NADH oxidation using carbo-naceous electrodes modified with dibenzo-dithia-diazapentacene. Electroanalysis, 15 (2003): 383-391.

[165] E. S. Gil and L. T. Kubota, Electrochemical properties of Doyle catalyst immobilized on carbon paste in the presence of DNA. Bioelectrochemistry, 51 (2001): 145-149.

[166] V. Parra, T. del Cano, M. L. Rodríguez Mendez, J. A. de Saja, and R. F. Aroca, Electrochemical characterization of two perylenetetracarboxylic diimides: Langmuir-Blodgett films and carbon paste electrodes. Chemistry of Materials, 16 (2004): 358-364.

[167] C.-X. Lei, S.-Q. Hu, G.-L. Shen, and R.-Q. Yu, Immobilization of horseradish peroxidase to a nano-Au monolayer / chitosan- modified carbon paste electrode for the detection of hydrogen peroxide. Talanta, 59 (2003): 981-988.

[168] J. Li, L.-T. Xiao, X.-M. Liu, G.-M. Zeng, G.-H. Huang, G.-.L. Shen, and R.-Q. Yu, Amperometric biosensor with HRP immobilized on a sandwiched nano-Au polymerized film and ferrocene mediator. Analytical and Bioanalytical Chemistry, 376 (2003): 902-907.

[169] H. Remita, P. F. Siril, I. M. Mbomekalle, B. Keita, and L. Nadjo, Activity evaluation of carbon paste electrodes loaded with Pt-nanoparticles prepared in different radiolytic conditions. Journal of Solid State Electrochemistry, 10 (2006): 506-511.

[170] J.-Z. Xu, J.-J. Zhu, H. Wang, and H.-Y. Chen, Nano-sized copper oxide modified carbon paste electrodes as an amperometric sensor for amikacin. Analytical Letters, 36 (2003): 2723-2733.

[171] D. R. do Carmo, L. L. Paim, N. L. Dias, and N. R. Stradiotto, Preparation, characte-rization and application of a nanostructured composite: Octakis-(cyanopropyldimethyl-siloxy)octa-silsesquioxane. Applied Surface Science, 253 (2007): 3683-3689.

[172] D.-P. Tang, R. Yuan, and Y.-Q. Chai, Magnetic core-shell Fe3O4@Ag nanoparticles coated carbon paste interface for studies of carcinoembryonic antigen in clinical immunoassay. Journal of Physical Chemistry B, 110 (2006): 11640-11646.

[173] W. Sun, D.-D. Wang, J.-H. Zhong, and K. Jiao, Electrocatalytic activity of hemoglobin in sodium alginate / SiO_2 nanoparticle / ionic liquid BMIM-PF_6 composite film. Journal of Solid State Electrochemistry, 12 (2008): 655-661.

[174] X.-L, Wang., Z.-H. Kang, E.-B. Wang, C.-W. Hu, Preparation of chemically bulk-modified electrode based on hybrid silicomolybdate nanoparticles for the detection of nitrite. Material Letters, 56 (2002): 393-396.

[175] X.-L. Wang., Z.-H. Kang, E.-B. Wang, C.-W. Hu, Inorganic-organic hybrid 18-molybdo-diphosphate nanoparticles bulk-modified carbon paste electrode and its electro-catalytic properties. Chinese Journal of Chemistry (Shanghai), 20 (2002): 777-783.

[176] X.-L. Wang., Z.-H. Kang, Y. Lan, and E.-B. Wang, Molybdo-vanado-phosphate tetraethyl-ammonium nanoparticles bulk-modified carbon paste electrode and its electro-catalysis toward the reduction of hydrogen peroxide. Fenxi Huaxue (Chinese Journal of Analytical Chemistry, 31 (2003): 941-944.

[177] L. Wang, M. Jiang, E.-B. Wang, S.-Y. Lian, L. Xu, and Z. Li, Synthesis and characte-rization of nanoporous ultrathin multilayer films based on molybdenum polyoxometalate $(Mo\text{-}36)_n$. Material Letters, 58 (2004): 683-687.

[178] X.-L. Wang, H.-Y. Zhao, and Y.-F. Wang, Preparation, electrochemical property and

application in bulk-modified electrode of Dawson-type phosphomolybdate-doped polypyrrole composite nanoparticles. Gaodeng Xuexiao Huaxue Xuebao (Chemical Research in Chinese Universities), 22 (2006): 556-559.

[179] Z.-G. Han, Y.-L. Zhao, J. Peng, Q. Liu, and E.-B. Wang, Inorganic-organic hybrid polyoxo-metalate containing supramolecular helical chains: Preparation, characterization and application in chemically bulk-modified electrode. Electrochimica Acta, 51 (2005): 218-224.

[180] A. Curulli, F.Valentini, S. Orlanducci, M. L. Terranova, C. Paoletti, G. Palleschi, Electrosynthesis of non conventional-polymer nanotubules: A new nanostructured material for analytical applications. Sensors & Actuators B, Chemical; 100 (2004) 65-71.

[181] S.-Y. Zhu, L.-S. Fan, X.-Q. Liu, L-H. Shi, H.-J. Li, S. Han, and G.-B. Xu, Determination of concentrated hydrogen peroxide at single-walled carbon nanohorn paste electrode. Electrochemistry Communications, 10 (2008): 695-698.

[182] M. B. González García, and A. Costa García, Adsorptive stripping voltammetric behavior of colloidal gold and immunogold on a carbon paste electrode. Bioelectrochemistry & Bioenergetics, 38 (1995): 389-395.

[183] D. Hernández Santos, M. B. González García, and A. Costa Garcia, Metalnano-particles based electroanalysis. A Review. Electroanalysis, 14 (2002): 1225-1235.

[184] S.-Q. Liu and H.-X. Ju, Reagentless glucose biosensor based on colloidal gold modified carbon paste electrode. Biosensors & Bioelectronics, 19 (2003): 177-183.

[185] S.-Q. Liu and H.-X. Ju, Electrocatalysis via direct electrochemistry of myoglobin immobilized on colloidal gold nanoparticles. Electroanalysis, 15 (2003): 1488-1493.

[186] T. Grygar, F. Marken, U. Schröder, and F. Scholz, Electrochemical analysis of solids. A Review. Collection of Czechoslovak Chemical Communications, 67 (2002): 163-208.

[187] V. Vivier, A. Regis, G. Sagon, J. Y. Nedelec, L. T. Yu, and C. Cachet Vivier, Cyclic voltammetry study of bismuth oxide powder by means of a cavity microelectrode coupled with Raman microspectrometry. Electrochimica Acta, 46 (2001): 907-914.

[188] V. B. Fetisov, G. A. Kozhina, A. N. Ermakov, A. V. Fetisov, and E. G. Miroshnikova, Electrochemical dissolution of Mn3O4 in acid solutions. Journal of Solid State Electrochemistry, 11 (2007): 1205-1210.

[189] G. Cepria, J. J. Cepria, J. Ramajo, Fast and simple electroanalytical identification of iron oxides in geological samples. Microchimica Acta, 144 (2004): 139-145.

[190] K. E. Jaya, S. Berckman, V. Yegnaraman, and P. N. Mohandes, Electrochemical investigation of the rusting reaction of ilmenite using CV-studies. Hydrometallurgy, 65 (2002): 217-225.

[191] E. Barrado, F. Prieto, F. J. Garay, J. Medina, and M. Vega, Characterization of nickel-bearing ferrites obtained as by-products of hydrochemical wastewater purification processes. Electrochemica Acta 47 (2002) 1959-1965.

[192] E. Barrado, F. Prieto, J. Medina, and R. Pardo, Purification of cadmium waste water: Characterization and electrochemical behaviour of ferrites bearing cadmium(II). Quimica Analytica, 20 (2001): 47-53.

[193] J. L. Nava, M. T. Oropeza, and I. González, Oxidation of mineral species as a function of the anodic potential of zinc sulphide concentrate in sulfuric acid. Journal of Electro-analytical Chemistry Society, Section B; 151 (2004): B387-B393.

[194] S.-Y. Shi, Z.-H. Fang, and J.-R. Ni, Comparative study on the bioleaching of zinc sulphides. Process Biochemistry, 41 (2006): 438-446.

[195] S.-Y. Shi, Z.-H. Fang, and J.-R. Ni, Electrochemistry of marmatite-containing carbon paste electrode in the presence of bacterial strains. Bioelectrochemistry, 68 (2006): 113-118.

[196] J. L. Nava, M. T. Oropeza, and I. González, Electrochemical characterisation of sulfur species formed during anodic dissolution of galena concentrate in perchlorate medium. Electrochimica Acta, 47 (2002): 1513-1525.

[197] J. L. Nava and I. González, The role of the carbon paste electrodes in the electro-chemical study of metallic minerals. Quimica Nova, 28 (2005): 901-909.

[198] D. Nava and I. González, Electrochemical characterization of chemical species formed during the electrochemical treatment of chalcopyrite in sulfuric acid. Electrochimica Acta, 51 (2005): 5295-5303.

[199] E. A.Holley, A. J. McQuillan, D. Craw, J. P. Kim, and S. G. Sander, Mercury mobilization by oxidative dissolution of alpha cinnabar and

beta-cinnabar. Chemical Geology, 240 (2007): 313-325.

[200] C. M. V. B. Almeida and B. F. Giannetti, Electrochemical study of arsenopyrite weathering. Physical Chemistry / Chemical Physics, 5 (2003): 604-610.

[201] G. Cepria, N. Alexa, E. Cordos, and J. R. Castillo, Electrochemical screening procedure for arsenic contaminated soils. Talanta, 66 (2005): 875-881.

[202] I. Galfi, J. Aromaa, and O. Forsen, Laboratory tool for electrochemical study of sulphide minerals. Physicochemical Problems in Mineral Processing, 41 (2007): 301-312.

[203] C. M. V. B. Almeida and B. F. Giannetti, A new and practical carbon paste electrode for insoluble and ground samples. Electrochemistry Communications, 4 (2002): 985-988.

[204] G. Cepria, L. Irigoyen, and J. R. Castillo, A microscale procedure to test the metal sorption properties of biomass sorbents: A time and reagents saving alternative to conventional methods. Microchimica Acta, 154 (2006): 287-295.

[205] D. R. do Carmo, R. M. da Silva, and Stradiotto N. R., Electrochemical study of $Fe[Fe(CN)_5NO]$ in a graphite paste electrode. Ecletica Quimica (Brazil), 27 (2002): 197-210.

[206] M. Shamsipur, A. Salimi, S. M. Golabi, H. Sharghi, and M. F. Mousayi, Electro-chemical properties of modified carbon paste electrodes containing some amino derivatives of 9,10-anthraquinone. Journal of Solid State Electro-chemistry, 5 (2001): 68-72.

[207] A. Vlasa, S. Varvara, and L. M. Muresan, Electrochemical investigation of the influence of two thiadiazole deriva-tives on the patina of an archaeological bronze artefact using a carbon paste electrode. Studies of University Babes-Bolyai, Series Chemical (Cluj-Napoca); 52 (2007): 63-71.

[208] G.-Y. Shi, K. Yamamoto, T.-.S. Zhou, F. Xu, T. Kato, J.-Y. Jin, and L.-T. Jin, On-line biosensors for simultaneous determination of glucose, choline, and glutamate integrated with a microseparation system. Electrophoresis, 24 (2003): 3266-3272.

[209] S.-Y. Ly, Real-time voltammetric assay of cadmium ions in plant tissue and fish brain core. Bulletin of the Korean Chemistry Society, 27 (2006): 1613-1617.

[210] S. Y. Ly, Diagnosis of Cu(II) ions in vascular tracts by a F-doped carbon nanotube sensor. Talanta, 74 (2008): 1635-1641.

[211] S.-Y. Ly, Y.-S. Jung, C.-H. Lee, and B.-W. Lee, Administering pesticide assays with the aid of in-vivo implanted biosensors. Australian Journal of Chemistry, 61 (2008): 826-832.

[212] L. Lvova, S.-S. Kim, A. Legin, Y. Vlasov, J.-S. Yang, G.-S. Cha, and H. Nam, Solid-state electronic tongue and its application for beverage analysis. Analytica Chimica Acta, 468 (2002): 303-314.

[213] A. Arrieta, M. L. Rodríguez Mendéz, and J. A. de Saja, Langmuir-Blodgett film and carbon paste electrode based on phthalocyanines as sensing units for taste. Sensors & Actuators B, Chemical; 95 (2003): 357-365.

[214] V. Parra, A. A. Arrieta, J. A. Fernández Escudero, M. Iníguez, J. A. de Saja, and M. M. L. Rodríguez, Monitoring of the ageing of red wines in oak barrels by an hybrid electronic tongue. Analytica Chimica Acta, 563 (2006): 229-237.

[215] M. L. Rodríguez Mendez, V. Parra, C. Apetrei, S. Villanuevam, M. Gay, N. Prieto, J. Martínez, and J. A. de Saja, Electronic tongue based on voltammetric electrodes modified with materials showing complementary electroactive properties. Characterization and Applications. Microchimica Acta, 163 (2008): 23-31.

[216] C. Apetrei, F. Gutieréz, M. L. Rodríguez Mendéz, and J. A. de Saja, Novel method based on carbon paste electrodes for the evaluation of bitterness in extra virgin olive oils. Sensors & Actuators B, Chemical, 121 (2007): 567-575.

[217] Y. Kureishi, H. Shiraishi, and H. Tamiaki, Self-aggregates of synthetic zinc chlorins as the photo-sensitizer on carbon paste electrodes for a novel solar cell. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 496 (2001): 13-20.

[218] M. Torimura, A. Miki, A. Wadano, K. Kano, and T. Ikeda, Electrochemical investigation of photoreduction catalyzed by cyanobacteria Synechococcus sp. (PCC-7942) in exogenous quinones and photoelectrochemical oxidation of water. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 496 (2001): 21-28.

[219] T.-S. Oh, J.-H. Lee, S.-E. Lee, K.-W. Min, S.-K. Kang, J.-B. Yoo, C.-Y. Park, and J.-M. Kim, A field-emission display with an asymmetric electrostatic-quadrupole lens structure. Japanese Journal of Applied Physics, 44 (2005): 8692-8697.

[220] S. Křížková, P. Ryant, O. Kryštofová, V. Adam, V. Galiová, M. Beklová, P. Babula, J. Kaiser,

K. Novotný, J. Novotný, M. Liška, R. Malina, J. Zehnálek, J. Hubálek, L. Havel, R. Kizek, Multi-instrumental analysis of tissues of sunflower plants treated with silver(I) ions: Plants as bioindicators of environmental pollution. Sensors, 8 (2008): 445-463.

[221] A. Economou and P. R. Fielden, Mercury film electrodes: developments, trends and potentialities for electroanalysis (Review). Analyst (UK), 128 (2003): 205–212.

[222] A. Walcarius, Zeolite-modified electrodes in electroanalytical chemistry. Analytica Chimica Acta, 384 (1999): 1-16.

[223] A. Walcarius, Electroanalysis with pure, chemically modified, and sol-gel-derived silica-based materials. Electroanalysis, 13 (2001): 701-718.

[224] A. Walcarius, Electrochemical applications of silica-based organic-inorganic hybrid materials. Chem. Mater., 13 (2001): 3351-3372.

[225] A.Walcarius, Electroanalytical applications of microporous zeolites and mesoporous (organo) silicas: Recent trends. Electroanalysis, 20 (2008): 711-738.

[226] A. Walcarius, P. Mariaulle, and L. Lamberts, Zeolite-modified solid carbon paste electrodes. Journal of Solid State Electrochemistry, 7 (2003): 671-677.

[227] A. Walcarius, Zeolite-modified paraffin-impregnated graphite electrode. Journal of Solid State Electrochemistry, 10 (2006): 469-478.

[228] S. Sayen, M. Etienne, J. Bessière, and A. Walcarius, Tuning the sensitivity of electrodes modified with an organic-inorganic hybrid by tailoring the structure of the nano-composite material. Electroanalysis, 14 (2002): 1521-1525.

[229] A. Walcarius, M. Etienne, S. Sayen, and B. Lebeau, Grafted silicas in electroanalysis: A Study on amorphous versus ordered mesoporous materials. Electroanalysis, 15 (2003): 414-421.

[230] M. Etienne, J. Bessière, and A. Walcarius, Voltammetric detection of copper(II) at a carbon paste electrode containing an organically modified silica. Sensors & Actuators B, Chemical; 76 (2001): 531-538.

[231] S. Sayen, C. Gérardin, L. Rodehuser, and A. Walcarius, Electrochemical detection of copper(II) at an electrode modified by a carnosine-silica hybrid material. Electro-analysis, 15 (2003): 422-430.

[232] V. Ganesan and A. Walcarius, Surfactant templated sulfonic acid-functionalized silica microspheres as new efficient ion-exchangers and electrode modifiers. Langmuir, 20 (2004): 3632-3640.

[233] S. Goubert-Renaudin, M. Etienne, Y. Rousselin, F. Denat, B. Lebeau, and A. Walcarius, Cyclam-functionalized silica-modified electrodes for selective determination of Cu(II). Electroanalysis, in press.

[234] M. Etienne, C. Delacôte, and A. Walcarius, Interest of mesoporous organic-inorganic hybrids in electroanalysis: Illustration for mercury binding to thiol-functionalized silica-based materials; in Progress in Electrochemistry Research, ed. M. Nuñéz. (Hauppauge (NY): Nova Science Publishers, 2005), pp.145-184.

[235] W. Yantasee, C. Timchalk, G. E. Fryxell, B. P. Dockendorff, and Y. Lin, Automated portable analyzer for lead(II) based on sequential flow injection and nano-structured electrochemical sensors. Talanta, 68 (2005): 256-261.

[236] L.-D. Li, W.-J. Li, C.-Q Sun, and L.-S. Li, Fabrication of carbon paste electrode containing 1:12 phosphomolybdic anions encapsulated in modified mesoporous molecular sieve MCM-41 and its electrochemistry. Electroanalysis, 14 (2002): 368-375.

[237] C. Delacôte, J.-P. Bouillon, and A. Walcarius, Voltammetric responses of ferrocene-grafted mesoporous silica. Electrochimica Acta, 51 (2006): 6373-6383.

[238] M. Zendehdel, A. Babaei, and S. Alami, Intercalation of xylenol orange, morin, and calmagite into NaY-zeolite and their application in a dye / zeolite modified electrode. Journal of Inclusion Phenomena and Macrocyclic Chemistry, 59 (2007): 345-349.

[239] D. Gligor, L. M. Muresan, A. Dumitrum, and I. C. Popescu, Electrochemical behavior of carbon paste electrodes modified with methylene green immobilized on two different X-type zeolites. Journal of Applied Electrochemistry, 37 (2007): 261-267.

[240] J. Li, M.-H. Huang, X.-Q. Liu, H. Wei, Y.-H. Xu, G.-B. Xu, and E.-K. Wang, Enhanced electrochemiluminescence sensor from tris(2,2'-bipy)Ru^{II} incorporated into MCM-41 and ionic liquid-based carbon paste electrode. Analyst (UK), 132 (2007): 687-691.

[241] I. Švancara, K. Kalcher, and K. Vytřas, Solid Electrodes Plated with Metallic Films. Scientific Papers of the University of Pardubice, Series A; 3 (1997): 207-225.

[242] I. Švancara, R. Pazdera, R. Metelka, E. Norkus, and K. Vytřas, Some aspects of using stripping

potentiometry for measurements with carbon paste electrodes plated with mercury- and gold films; in Monitoring of Environmental Pollutants – III (in Czech), eds. K. Vytřas, J. Kellner, and J. Fischer (University of Pardubice, 2001), pp. 123-134.

[243] I. Švancara, M. Fairouz, Kh. Ismail, R. Metelka, and K. Vytřas, A contribution to the characterisation of mercury- and bismuth film carbon paste electrodes in stripping voltammetry. Scientific Papers of the University of Pardubice, Series A; 9 (2003): 31-48.

[244] I. Švancara, M. Fairouz, Kh. Ismail, J. Šrámková, R. Metelka, and K. Vytřas: Applicability of electrochemical stripping analysis at mercury- and bismuth-film carbon paste electrodes to crude oil digests. Scientific Papers of the University of Pardubice, Series A; 10 (2004): 5-20.

[245] E. Tesařová, A. Królicka, A. Bobrowski, I. Švancara, and K. Vytřas, A study on simultaneous determination of indium and cadmium at mercury-based and bismuth film-plated electrodes, Scientific Papers of the University of Pardubice, Series A; 10 (2004): 21-32.

[246] I. Švancara, E. Tesařová, and R. Metelka, Stripping voltammetry at mercury-film plated carbon paste electrodes: Ten years of advanced laboratory exercises for students at the University of Pardubice. Scientific Papers of the University of Pardubice, Series A; 11 (2005): 343-361.

[247] I. Švancara, K. Vytřas, A. Bobrowski, and K. Kalcher, Determination of arsenic at a gold-plated carbon paste electrode using constant current stripping analysis. Talanta, 56 (2002): 45-55.

[248] A. Królicka, R. Pauliukaitė, I. Švancara, R. Metelka, E. Norkus, A. Bobrowski, K. Kalcher, and K. Vytřas, Bismuth film-plated carbon paste electrodes, Electrochemistry Communications, 4 (2002): 193-196.

[249] K. Vytřas, I. Švancara, and R. Metelka, A novelty in potentiometric stripping analysis: Total replacement of mercury by bismuth. Electroanalysis, 14 (2002): 1359-1364.

[250] S. A. A. Elsuccary, I. Švancara, R. Metelka, L. Baldrianová, M. E. M. Hassouna, and K. Vytřas, Applicability of bismuth film carbon paste electrodes in highly alkaline media. Scientific Papers of the University of Pardubice, Series A; 9 (2003): 5-17.

[251] I. Švancara, L. Baldrianová, E. Tesařová, S. A. A. Elsuccary, A. Economou, S. Sotiropoulos, A. Bobrowski, and K. Vytřas, Stripping voltammetry of metal-ion mixtures at bismuth film-plated electrodes; in Monitoring of Environmental Pollutants – VI (in Czech), eds. K. Vytřas, J. Kellner, and J. Fischer (University of Pardubice, 2004), pp. 229-246.

[252] I. Švancara, L. Baldrianová, M. Vlček, R. Metelka, and K. Vytřas, A role of the plating regime in the deposition of bismuth films onto a carbon paste electrode: Microscopic study. Electroanalysis, 17 (2005): 120-126.

[253] E. Tesařová, L. Baldrianová, A. Królicka, I. Švancara, A. Bobrowski, and K. Vytřas, Role of supporting electrolyte in anodic stripping voltammetry of In(III) in the presence of Cd(II) and Pb(II) using bismuth film electrodes; in Sensing in Electroanalysis, eds. K. Vytřas and K. Kalcher. (Pardubice: University of Pardubice, 2005), pp. 75-87.

[254] K. Vytřas, L. Baldrianová, E. Tesařová, A. Bobrowski, and I. Švancara, Comments to Stripping voltammetric determination of copper(II) at bismuth-modified carbon substrate electrodes; in Sensing in Electroanalysis, eds. K. Vytřas, K. Kalcher. (Pardubice: University of Pardubice, 2005), pp. 49-58.

[255] I. Švancara, L. Baldrianová, E. Tesařová, T. Mikysek, and K. Vytřas, Determination of tin(II) at bismuth-modified carbon paste electrodes: An initial study; in: Monitoring of Environmental Pollutants – VII (in Czech), eds.: K. Vytřas, J. Kellner, and J. Fischer. (Pardubice: University of Pardubice, 2005), pp. 139-148.

[256] I. Švancara, L. Baldrianová, E. Tesařová, S. B. Hočevar, S. A. A. Elsuccary, A. Economou, S. Sotiropoulos, B. Ogorevc, and K. Vytřas, Recent advances in anodic stripping voltammetry with Bi-modified carbon paste electrodes. Electroanalysis, 18 (2006): 177-185.

[257] L. Baldrianová, I. Švancara, M. Vlček, A. Economou, and S. Sotiropoulos, Effect of Bi(III) concentration on the stripping voltammetric response of in-situ bismuth-coated carbon paste and gold electrodes. Electrochimica Acta, 52 (2006): 481-490.

[258] I. Švancara, L. Baldrianová, E. Tesařová, T. Mikysek, and K. Vytřas, Anodic stripping voltammetry at bismuth-modified electrodes in ammonia-buffered media. Scientific Papers of University of Pardubice, Series A; 12 (2006): 5-19.

[259] L.-Y. Cao, J.-B. Jia, and Z.-H. Wang, Sensitive determination of Cd(II) and Pb(II) by differential

pulse stripping voltammetry with in-situ bismuth-coated zeolite doped carbon paste electrodes. Electrochimica Acta, 53 (2007): 2177-2182.

[260] I. Adraoui, M. E. Rhazi, and A. Amine, Fibrinogen-coated bismuth film electrodes for voltammetric analysis of lead and cadmium using the batch injection analysis, Analytical Letters, 40 (2007): 349-367.

[261] I. Švancara, L. Baldrianová, E. Tesařová, M. Vlček, K. Vytřas, and S. Sotiropoulos, Microscopic studies with bismuth-modified carbon paste electrode substrates: Morphological transformations of bismuth microstructures and related observations; in Sensing in Electro-analysis – 2, eds. K. Vytřas and K. Kalcher. (University of Pardubice, 2007), pp. 35-58.

[262] L. Baldrianová, I. Švancara, K. Vytřas, and S. Sotiropoulos, Variation of the metal analyte-to-bismuth peak ratio with deposition time in anodic stripping voltammetry at in-situ bismuth-coated carbon paste electrodes, in Sensing in Electroanalysis – 2, eds. K. Vytřas and K. Kalcher. (Pardubice: University of Pardubice, 2007), pp. 59-74.

[263] R. Pauliukaitė, R. Metelka, I. Švancara, A. Królicka, A. Bobrowski, K. Vytřas, E. Norkus, and K. Kalcher, Carbon paste electrodes modified with Bi2O3 as sensors for the determination of cadmium and lead. Analytical and Bioanalytical Chemistry, 374 (2002): 1155-1158.

[264] S. B. Hočevar, I. Švancara, B. Ogorevc, and K. Vytřas, Novel electrode for electro-chemical stripping analysis based on carbon paste modified with bismuth powder. Electro-chimica Acta, 51 (2005): 706-710.

[265] L. Baldrianová, P. Agrafiotou, I. Švancara, K. Vytřas, and S. Sotiropoulos, The determination of cysteine at bismuth-powder carbon paste electrodes by cathodic stripping voltammetry. Electrochemistry Communications, 10 (2008): 918-921.

[266] K. Vytřas, I. Švancara, and R. Metelka, Bismuth-based electrodes in electrochemical stripping analysis: A review; in Monitoring of Environmental Pollutants – IV (in Czech), eds. K. Vytřas, J. Kellner, and J. Fischer. (University of Pardubice, 2002). pp. 159-170.

[267] A. Economou, Bismuth-film electrodes: recent developments and potentialities for electroanalysis (A review). Trends in Analytical Chemistry, 24 (2005): 334-340.

[268] J. Wang, Stripping analysis at bismuth electrodes: A Review. Electroanalysis, 17 (2005): 1341-1346.

[269] I. Švancara and K. Vytřas, Electroanalysis with bismuth electrodes: State of the art and future prospects (in Czech). Chemické Listy, 100 (2006): 90-113.

[270] C. Kokkinos and A Economou, Stripping analysis at bismuth-based electrodes. Current Analytical Chemistry, 4 (2008): 183-190.

[271] C. Gouveia Caridade, R. Pauliukaitė, and C. M. A. Brett, Influence of Nafion coatings and surfactant on the stripping voltammetry of heavy metals at bismuth-modified carbon film electrodes. Electroanalysis, 18 (2006): 854-861.

[272] R. Kalvoda, Is polarography still attractive? (A Review). Chemia Analyticzna (Warsaw), 52 (2007): 869-873.

[273] I. Švancara, S. B. Hočevar, L. Baldrianová, E. Tesařová, and K. Vytřas, Antimony-modified carbon paste electrodes: Initial studies and prospects. Scientific Papers of the University of Pardubice, Series A; 13 (2007): 5-19.

[274] R. Pauliukaitė and K. Kalcher, On using of CPE and SPCE modified by Bi2O3 and Sb2O3 for trace analysis of some heavy metals; in YISAC '01: 8th Young Investigators' Seminar on Analytical Chemistry, Book of Abstracts (University of Pardubice, 2001), pp. 10-11.

[275] A. Bobrowski, A. Królicka, and E. Łyczkowska, Carbon paste electrode plated with lead film: Electrochemical characteristics and application in adsorptive stripping voltammetry. Electroanalysis, 20 (2008): 61-67.

[276] A. Economou and A. Voulgaropoulos, A study of the square-wave modulation for the determination of trace metals by anodic and adsorptive stripping voltammetry with bismuth film electrodes. Scientific Papers of the University of Pardubice, Series A; 10 (2004): 33-46.

[277] R. Pauliukaite and K. Kalcher, Determination of Traces of Cd(II) and Pb(II) Using a Bi-Modified Carbon Paste and Screen-Printed Carbon Electrodes; in US-CZ Workshop on Electrochemical Sensors – Prague '01, Book of Abstracts; eds. J. Barek and J. Drašar J. (Prague: Czech Chemical Society, 2001), pp. 30-31.

[278] R. Pauliukaitė, R. Metelka, I. Švancara, A. Królicka, A. Bobrowski, E. Norkus, K. Kalcher, K. Vytřas, Screen-printed carbon electrodes bulk-modified with Bi2O3 or Sb2O3 for trace determination of heavy metals. Scientific Papers of the University of Pardubice, Series A; 10 (2004): 47-58.

[279] R. Metelka, M. Stočes, J. Krejčí, M. Bartoš, I. Švancara, P. Kotzian, and K. Vytřas, Development and characterization of new types of screen-printed bismuth-based sensors; in:

Sensing in Electroanalysis – 2, eds. K. Vytřas and K. Kalcher. (Pardubice: University of Pardubice, 2007), pp. 169-179.

[280] K. Kalcher, I. Švancara, M. Buzuk, K. Vytřas, and A. Walcarius, Electrochemical sensors and biosensors based on heterogeneous carbon materials. Monatshefte fur Chemie – Chemical Monthly, 140 (2009): 861-889.

[281] J. Růžička, C. G. Lamm, and J. C. Tjell, Selectrode™ – the universal ion-selective electrode: Concept, construction and materials. Analytica Chimica Acta, 62 (1972): 15-28.

[282] K. Vytřas and I. Švancara, Carbon paste-based ion-selective electrodes, in Sensing in Electroanalysis – 2, eds. K. Vytřas and K. Kalcher. (University of Pardubice, 2007), pp. 7-22.

[283] R. P. Buck, Electrochemical Methods: Ion-Selective Electrodes, in Water Analysis, Vol. II, eds. R. A. Minear and L. H. Keith. (Orlando: Academic Press, 1984), pp. 249-321.

[284] K. Vytřas, J. Kalous, V. Dlabka, and J. Ježková, Studies on potentiometric titrations using simple liquid membrane-based electrodes: Coated-wires versus carbon pastes. Scientific Papers of the University of Pardubice, Series A; 3 (1997): 307-321.

[285] K. Vytřas, J. Kalous, and J. Ježková: Automated potentiometry as an ecologic alternative to two-phase titrations of surfactants. Egyptian Journal of Analytical Chemistry, 6 (1997): 107-123.

[286] L. Tymecki, M. Jakubowska, S. Achmatowicz, R. Koncki, and S. Glab, Potentiometric thick-film graphite electrodes with improved response to copper ions. Analytical Letters, 34 (2001): 71-78.

[287] A. Abbaspour and S. S. M. Moosavi, Chemically modified carbon paste electrode for determination of copper(II) by potentiometric method. Talanta, 56 (2002): 91-96.

[288] M. Javanbakht, A. Badiei, M. R. Ganjali, P. Norouzi, A. Hasheminasab, and M. Abdouss, Use of organo-functionalized nanoporous silica gel to improve the lifetime of carbon paste electrode for determination of Cu(II). Analytica Chimica Acta, 601 (2007): 172-182.

[289] H. M. Abu-Shawish and S. M. Saadeh, A new chemically modified carbon paste electrode for determination of copper based on N,N'-disalicylidenehexametylene-diaminate copper(II) complex. Sensor Letters, 5 (2007): 565-571.

[290] M. J. Gismera, M. T. Sevilla, and J. R. Procopio, Flow and batch systems for copper(II) potentiometric sensing. Talanta, 14 (2008): 190-197.

[291] R. Chaisuksant, L. Pattanarat, and K. Grudpan, Naphthazarin modified carbon paste electrode for determination of copper(II). Microchimica Acta, 162 (2008): 181-188.

[292] M. H. Mashhadizadeh, K. Eskandari, A. Foroumadi, and A. Shafiee, Copper(II) modified carbon paste electrodes based on self-assembled mercapto compounds-gold-nanoparticle. Talanta, 76 (2008): 497-502.

[293] M. Javanbakht, M. R. Ganjali, P. Norouzi, A. Badiei, A. Hasheminasab, and M. Abdouss, Carbon paste electrode modified with functionalized nanoporous silica gel as a new sensor for determination of silver ion. Electroanalysis, 19 (2007): 1307-1314.

[294] M. N. Abbas and G. A. E. Mostafa, New triiodomercurate-modified carbon paste electrode for the potentiometric determination of mercury(II). Analytica Chimica Acta, 478 (2003): 329-335.

[295] M. H. Mashhadizadeh, M. P. Talakesh, Mahnaz, and H. M. M. Hamidian, A novel modified carbon paste electrode for potentiometric determination of mercury(II) ion. Electroanalysis, 18 (2006): 2174-2179.

[296] M. J. Gismera, J. R. Procopio, and M. T. Sevilla, Characterization of mercury-humic acids interaction by potentiometric titration with a modified carbon paste mercury sensor. Electroanalysis, 19 (2007): 1055-1061.

[297] M. J. Gismera, M. T. Sevilla, and J. R. Procopio, Potentiometric carbon paste sensors for lead(II) based on dithiodibenzoic and mercaptobenzoic acids. Analytical Sciences (Japan), 22 (2006): 405-410.

[298] M. M. Ardakani, M. A. Karimi, M. H. Mashhadizadeh, M. Pesteh, M. S. Azimi, and H. Kazemian, Potentiometric determination of monohydrogen arsenate by zeolite-modified carbon-paste electrode. International Journal of Environmental Analytical Chemistry, 87 (2007): 285-294.

[299] G. A. E. Mostafa, Development and characterization of ion selective electrode for the assay of antimony. Talanta, 71 (2007): 1449-1454.

[300] G. A. E. Mostafa and A. M. Homoda, Potentiometric carbon paste electrodes for the determination of bismuth in some pharmaceutical preparations. Bulletin of the Chemical Society of Japan, 81 (2008): 257-261.

[301] H. R. Pouretedal and M. H Keshavarz, Cyclam modified carbon paste electrode as

a potentiometric sensor for determination of cobalt(II) ions. Gaodeng Xuexiao Huaxue Xuebao (Chemical Research in Chinese Universities), 21 (2005): 28-31.

[302] M. Galík, M. Cholota, I. Švancara, A. Bobrowski, and K. Vytřas, A Study on stripping voltammetric determination of osmium(IV) at a carbon paste electrode modified in situ with cationic surfactants. Electroanalysis, 18 (2006): 2218-2224.

[303] M. F. S. Teixeira, E. T. G. Cavalheiro, M. F. Bergamini, F. C. Moraes, and N. Bocchi, Use of a carbon paste electrode modified with spinel-type manganese oxide as a potentiometric sensor for lithium ions in flow injection analysis. Electroanalysis, 16 (2004): 633-639.

[304] C. F. B. Coutinho, A. A. Muxel, C. G. Rocha, D. A. de Jesus, R. V. S. Alfaya, F. A. S. Almeida, Y. Gushikem, and A. A. S. Alfaya, Ammonium ion sensor based on SiO2 / ZrO2 / phosphate-NH4+ composite for quantification of ammonium ions in natural waters. Journal of Brazilian Chemical Society, 18 (2007): 189-194.

[305] M. N. Abbas, Chemically modified carbon paste electrode for iodide on the basis of cetyltrimethylammonium iodide ion-pair. Analytical Sciences (Japan), 19 (2003): 229-233.

[306] J. Tan, J. H. Bergantini, A. Merkoci, S. Alegret, and F. Sevilla, Oil dispersion of AgI/Ag2S salts as a new electroactive material for potentiometric sensing of iodide and cyanide. Sensors & Actuators B, Chemical; 101 (2004): 57-62.

[307] A. Abbaspour, M. Asadi, A. Ghaffarinejad, and E. Safaei, A selective modified carbon paste electrode for determination of cyanide using tetra-3,4-pyridinoporphyrazinato-cobalt(II). Talanta, 93 (2005): 931-936.

[308] M. Shamsipur, S. Ershad, N. Samadi, A. Moghimi, and H. Aghabozorg, A novel chemically modified carbon paste electrode based on a new mercury(II) complex for selective potentiometric determination of bromide ion. Journal of Solid State Electro-chemistry, 9 (2005): 788-793.

[309] A. Soleymanpour, E. H. Asl, and M. A. Nasseri, Chemically modified carbon paste electrode for determination of sulfate ion, SO42-, by potentiometric method. Electroanalysis, 18 (2006): 1598-1604.

[310] K. Vytřas, Potentiometric titrations based on ion-pair formation. Ion-Selective Electrode Reviews, 7 (1985): 77-164.

[311] H. Ibrahim, Y. M. Issa, and H. M. Abu Shawish, Chemically modified CPE for the potentiometric determination of Dicylomine hydrochloride under batch and in FIA conditions. Analytical Sciences (Japan), 20 (2004): 911-916.

[312] S. I. M. Zayed, New plastic membrane and carbon paste ion selective electrodes for potentiometric determination of Triprolidine. Analytical Sciences, 20 (2004): 1043-1048.

[313] H. Ibrahim, Chemically modified carbon paste electrode for the potentiometric FIA of Piribedil in pharmaceutical preparation and urine. Journal of Pharmaceutical and Biomedical Analysis, 38 (2005): 524-632.

[314] Y. M. Issa, H. Ibrahim, and H. M. Abu Shawish, Carbon paste electrode for the potentiometric flow injection analysis of Drotaverine in serum and urine. Microchimica Acta, 150 (2005): 47-54.

[315] M. N. Abbas and G. A. E. Mostafa, Gallamine-tetraphenylborate-modified carbon paste electrode for potentio-metric determination of gallamine triethiodide (Flaxedil). Journal of Pharmaceitical and Biomedical Analysis, 31 (2003): 819-826.

[316] K. I. Ozomena, R. I. Stefan, J. F. van Staden, and H. Y. Aboul Enein, Enantioanalysis of S-Perindopril using different cyclodextrin-based potentiometric sensors. Sensors & Actuators B, Chermical; 105 (2005): 425-429.

[317] R. I. Stefan van Staden, R. G. Bokretsion, K. I. Ozomena, J. F. van Staden, and H. Y. Aboul Enein, Enantioselective, potentiometric membrane electrodes based on different cyclodextrins as chiral selectors for the assay of S-Flurbiprofen. Electroanalysis, 18 (2006): 1718-1721.

[318] R. I. Stefan van Staden, R. G. Bokretsion, and K. I. Ozomena, Utilization of maltodextrin-based enantioselective, potentiometric membrane electrodes for the enantio-selective assay of S-Flurbiprofen. Analytical Letters, 39 (2006): 1065-1073.

[319] V. V. Cosofret and R. P. Buck, Drug-Type Substances analysis with membrane electrodes, Ion-Selective Electrode Reviews, 6 (1984): 59-121.

[320] K. Vytřas, The use of ion-selective electrodes in the determination of drug substances. Journal of Pharmaceutical and Biomedical Analysis, 7 (1989): 789-812.

[321] K. I. Ozomena and R. I. Stefan, Enantioselective potentiometric electrodes based on alpha-, beta-, and gamma-cyclodextrins as chiral selectors for

the assay of L-proline. Talanta, 66 (2005): 501-504.

[322] M. K. Amini, S. Shahrokhian, S. Tangestaninejad, and V. Mirkhani, Iron(II) phthalocyanine-modified carbon paste electrode for potentiometric detection of ascorbic acid. Analytical Biochemistry, 290 (2001): 277-282.

[323] B. N. Barsoum, W. M. Watson, I. M. Mahdi, and E. Khaled, Electrometric assay for the determination of acetylcholine using a sensitive sensor based on carbon paste. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 567 (2004): 277-281.

[324] M. K. Amini, J. H. Khorasani, S. S. Khaloo, and S. Tangestaninejad, Cobalt(II) salophen-modified carbon paste electrode for potentiometric and voltammetric determination of cysteine. Analytical Biochemistry, 320 (2003): 32-38.

[325] S. S. Khaloo, M. K. Amini, S. Tangestaninejad, S. Shahrokhian, and R. Kia, Voltam-metric and potentiometric study of cysteine at Co(II)-phthalocyanine modified carbon paste electrode. Journal of Iranian Chemical Society, 1 (2004): 128-135.

[326] S. Shahrokhian and J. Yazdani, Electrocatalytic oxidation of thioglycolic acid (TGA) at carbon paste electrode modified with Co(II)-phthalocyanine: Applications as a potentiometric sensor. Electrochimica Acta, 48 (2003): 4143-4148.

[327] M. K. Amini, S. Shahrokhian, S. Tangestaninejad, and I. M. Baltork, Voltammetric and potentiometric behavior of 2-pyridinethiol, 2-mercaptoethanol and sulfide at iron(II) phthalocyanine modified carbon-paste electrode. Iranian Journal of Chemistry & Chemical Engineering, 20 (2001): 29-36.

[328] H. Ibrahim and A. Khorshid, Modified Carbon paste sensor for cetyltrimethyl-ammonium ion based on its ion-associate with tetrachloropalladate(II). Analytical Sciences (Japan), 23 (2007): 573-579.

[329] J. Konvalina and K. Vytřas, The present use of (chrono)potentiometric stripping analysis (In Czech). Chemické Listy, 95 (2001): 344-352.

[330] I. Švancara and K. Vytřas, Voltammetry with carbon paste electrodes containing membrane plasticizers used for PVC-based ion-selective electrodes. Anal Chim. Acta, 273 (1993): 195-204.

[331] K. Vytřas and J. Konvalina, New possibilities of potentiometric stripping analysis based on ion-pair formation and accumulation of analyte at carbon paste electrodes (Preliminary note). Electroanalysis, 10 (1998): 787-790.

[332] K. Vytřas, Ion-pairing principles in the light of construction of ion-selective electrodes and sensors for both voltammetric and potentiometric stripping analysis, in Electroanalytical Chemistry and Allied Topics, eds. S. K. Aggarwal, H. S. Sharma, N. Gopinath, and D. S. C. Purushotham. (Mumbai: SAEST, 2000), pp. 127-130.

[333] J. Konvalina and K. Vytřas, Determination of thallium(III) at a carbon paste electrode with the aid of potentiometric stripping analysis, in Monitororing of Environmental Pollutants (in Czech), eds. K. Vytřas, J. Kellner, J. Fischer. (Univerzita Pardubice, 1999), pp. 99-104.

[334] I. Švancara, B. Ogorevc, S. B. Hočevar, and K. Vytřas, Perspectives of carbon paste electrodes in stripping potentiometry. Analytical Sciences (Japan), 18 (2002): 301-305.

[335] J. Konvalina, E. Khaled, and K. Vytřas, Carbon paste electrode as a support for mercury film in potentiometric stripping determination of heavy metals. Collection of Czechoslovak Chemical Communications, 65 (2000): 1047-1054.

[336] E. Khaled, J. Konvalina, K. Vytřas and H. N. A. Hassan, Investigation of carbon paste electrodes as supports for gold films in stripping potentiometry of Cu(II) and Hg(II) traces. Scientific Papers of the University of Pardubice, Series A; 9 (2003): 19-29.

[337] E. Tesařová and K. Vytřas, Potentiometric stripping analysis with antimony film electrodes. Electroanalysis, 21 (2009): 1075-1080.

[338] J.-M. Zen, A. S. Kumar, and D.-M. Tsai, Recent updates of chemically modified electrodes in analytical chemistry (Review). Electroanalysis, 15 (2003): 1073-1087.

[339] N. Y. Stozhko, N. A. Malakhova, M. V. Fyodorov, and Kh. Z. Brainina, Modified carbon-containing electrodes in stripping voltammetry of metals. Part I: Glassy carbon and carbon paste electrodes. Journal of Solid State Electrochemistry, 12 (2008): 1185-1204.

[340] N. Y. Stozhko, N. A. Malakhova, M. V. Fyodorov, and Kh. 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.

[341] K. Vytřas, K. Kalcher, I. Švancara, E. Khaled, J. Ježková, J. Konvalina, and R. Metelka, Recent applications of carbon paste electrodes

in potentiometry and stripping analysis; in Chemical Sensors and Analytical Methods, Book of Proceedings; eds. M. Butler, P. Vanýsek, and N. Yamazoe. (Pennigton: Electrochemical Society, 2001), pp. 277-283.

[342] A. Bobrowski and J. Zarebski, Catalytic adsorptive stripping voltammetry at film electrodes. Current Analytical Chemistry, 4 (2008), 191-201.

[343] C. Locatelli, Voltammetric analysis of trace levels of platinum group metals: Principles and applications (Review). Electroanalysis, 19 (2007): 2167-2175.

[344] J. Zima, I. Švancara, J. Barek, and K. Pecková, Carbon Paste Electrodes for the Determination of Detrimental Substances in Drinking Water, in: Progress on Drinking Water Research, eds. M. H. Lefebvre and M. M. Roux. (New York: Nova Science Publ., in press; https://www.novapublishers.com/catalog/product_info.php?cPath=23_597_703&products_id=7407&osCsid=cf1cb6ee708126d565c89956e2512406; January 30, 2008.

[345] Kh. Z. Brainina, Electroanalysis: From laboratory to field versions (Review). Journal of Analytical Chemistry, 56 (2001): 303-312.

[346] N. Serrano, J. M. Díaz Cruz, C. Ariño, and M. Esteban, Stripping chronopotentiometry in environmental analysis (Review). Electroanalysis, 19 (2007): 2039-2049.

[347] D. Lowinsohn and M. Bertotti, Electrochemical sensors: Fundamentals and applications in micro-environments. Quimica Nova, 29 (2006): 1318-1325.

[348] O. D. Renedo, M. A. Alonso Lomillo, and M. J. A. Martinez, Recent developments in the field of screen-printed electrodes and their related applications (Review). Talanta, 73 (2007): 202-219.

[349] Z. Navrátilová and P. Kula, Clay modified electrodes: Present applications and prospects. Electroanalysis, 15 (2003): 837-846.

[350] S. E. W. Jones and R. G. Compton, Fabrication and applications of nanoparticle-modified electrodes in stripping analysis. Current Analytical Chemistry, 4 (2008): 177-182.

[351] P. Kula and Z. Navrátilová, Anion exchange of gold chloro complexes on carbon paste electrode modified with montmorillonite for determination of gold in pharmaceuticals. Electroanalysis, 13 (2001): 795-798.

[352]. K.-S. Ha, J.-H. Kim, Y.-S. Ha, S.-S. Lee, and M.-L. Seo, Anodic stripping voltam-metric determination of silver(I) at a carbon paste electrode modified with S2O2-donor podand. Analycal Letters, 34 (2001): 675-686.

[353] S.-B. Zhang, X.-J. Zhang, and X.-Q. Lin, An ethylenediaminetetraacetic acid modified carbon paste electrode for the determination of silver ion. Fenxi Huaxue (Chinese Journal of Analytical Chemistry), 30 (2002): 745-747.

[354] M.-S. Won, J.-S. Yeom, J.-H. Yoon, E.-D. Jeong, and Y.B. Shim, Determination of Ag(I) ion at a modified carbon paste electrode containing N,N'-diphenyl oxamide. Bulletin of the Korean Chemical Socienty, 24 (2003): 948-952.

[355] C.-H. Yang, W.-S. Huang, and S.-H. Zhang, Highly sensitive electrochemical determination of trace Pb2+ and Ag+ in the presence of cetyltrimethylamonium bromide. Fenxi Huaxue (Chinese Journal of Analytical Chemistry), 31 (2003): 794-798.

[356] Y.-H. Li, H.-Q. Xie, and F.-Q. Zhou, Alizarin violet modified carbon paste electrode for the determination of trace silver(I) by adsorptive voltammetry. Talanta, 67 (2005): 28-33.

[357] A. Mohadesi and M. A. Taher, Stripping voltammetric determination of silver(I) at carbon paste electrode modified with 3-amino-2-mercapto quinazolin-4(3H)-one. Talanta, 71 (2007): 615-619.

[358] A. V. Laganovsky, Z. O. Kormosh, A. O. Fedorchuk, V. P. Sachanyuk, and O. V. Parasyuk, AgCrTiS4: Synthesis, Properties, and Analytical Application. Metallurgic Material Transactions – B, 39 (2008): 155-159.

[359] W. Huang, C. Yang, and S. Zhang, Anodic stripping voltammetric determination of mercury by use of a sodium montmorillonite-modified carbon-paste electrode. Analytical and Bioanalytical Chemistry, 274 (2002): 998-1001.

[360] Y.-T. Kong, G.-H. Choi, M.-S. Won, and Y.-B. Shim, Determination of Hg2(2+) ions using the specific reaction with a picolinic acid N-oxide modified electrode. Chemical Letters, 31 (2002): 54-55.

[361] A. Walcarius, M. Etienne, and C. Delacôte, Uptake of inorganic HgII by organically modified silicates: Influence of pH and chloride concentration on the binding pathways and electrochemical monitoring of the processes. Analytica Chimica Acta, 508 (2004): 87-98.

[362] M. Colilla, M. A. Mendiola, J. R. Procopio, and M. T. Sevilla, Application of a carbon paste electrode modified with a Schiff base ligand to mercury speciation in water. Electroanalysis, 17 (2005): 933-940.

[363] N. L. Dias and D. R. Do Carmo, Stripping

voltammetry of mercury(II) with a chemically modified carbon paste electrode containing silica gel functionalized with 2,5-dimercapto-1,3,4-thiadiazol. Electroanalysis, 17 (2005): 1540-1546.

[364] I. K. Tonle, E. Ngameni, and A. Walcarius, Preconcentration and voltammetric analysis of Hg(II) at carbon paste electrode modified with natural smectite-type clays grafted with organic chelating groups. Sensors & Actuators B, Chemical; 110 (2005): 195-203.

[365] N. L. D. Filho, D. R. do Carmo, F. Gessner, and A. H. Rosa, Preparation of a clay-modified carbon paste electrode based on 2-thiazoline-2-thiol-hexadecylammonium sorption for the sensitive determination of Hg(II) ion. Analytical Sciences, 21 (2005): 1309-1316.

[366] F. Dias, L. Newton, L. D. R. do Carmo, and A. H. Rosa, An electroanalytical application of 2-aminothiazole-modified silica gel after adsorption and separation of Hg(II) from heavy metals in aqueous solution. Electrochimica Acta, 52 (2006): 965-972.

[367] N. L. Dias, L. Caetano, D. R. do Carmo, and A. H. Rosa, Preparation of a silica gel modified with 2-amino-1,3,4-thiadiazole for adsorption of metal ions and electroanalytical application. Journal of Brazilian Chemical Society, 17 (2006): 473-481.

[368] N. L. Dias, D. R. do Carmo, and A. H. Rosa, Selective sorption of mercury(II) from aqueous solution with an organically modified clay and its electroanalytical application. Separation Sciences Technology, 41 (2006): 733-746

[369] L. H. Marcolino, B. C. Janegitz, B. C. Lourencao, and O. Fatibello, Anodic stripping voltammetric determination of mercury in water using a chitosan-modified sarbon paste electrode. Analytical Letters, 40 (2007): 3119-3128.

[370] H. Zejli, J. de Cisneros, I. N. Rodríguez, H. Elbouhouti, M. Choukairi, D. Bouchta, and K. R. Temsamani, Electrochemical analysis of mercury using a cryptofix carbon-paste electrode. Analytical Letters, 40 (2007): 2788-2798.

[371] M. C. Rizea, A. F. Danet, and S. Kalinowski, Determination of mercury(II) after its preconcentration on a carbon paste electrode modified with Cadion A. Revista de Chimie (Bucharest), 58 (2007): 266-269.

[372] E. Sar, H. Berber, B. Asct, and H. Cankitrtaran, Determination of some heavy metal ions with a carbon paste electrode modified by poly(glycidylmethacrylate-methyl-methacrylate-divinylbenzene) microspheres functionalized by 2-aminothiazole. Electro-analysis, 20 (2008): 1533-1541.

[373] I. Cesarino, G. Marino, J. D. Matos, and E. T. G. Cavalheiro, Evaluation of a carbon paste electrode modified with organofunctionalised SBA-15 nanostructured silica in the simultaneous determination of lead, copper and mercury ions. Talanta, 15 (2008): 15-21.

[374] J Ruiperéz, M. A. Mendiola, M. Tereza Sevilla, J. R. Procopio, L. Hernández, Application of a macrocyclic thio-hydrazone modified carbon paste electrode to copper speciation in water samples. Electroanalysis, 14 (2002): 532-539.

[375] A. Abbaspour and S. S. M. Moosavi, Chemically modified carbon paste electrode for determination of copper(II) by potentiometric method. Talanta, 56 (2002): 91-96.

[376] Y. Zhang, X. Q. Lu, K. M. Zhu, Z. H. Wang, and J. W. Kang, Voltammetric detection of traces of copper using a casbon paste electrode modified with tetraphenylporphyrin. Analytical Letters, 35 (2002): 369-381.

[377] C. T. Gautier, W. T. L. da Silva, M. O. O. Rezende, and N. El Murr, Sensitive and reproducible quantification of Cu^{2+} by stripping with a carbon paste electrode modified with humic acid. Journal of Environmental Science Health, Part A; 38 (2003): 1811-1823.

[378] S. Yang, X.-Q. Lu, Y.-H. Xue, X.-Q. Feng, and X.-F. Wang, 4-methoxy-2,5-bis(3,5-dimethylpyrazoyl)-1,3,5-triazine modified carbon paste electrode for trace Cu(II) determination by differential pulse voltammetry. Rare Metals, 22 (2003): 250-253.

[379] I. Jureviciutė and A. Malinauskas, Preparation of 2-mercaptobenzothiazole modified carbon paste electrode and its application to the stripping analysis of copper. Chemia Analyticzna (Warsaw), 49 (2004): 339-349.

[380] A. F. Danet, D. Neagu, M. P. Dondoi, and N. Iliescu, Anodic stripping voltammetric determination of copper(II) with salicylaldoxime carbon paste electrodes. Revista de Chimie (Bucharest), 55 (2004): 1-4.

[381] S. Kilinc Alpat, Ü. Yuksel, and H. Akçay, Development of a novel carbon paste electrode containing a natural zeolite for the voltammetric determination of copper. Electrochemistry Communications, 7 (2005): 130-134.

[382] N. Liu and J. F. Song, Catalytic adsorptive stripping voltammetric determination of copper(II) on a carbon paste electrode. Analytical and Bioanalytical Chemistry, 383 (20050: 358-364.

[383] E. C. Canpolat, E. Sar, N. Y. Coskun, and

H. Cankurtaran, Determination of trace amounts of copper in tap water samples with a calix[4] arene modified carbon paste electrode by differential pulse anodic stripping voltammetry. Electroanalysis, 19 (2007): 1109-1115.

[384] J. H. Yoon, G. Muthuraman, S. B. Yoon, and M. S. Won, Pt-nanoparticle incorporated carbon paste electrode for the determination of Cu(II) ion by anodic stripping voltammetry. Electroanalysis, 19 (2007): 1160-1166.

[385] B. C. Janegitz, L. H. Marcolino, and O. Fatibello Filho, Anodic stripping voltammetric determination of copper (II) in wastewaters using a carbon paste electrode modified with chitosan. Quimica Nova 30 (2007): 1673-1676.

[386] M. A. Taher, M. Esfandyarpour, S. Abbasi, and A. Mohadesi, Indirect determination of trace copper(II) by adsorptive stripping voltammetry with zincon at a carbon paste electrode. Electroanalysis, 20 (2008): 374-278.

[387] H. M. Abu Shawish, S. M. Saadeh, and A. R. Hussein, Enhanced sensitivity for Cu(II) ions by a salicylidine-functionalized polysiloxane carbon paste electrode. Talanta, 76 (2008): 941-948.

[388] S. K. Alpat, S. Alpat, B. Kutlu, O. Ozbayrak, and H. B. Buyukisik, Development of biosorption-based algal biosensor for Cu(II) using Tetraselmis chuii. Sensors & Actuators B, Chemical; 128 (2008): 273-278.

[389] K. H. Lubert and L. Beyer, Carbon paste electrode modified with the copper(II) complex of N-benzoyl-N',N'-Di-N-butyl-thiourea—voltammetric behavior and response to copper(II). Solvent Extraction and Ion Exchange, 26 (2008): 321-331.

[390] G. Marino, M. F. Bergamini, M. F. S. Teixeira, and E. T. G. Cavalheiro, Evaluation of a carbon paste electrode modified with organofunctionalized amorphous silica in the cadmium determination in a differential pulse anodic stripping voltammetric procedure. Talanta, 59 (2003): 1021-1028.

[391] E. Shams and R. Torabi, Determination of nanomolar concentrations of cadmium by anodic-stripping voltammetry at a carbon paste electrode modified with zirconium phosphated amorphous silica. Sensors & Actuators B, Chemical; 117 (2006): 86-92.

[392] I. Cesarino, G. Marino, J. D. R. Matos, and E.T.G.Cavalheiro, Using the organofunctionalised SBA-15 nanostructured silica as a carbon paste electrode modifier: Determination of cadmium ions by differential anodic pulse stripping voltammetry. Journal of Brazilian Chemical Society, 18 (2007): 810-817.

[393] M. H. Mashhadizadeh, K. Eskandari, A. Foroumadi, and A. Shafiee, Self-assembled mercapto-compound-gold-nanoparticle-modified carbon paste electrode for potentiometric determination of cadmium(II). Electroanalysis, 20 (2008): 1891-1896.

[394] Y.-F. Kuang, J.-L. Zou, L.-Z. Ma, Y.-J. Feng, and P.-H. Deng, Determination of trace Cd(II) in water sample using 1,10-phenanthroline-5,6-dione modified carbon paste electrode. Fenxi Huaxue (Chinese Journal of Analytical Chemistry), 36 (2008): 103-106.

[395] K. Fanta and B. S. Chandravanshi, Differential pulse anodic stripping voltammetric determination of cadmium(II) with N-p-chlorophenyl-cinnamohydroxamic acid modified carbon paste electrode. Electroanalysis, 13 (2001): 484-492.

[396] W. Yantasee, Y.-H. Lin, G. E. Fryxell, and B. J. Busche, Simultaneous detection of cadmium, copper, and lead using a carbon paste electrode modified with carbamoyl-phosphonic acid self-assembled monolayer on mesoporous silica (SAMMS). Analytica Chimica Acta, 502 (2004): 207-212.

[397] I. Adraoui, M. E. Rhazi, and A. Amine, Fibrinogen-coated bismuth film electrodes for voltammetric analysis of lead and cadmium using the batch injection analysis. Analytical Letters, 40 (2007): 349-368.

[398] L.-Y. Cao, J.-B. Jia, and Z.-H. Wang, Sensitive determination of cadmium and lead by using differential pulse stripping voltammetry with in-situ bismuth-modified zeolite doped carbon paste electrodes. Electrochimica Acta, 53 (2008): 2177-2182.

[399] C.-G. Hu, K.-B. Wu, X. Dai, and S.-S. Hu, Simultaneous determination of lead(II) and cadmium(II) at a diacetyl-dioxime modified carbon paste electrode by differential pulse stripping voltammetry. Talanta, 60 (2003): 17-24.

[400] M. G. Roa, S. M. T. Ramirez, M. A. R. Romero, and L. Galicia, Determination of lead and cadmium using a poly-cyclodextrin-modified carbon paste electrode with anodic stripping voltammetry. Analytical and Bioanalytical Chemistry, 377 (2003): 763-769.

[401] V. S: Ijeri and A. K. Srivastava, Voltammetric determination of lead at chemically modified electrodes based on crown ethers. Analytical Sciences (Japan), 17 (2001): 605-608.

[402] W. Yantasee, Y. H. Lin, T. S. Zemanian, and G. E. Fryxell, Voltammetric detection of lead(II) and mercury(II) using a carbon paste electrode

modified with thiol self-assembled monolayer on mesoporous silica (SAMMS). Analyst (UK), 128 (2003): 467-462.

[403] W. Ouangpipat, T. Lelasattarathkul, C. Dongduen, and S. Liawruangrath, Bioaccu-mulation and determination of lead using treated-pennisetum-modified carbon paste electrode. Talanta, 61 (2003): 455-464.

[404] S. Majid, M. El Rhazi, A. Amine, A. Curulli, and G. Palleschi, Carbon paste electrode bulk-modified with the conducting polymer poly(1,8-diaminonaphthalene): Application to lead determination. Microchimica Acta, 143 (2003): 195-204.

[405] A. Rahmani, M. F. Mousavi, S. M. Golabi, M. Shamsipur, H. Sharghi, Voltammetric determination of lead(II) using chemically modified carbon paste with bis[1-hydroxy-9,10,-anthraquinone-2-methyl]sulfide. Chemia Analyticzna (Warsaw), 49 (2004): 359-368.

[406] I. Adraoui, M. El Rhazi, A. Amine, L. Idrissi, A. Curulli, and G. Palleschi, Lead determination by anodic stripping voltammetry using a p-phenylenediamine modified carbon paste electrode. Electroanalysis, 17 (2005): 685-693.

[407] E. Shams, F. Alibeygi, and R. Torabi, Determination of nanomolar concentrations of Pb(II) using carbon paste electrode modified with zirconium phosphated amorphous silica. Electroanalysis, 18 (2006): 773-778.

[408] R. Torabi, E. Shams, M. A. Zolfigol, and S. Afshar, Anodic stripping voltammetric determination of lead(II) with a 2-aminopyridinated-silica modified carbon paste electrode. Analytical Letters, 39 (2006): 2643-2655.

[409] M. D. Vásquez, M. L. Tascón, L. Deban, Determination of Pb(II) with a dithizone-modified carbon paste electrode. Journal of Enviromental Sciences, 41 (2006): 2735-274

[410] R. E. Mojica Elmer, S. P. Gomez, J. R. L. Micor, and C. C. Deocaris, Lead detection using a pineapple bioelectrode. Philippine Agricultural Sciences, 89 (2006): 134-140.

[411] M. Ghlaci, B. Rezaei, and R. J. Kalbasi, High selective SiO2–Al2O3 mixed-oxide modified carbon paste electrode for anodic stripping voltammetric determination of Pb(II). Talanta, 73 (2007): 37-45.

[412] D. Sun, C.-D. Wan, G. Li, and K.-B. Wu, Electrochemical determination of lead(II) using a montmorillonite calcium-modified carbon paste electrode. Microchimica Acta, 158 (2007): 255-260.

[413] M. B. Gholivand and M. Malekian, Determination of trace amount of lead(II) in sweet fruit-flavored powder drinks by differential pulse adsorptive stripping voltammetry at carbon paste electrode. Electroanalysis, 20 (2008): 367-373.

[414] T. Mikysek, I. Švancara, K. Vytřas, and B. G. Banica, F. G, Functionalised resin-modified carbon paste sensor for the voltammetric determination of Pb(II) within a wide concentration range. Electrochemistry Communications, 10 (2008): 242-245.

[415] R. Y. A. Hassan, I. H. I. Habib, and H. N. A. Hassan, Voltammetric determination of lead (II) in medical lotion and biological samples ising chitosan-carbon paste electrode. International Journal of Electrochemical Sciences, 3 (2008): 935-945.

[416] J. Konvalina, Carbon Paste Electrodes in Stripping Potentiometry, Dissertation Thesis (in Czech). (Pardubice: University of Pardubice, 2001), pp. 75-85.

[417] H.-Q. Xie, Y.-H. Li, F.-Q. Zhou, H.-S. Guo, and B. Yi, Determination of trace tin by adsorptive voltammetry at an alizarin violet modified carbon paste electrode. Fenxi Huaxue (Chinese Journal of Analytical Chemistry), 29 (2001): 822-824.

[418] Y.-H. Li, H.-Q. Xie, F.-Q. Zhou, and H. S. Guo, Determination of trace tin by anodic stripping voltammetry at a carbon paste electrode. Electroanalysis, 18 (2006): 976-980.

[419] W.-S. Huang, Voltammetric determination of bismuth in water and nickel metal samples with a sodium montmoril-lonite (SWy-2) modified carbon paste electrode. Microchimica Acta, 14 (2004): 125-129.

[420] H.-S. Guo, Y.-H. Li, P.-F. Xiao, and N.-Y. He, Determination of trace amount of bismuth(III) by adsorptive anodic stripping voltammetry at carbon paste electrode. Analytica Chimica Acta, 534 (2005): 143-147.

[421] H.-S. Guo, Y.-H. Li, X.-K. Chen, L.-B. Nie and N.-Y. He, Determination of trace antimony(III) by adsorption stripping voltammetry at carbon paste electrode. Sensors, 5 (2005): 284-292.

[422] D. Watanabe, T. Furuike, M. Midorikawa, and T. Tanaka, Simultaneous determination of copper and antimony by differential pulse anodic stripping voltammetry with a carbon-paste electrode. Bunseki Kagaku (Japan Analyst), 54 (2005): 907-912.

[423] C. D. Mattos, D. R. do Carmo, M. F. de Oliveira, and N. R. Stradiotto, Voltammetric determination of total iron in fuel ethanol using a 1,10-fenanthroline / Nafion carbon paste-modified electrode. International Journal of

Electrochemical Science, 3 (2008): 338-345.
[424] H. R. Pouretedal and M. H Keshavarz, Cyclam modified carbon paste electrode as a potentiometric sensor for determination of cobalt(II) ions. Gaodeng Xuexiao Huaxue Xuebao (Chemical Research in Chinese Universities), 21 (2005): 28-31.
[425] M. M. Ardakani, Z. Akrami, H. Kazemian, and H. R. Zare, Accumulation and voltammetric determination of cobalt at zeolite-modified electrodes. Journal of Analytical Chemistry, 63 (2008): 184-191.
[426] P. S. González, V. A. Cortínez, and C. A. Fontan, Determination of nickel by anodic adsorptive stripping voltammetry with a cation exchanger-modified carbon paste electrode. Talanta, 58 (2002): 679-690.
[427] T. F. Oliveira, M. F. de Oliveira, B. V. Roberto, and S. N Ramos, Determination of nickel in fuel ethanol using a carbon paste modified electrode containing dimethylglyoxime. Microchimica Acta, 155 (2006): 397-401.
[428] M. Galík, I. Švancara, and K. Vytřas, Stripping voltammetric determination of platinum metals at carbon paste electrodes modified with cationic surfactants; in Sensing in Electroanalysis, eds. K. Vytřas and K. Kalcher. (University of Pardubice, 2005), pp. 89-107.
[429] I. Švancara, M. Galík, and K. Vytřas, Stripping voltammetric determination of platinum metals at a carbon paste electrode modified with cationic surfactants. Talanta, 72 (2007): 512-518.
[430] B. Rezaei; M. Ghiaci, and M. E. Sedaghat, A selective modified bentonite–porphyrin carbon paste electrode for determination of Mn(II) by using anodic stripping voltammetry. Sensors & Actuators B, Chemical; 131 (2008): 439-447.
[431] M. Rievaj, P. Tomčík, Z. Janošíková, D. Bustin, and R. G. Compton, Determination of trace Mn(II) in pharma-ceutical diet supplements by cathodic stripping voltammetry on bare carbon paste electrode. Chemia Analyticzna (Warsaw), 53 (2008): 153-161.
[432] I. Švancara, P. Foret, and K. Vytřas, A Study on the determination of chromium as chromate at a carbon paste electrode modified with surfactants. Talanta, 64 (2004): 844-852.
[433] A. M. Gevorgyan, S. V. Vakhnenko, and A. T. Artykov, Thick-film graphite-containing electrodes for determining selenium by stripping voltammetry. Journal of Analytical Chemistry, 59 (2004): 371-380.
[434] M. E. Sánchez Fernández, L. M. Cubillana Aguilera, J. M. Palacios Satander, I. Naranjo Rodríguez, and J. L. H. H.de Cisnéros, An oxidative procedure of the electrochemical determination of chromium(VI) using modified carbon paste electrodes. Bulletin of Electrochemistry, 21 (2005): 529-535.
[435] X.-W. Zheng, Z.-J. Zhang, Q. Wang, and H.-C. Ding, Electrogenerated chemiluminescence determination of Mo(VI) based on its sensitizing effect in electrochemical reduction luminol. Fenxi Huaxue (Chinese Journal of Analytical Chemistry), 31 (2003): 1076-1078.
[436] Y.-H. Li, Y.-X. Wang, and M.-H. Huang, Determination of trace vanadium by adsorptive stripping voltammetry at a carbon paste electrode. Electroanalysis, 20 (2008): 1440-1444.
[437] J.-N. Li, J. Zhang, P.-H. Deng, and J.- J. Fei, Carbon paste electrode for trace zirconium(IV) determination by adsorption voltammetry. Analyst (UK), 126 (2001): 2032-2035.
[438] J.-N. Li, J. Zhang, P.-H. Deng, and Y.-Q. Peng, Adsorption voltammetry of the mix-polynuclear complex of zirconium-calcium-alizarin red S at a carbon paste electrode. Analytica Chimica Acta, 431 (2001): 81-87.
[439] Y.-H. Li, Q.-L. Zhao, and M.-H: Huang, Adsorptive anodic stripping voltammetry of zirconium(IV)-alizarin red S complex at a carbon paste electrode. Microchimica Acta, 157 (2007): 245-249.
[440] S.-M. Liu, J.-N. Li and X. Mao, Stripping voltammetric determination of zirconium with complexing preconcentration of zirconium(IV) at a morin-modified carbon paste electrode. Electroanalysis, 15 (2003): 1751-1755.
[441] S.-M. Liu, J.-N. Li, and X. Mao, Determination of zirconium by second-order derivative adsorption voltammetry of zirconium (IV)-morin complex at a carbon paste electrode. Fenxi Huaxue (Chinese Journal of Analytical Chemistry), 32 (2004): 195-197.
[442] S. M. Liu, J.-N. Li, S.-J. Zhang, and J. Q. Zhao, Study on the adsorptive stripping voltammetric determination of trace cerium at a carbon paste electrode modified in situ with cetyltrimethylammonium bromide. Applied Surface Science, 252 (2005): 2078-2084.
[443] J.-N. Li, S.-M. Liu, Z.-H. Yan, X. Mao, and P. Gao, Determination of trace metals in industrial boron carbide by solid sampling optical emission spectrometry. Optimization of DC arc excitation. Microchimica Acta, 154 (2006): 241-243.
[444] M. Javanbakht, H. Khoshsafar, M. R. Ganjali,

P. Norouzi, A Badei, and A. Hashe-minasa, Stripping voltammetry of Ce(III) with a chemically modified carbon paste electrode containing functionalized nanoporous silica gel. Electro-analysis, 20 (2008): 203-206.

[445] S.-M. Liu, L.-H. Yi, and J.-N. Li, Studies on anodic adsorptive stripping voltammetry of gallium(III)-alizarin complexone at carbon paste electrodes and its application. Chinese Journal of Analytical Chemistry, 31 (2003): 1489-1492.

[446] Y.-H. Li, Q.-L. Zhao, and M.-H. Huang, Cathodic adsorptive voltammetry of gallium-alizarin red S complex at a carbon paste electrode. Electroanalysis, 17 (2005): 343-347.

[447] J. Zhang, J.-N. Li, and P.-H. Deng, Adsorption voltammetry of the scandium-alizarin red S complex onto a carbon paste electrode. Talanta, 54 (2001): 561-566.

[448] J.-N. Li, F.-Y. Yi, D.-S. Shen, and J. J. Fei, Adsorptive stripping voltammetric study of scandium-alizarin complexan complex at a carbon paste electrode. Analytical Letters, 35 (2002): 1361-1372.

[449] S.-M. Liu, J.-N. Li, and P. Gao, Anodic adsorptive stripping voltammetry at a carbon paste electrode for determination of trace thorium. Analytical Letters, 36 (2003): 1381-1392.

[450] J.-N. Li, F.-Y. Yi, Z.-M. Jiang, and J.-J. Fei, Adsorptive voltammetric study of Th(IV) alizarin complex at a carbon paste electrode. Microchimica Acta, 143 (2003): 287-292.

[451] K.-B. Ji and S.-S. Hu, Square wave voltammetric determination of trace amounts of europium(III) at montmoril-lonite-modified carbon paste electrodes. Collection of Czecho-slovak Chemical Communations, 69 (2004): 1590-1599.

[452] J.-N. Li, S.-M. Liu, X. Mao, P. Gao, and Z.-H. Yan, Trace determination of rare earths by adsorption voltammetry at a carbon paste electrode. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 561 (2004): 137-142.

[453] O. A. Farghaly, A novel method for determination of magnesium in urine and water samples with mercury film-plated carbon paste electrode. Talanta, 63 (2004): 497-501.

[454] N. Liu and J.-F. Song, Determination of free calcium at a carbon paste electrode adsorptive stripping voltam-metric method. Fenxi Huaxue (Chinese Journal of Analytical Chemistry), 33 (2005): 1261-1264.

[455] M. F. S. Teixeira, F. C. Moraes, O. F. Filho, and N. Bocchi, Voltammetric determination of lithium ions in pharma-ceutical formulation using a L-MnO2-modified carbon-paste electrode. Analytica Chimica Acta, 443 (2001): 249-255.

[456] M. F. S. Teixeira, F. C. Moraes, E. T. G. Cavalheiro, and N. Bocchi, Differential pulse anodic voltammetric determination of lithium ions in pharmaceutical formulations using a carbon paste electrode modified with spinel-type manganese oxide. Journal of Pharmaceutical and Biomedical Analysis, 31 (2003): 537-543.

[457] M. F. S. Teixeira, M. F. Bergamini, and N. Bocchi, Lithium ions determination by selective pre-concentration and differential pulse anodic stripping voltammetry using a carbon paste electrode modified with a spinel-type manganese oxid. Talanta, 62 (2004): 603-609.

[458] I. Szymanska, H. Radecka, J. Radecki, P. A. Gale, and C. N. Warriner, Ferrocene-substituted calix[4]pyrrole modified carbon paste electrodes for anion detection in water samples. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 591 (2006): 223-228.

[459] A. Walcarius, G. Lefévre, J. P. Rapin, G. Renaudin, and M. François, Voltammetric detection of iodide after accumulation by Friedel's salt. Electroanalysis, 13 (2001): 313-320.

[460] Q. He, J.-J. Fei, and S. H. Hu, Voltammetric method based on an ion-pairing reaction for the determination of trace amount of iodide at carbon-paste electrodes. Analytical Sciences (Japan), 19 (2003): 681-686.

[461] H. Hamidi, E. Shams, B. Yadollahi, and F. K. Esfahani, Fabrication of bulk-modified carbon paste electrode containing α-$PW_{12}O_{40}^{3-}$ polyanion supported on modified silica gel: Preparation, electrochemistry and electrocatalysis. Talanta, 74 (2008): 909-914.

[462] H. Wang, G. Xu, and S. Dong, Electrochemiluminescence of dichlorotris (1,10-phenanthroline) ruthenium(II) with peroxydisulfate in purely aqueous solution at carbon paste electrode. Microchemical Journal, 72 (2002): 43-48.

[463] J. B. Raoof, R. Ojani, and H. Karimi Maleh, Electrocatalytic determination of sulfite at the surface of new ferrocene derivative-modified carbon paste electrode. International Journal of Electrochemical Sciences, 2 (2007): 257-269.

[464] J. B. Raoof, R. Ojani, and H. Karimi-Maleh, Electrocatalytic determination of sulfite using 1-[4-(ferrocenyl-ethynyl)phenyl]-1-ethanone modified carbon paste electrode. Asian Journal of Chemistry, 20 (2008): 483-494.

[465] S. S. Kumar and S. S. Narayanan,

Electrocatalytic oxidation of sulfite on a nickel aquapentacyanoferrate modified electrode: Application for simple and selective determination. Electroanalysis, 20 (2008): 1427-1433.

[466] J. C. Quintana, L. Idrissi, G. Palleschi, P. Albertano, A. Amine, M. El Rhazi, and D. Moscone, Investigation of amperometric detection of phosphate: Application in seawater and cyanobacterial biofilm samples. Talanta, 63 (2004): 567-574.

[467] Y. Xue, X.-W. Zheng, and G.-X. Li, Determination of phosphate in water by means of a new electrochemi-luminescence technique based on the combination of liquid–liquid extraction with benzene-modified carbon paste electrode. Talanta, 72 (2007): 450-456.

[468] V. M. Ivama and S. H. P. Serrano, Rhodium-prussian blue modified carbon paste electrode (Rh-PBMCPE) for amperometric detection of hydrogen peroxide. Journal of Brazilian Chemical Society, 14 (2003): 551-555.

[469] C.-Y. Li, Y. Chen, C.-F. Wang, H.-B. Li, and Y.-Y. Chen, Electrocatalytic oxidation of H2O2 at a carbon paste electrode modified with a nickel (II)-5, 11, 17, 23-tetra-tert-butyl-25, 27-bis(Diethylcarbamoylmethoxy) calix[4]arene complex and its application. Wuhan University, Journal of Natural Sciences, 8 (2003): 857-860.

[470] Y. H. Lin, X. L. Cui, and L. Y. Li, Low-potential amperometric determination of hydrogen peroxide with a carbon paste electrode modified with nanostructured cryptomelane-type manganese oxides. Electrochemistry Communications, 7 (2005): 166-172.

[471] E. S. Ribeiro, S. L. P. Dias, Y. Gushikem, and L. T. Kubota, Cobalt(II) porphyrin complex immobilized on the binary oxide SiO_2/Sb_2O_3: electrochemical properties and dissolved oxygen reduction study. Electrochimica Acta, 49 (2004): 829-834.

[472] Q. He, C.-G. Hu, X.-P. Dang, Y.-L. Wei, and S. Hua, Electrocatalytic reduction of dioxygen at cetyltrimethyl-ammonium bromide modified carbon paste electrode. Electro-chemistry, 72 (2004): 5-8.

[473] M. P. Francisco, W. S. Cardoso, and Y. Gushikem, Carbon paste electrodes of the mixed oxide SiO2 / Nb2O5 prepared by sol–gel method: dissolved dioxygen sensor. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 574 (2005): 291-297.

[474] G.-H. Lu, D.-W. Long, T. Zhan, and H.-Y. Zhao, The electrochemical behavior of a ruthenium (II) - Polypyrindine complex and its electrocatalyis of nitrite. Fenxi Huaxue (Chinese Journal of Analytical Chemistry), 30 (2002): 1115-1118.

[475] S.-Q. Liu and H.-X. Ju, Nitrite reduction and detection at a carbon paste electrode containing hemoglobin and colloidal gold. Analyst (UK), 128 (2003): 1420-1424.

[476] M. Badea, A. Amine, M. Benzine, A. Curulli, D. Moscone, A. Lupu, G. Volpe, and G. Palleschi, Rapid and selective electrochemical determination of nitrite in cured meat in the presence of ascorbic acid. Microchimica Acta, 147 (2004): 51-58.

[477] W. S. Cardoso and Y. Gushikem, Electrocatalytic oxidation of nitrate on a carbon paste electrode modified with Co(II) porphyrion adsorbed on SiO2 / SnO2 / phosphate prepared by the sol-gel method. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 583 (2005): 300-306.

[478] L. Idrissi, A. Amine, M. El Rhazi, and F. E. Cherkaoui, Electrochemical detection of ntrite based on the reaction with 2,3-diaminonaphthalene. Analytical. Letters, 38 (2005): 1943-1955.

[479] R. Ojani, J. B. Raoof, and E. Zarei, Electrocatalytic reduction of nitrite using ferricyanide: Application for its simple and selective determination. Electrochim. Acta, 52 (2006): 753-759.

[480] R. Ojani, J. B. Raoof, and E. Zarei, Poly(o-toluidine) modified carbon paste electrode: A sensor for electrocatalytic reduction of nitrite. Electroanalysis, 20 (2008): 379-385.

[481] R. Ojani, V. Rahmanifar, and P. Naderi, Electrocatalytic reduction of nitrite by phosphotungstic heteropolyanion. application for its simple and selective determination. Electroanalysis, 20 (2008): 1092-1098.

[482] M. A. Kamyabi and F. Aghajanloo, Electrocatalytic oxidation and determination of nitrite on carbon paste electrode modified with oxovanadium(IV)-4-methyl salophen. Journal of Electroanalytical Chemistry and Interfacial Electro-chemistry, 614 (2008): 157-165.

[483] E. Casero, F. Pariente, E. Lorenzo, L. Beyer, and J. Losada, Electrocatalytic oxidation of nitric oxide at 6,17-diferrocenyldibenzo[b,i]5,9,14,18-tetraaza[14]annulen-Ni(II) modified electrodes. Electroanalysis, 13 (2001): 1411-1416.

[484] H. R. Zare and A. Nasirizadeh, Electrocatalytic characteristics of hydrazine and hydroxylamine oxidation at coumestan modified carbon paste electrode. Electroanalysis, 18 (2006): 507-512.

[485] C. A. Pessoa, Y. Gushikem, and S. Nagasaki,

Cobalt porphyrin immobilized on a niobium(V) oxide grafted - silica gel surface: Study of the catalytic oxidation of hydrazine. Electroanalysis, 14 (2002): 1072-1076.

[486] S. T. Fujiwara, Y. Gushikem, C. A. Pessoa, and S. Nakagaki, Electrochemical studies of a new iron porphyrin entrapped in a propylpyridiniumsilsesquioxane polymer immobilized on a SiO2 / Al2O3 surface. Electroanalysis, 17 (2005): 783-788.

[487] W. Siangproh, O. Chailapakul, R. Laocharoensuk, and J. Wang, Microchip capillary electrophoresis / electro-chemical detection of hydrazine compounds at a cobalt phthalo-cyanine modified electrochemical detector. Talanta, 67 (2005): 903-907.

[488] A. Abbaspour and M. A. Kamyabi, Electrocatalytic oxidation of hydrazine on a carbon paste electrode modified by hybrid hexacyanoferrates of copper and cobalt films. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 576 (2005): 73-83.

[489] J. B. Raoof, R. Ojani, and M. Ramine, Electrocatalytic oxidation and voltammetric determination of hydrazine on the tetrabromo-p-benzoquinone modified carbon paste electrode. Electroanalysis, 19 (2007): 597-603.

[490] C. D. C. Conceiçao, R. C. Faria, O. Fatibello, and A. A. Tanaka, Electrocatalytic oxidation and voltammetric determination of hydrazine in industrial boiler feed water using a cobalt phthalocyanine-modified electrode. Analytical Letters, 41 (2008): 1010-1021.

[491] Z. D. Chen and M. Hojo, Determination of phenol using a carbon paste electrode modified with overoxidized polypyrrole/polyvinylpyrrolidone films. Bunseki Kagaku, 56 (2007):669-673.

[492] X. Cheng, Q. J. Wang, S. Zhang, W. D. Zhang, P. G. He, and Y. Z. Fang, Determination of four kinds of carbamate pesticides by capillary zone electrophoresis with amperometric detection at a polyamide-modified carbon paste electrode. Talanta, 71 (2007):1083-1087.

[493] N. German, S. Armalis, J. Zima, and J. Barek, Voltammetric determination of fluoren-9-ol and 2-acetamidofluorene using carbon paste electrodes. Collection of Czechoslovak Chemical Communications, 70 (2005):292-304.

[494] S. Shahrokhian and M. Ghalkhani, Simultaneous voltammetric detection of ascorbic acid and uric acid at a carbon-paste modified electrode incorporating thionine-nafion ion-pair as an electron mediator. Electrochimica Acta, 51 (2006):2599-2606.

[495] A. G. Angelikaki and S. T. Girousi, Sensitive detection of tetracycline, oxytetra-cycline, and chlortetracycline in the presence of copper(II) ions using a DNA-modified carbon paste electrode. Chemia Analityczna, 53 (2008):445-454.

[496] J. Wang and X.-J. Zhang, Needle-type dual microsensor for the simultaneous monitoring of glucose and insulin. Analytical Chemistry, 73 (2001):844-847.

[497] J. B. Raoof, R. Ojani, and A. Kiani, Apple-modified carbon paste electrode: A biosensor for selective determination of dopamine in pharmaceutical formulations. Bulletin of Electrochemistry, 21 (2005):223-228.

[498] H. R. Zare, N. Nasirizadeh, M. Mazloum-Ardakani, and M. Namazian, Electrochemical properties and electro-catalytic activity of hematoxylin modified carbon paste electrode toward the oxidation of reduced nicotinamide adenine dinucleotide (NADH). Sensors and Actuators B-Chemical, 120 (2006):288-294.

[499] H. Qi, X.-X. Li, P. Chen, and C.-X. Zhang, Electrochemical detection of DNA hybridization based on polypyrrole/ss-DNA/multi-wall carbon nanotubes paste electrode. Talanta, 72 (2007):1030-1035.

[500] K. Jiao, Y. Ren, G. Y. Xu, and X. Z. Zhang, Voltammetric study on deoxyribonucleic acid immobilization and hybridization on stearic acid/aluminum ion films and the detection of specific gene related to phosphinothricin acethyl-transferase gene from Bacillus Amyloliquefaciens gene. Chinese Journal of Analytical Chemistry, 33 (2005):1381-1384.