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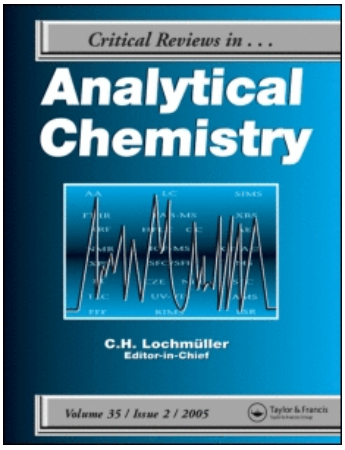

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Carbon Paste Electrodes in Modern Electroanalysis

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Dedicated to the Memory of Professor Jaroslav Heyrovský

on the Occasion of the 110th Anniversary of His Birth

ABSTRACT: Recent trends and advances in the electrochemistry with both unmodified and modified carbon paste electrodes are reviewed (247 refs.). Present day knowledge of their basic physico-chemical properties and characteristics is surveyed, including some specifics important in electrochemical measurements. Special attention is paid to the possibilities of carbon paste-based electrodes in electrochemical investigations and in modern electroanalysis of inorganic ions or molecules, organic substances, biologically important compounds, and pharmaceuticals.

KEY WORDS: carbon paste electrodes, electroanalysis, review.

ABBREVIATIONS: **ACV**, alternating current voltammetry; **A(C)SV,** anodic (cathodic) stripping voltammetry; **ADH,** alcohol dehydrogenase; **AdSV**, adsorptive stripping voltammetry; **AMP,** amperometry; **ASV**, anodic stripping voltammetry; **2-BP**, 2-butanone peroxide; **bpy**, bipyridyl; **CCSA**, constant current stripping analysis; **CMCPEs**, chemically modified CPE; **CNA**, chronoamperometry; **CNP,** chronopotentiometry; **CPEs**, carbon paste electrodes; **CPEEs,** carbon paste electroactive electrodes; **CP-ISEs,** carbon paste ion-selective electrodes; **CPyC,** cetylpyridinium chloride; **CP-UMEs,** carbon paste ultramicroelectrodes; **CTAB,** cetyltrimethylammonium bromide; **CV**, cyclic voltammetry; **DCSV**, direct current stripping voltammetry; **DME,** dropping mercury electrode; **DPDTC**, diphenyldithiocarbamate; **DPA(C)SV,** differential pulse anodic (cathodic) stripping voltammetry; **EIA**, enzyme immunoanalysis; **FIA,** flow injection analysis; **FDH,** fructose dehydrogenase; **GIDH,** glycerol dehydrogenase; **GOD**, glucose oxidase; **HRP,** horseradish peroxidase; **HTTA,** thiophenecarboxylic trifluoroacetone; **LADH**, lipoamide dehydrogenase; **LDH**, lactate dehydrogenase; **LOd**, lactate oxidase; **LSV**, linear scan voltammetry; **MCPE**, modified carbon paste electrode; **NPOE**, 2-nitrophenyl octyl ether; **NMP**, *N*-methylphenazonium; **NiTsPc**, nickel tetrasulfonated phthalocyanine; **Pf,** *Pseudomonas fluorescens*; **PAP**, poly(o-aminophenol); **PEG**, polyethylene glycol; **PEI,** polyethyleneimine; **PNA**, peptide nucleic acid; **POL,** polarography; **PPD**, poly(*o*-phenylenediamine); **PQQ**, pyrrolo quinoline quinone; **PSA**, potentiometric stripping analysis; **PVP**, poly(4-vinylpyridine); **R.S.D.,** relative standard deviation, **Septonex,** 1-ethoxycarbonylpentadecyl-trimethylammonium bromide; **SPEs,** screen printed electrodes; **SPPM**, spectrophotometry; **ST,** titanized silica gel; **SWV**, square wave voltammetry; **TCP,** tricresyl phosphate; **TEMPO**, 2,2,6,6-tetramethylpiperydinyloxy; **V**, voltammetry.

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I. INTRODUCTION

In 1958, shortly before Professor Jaroslav Heyrovský received the Nobel Prize for Chemistry and his polarographic method became known worldwide, Adams reported on a new type of electrode.[1] The proper material of this sensor was formed by a mixture of carbon powder with a liquid nonelectroactive binder and called simply "carbon paste". It is interesting to notice that the discovery of carbon paste had closely been connected with Heyrovský's polarography and his dropping mercury electrode (DME). Several years after the carbon paste had been first introduced, its inventor admitted that his original idea was to develop "dropping carbon electrode".[2] Such a sensor was to be constructed similarly like the DME, that is, from a reservoir with suspension of carbon powder in a liquid and connected to a capillary, allowing one to obtain periodically renewable droplets of "carbon electrode". The author hoped that this set-up could serve as a certain analogy to the DME for anodic oxidations of organic compounds where mercury-based electrodes were inapplicable. Although practical experiments with carbon dropping electrode failed, the above-mentioned mixture of carbon powder and a binder prepared in thicker consistency was presented as promising electrode material. Its perspectives were emphasized already in the pioneering report,[1] and the oncoming boom in the field of electrochemical sensors has confirmed such anticipations.

Carbon paste electrodes (CPEs) and related sensors underwent an attractive development. Its inspiring history, illustrating potentialities of electrochemistry as a whole and revealing numerous connections with the current trends, can be overviewed on some important moments and periods:

- *1959–1963: Introduction of Carbon Paste and Its First Applications*. The very beginnings of the electrochemistry at CPEs were associated with the research activity of Adams's group. They postulated first basic characteristics of carbon pastes and some rules for their usage. The initial stage is typical for a rather specialised field of applications; CPEs having been employed mainly in studying the mechanisms of electrode reactions of various organic compounds.[3] In that period, reviewed by Adams himself,[4] the publications of other authors had appeared only very rarely.
- *1964,1965: First Modifications of Carbon Pastes*. The composite nature of carbon pastes and their easy preparation were undoubtedly stimulating factors for altering the properties of originally binary mixtures by another component admixed in. Again, in Adams's laboratory,[3] two such novel carbon pastes had been born. The first type[5] containing an organic substance dissolved in the binder and serving to the study the electrode behavior of the substance itself is considered as a pioneering step in the field of carbon paste electroactive electrodes. The second one[6] prepared by rubbing a modifier into the paste had then represented apparently the first case when direct modification of a CPE had resulted in the aimed improving of the electrode performance.
- *1974: Appearance of Carbon Pastes with Electrolytic Binder*. The replacement of common non-electroactive pasting liquids by electrolyte

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solutions[7] opened the avenue for a specific branch of the electrochemistry of carbon paste electroactive electrodes, allowing one to investigate the redox behaviour as well as various structural and morphological changes of inorganic compounds dissolved directly in the electrolyte. At present, studies of this kind usually belong to a special field of the so-called solid-state electrochemistry.[8]

- *1981–1990: The Era of Chemically Modified Carbon Pastes*. The attempts to utilize favorable mechanical and electrochemical properties of carbon pastes for the preparation of a new generation of sensors culminated at the beginning of the 1980s. Modification of a carbon paste by impregnating the carbon particles with methanolic solution of dimethylglyoxime[9] represents another milestone in the history of CPEs. It was a first attempt when classic analytical reagent had served as selective modifier, thus initiating a very successful role of chemically modified carbon paste electrodes (CMCPEs) in electrochemical analysis, as shown in a review covering this period.[10] Since that time, the number of publications dealing with chemically modified carbon paste-based electrodes started to grow exponentially and this trend continued over the next decade when other review articles had appeared.[11-15]
- *1988: Biologically Modified Carbon Pastes as Enzymatic Biosensors*. Hand in hand with a rapid development of CMCPEs, favorable mechanical and electrochemical properties of carbon pastes were tested for the preparation of special sensors containing enzymes allowing one to monitor some enzymatically catalysed reactions of biologic substances. The priority in this area can be attributed to Matuszewski and Trojanowicz[16] who have reported on a CPE with glucose oxidase blended into the carbon paste. This way of anchoring enzymes to an electrode material immediately attracted biochemists and carbon paste-based enzymatic biosensors had rapidly come to the fore. Retrospectively, they have occupied a very significant position in the family of CPEs when having finally formed a specific independent area similarly like electroactive carbon pastes in the electrochemistry of solids. A comprehensive overview mapping the whole genesis of such biosensors was presented by Gorton,[17] some other articles have appeared more recently.[18,19]
- *1991: Robust Carbon Composites Competing with Carbon Pastes*. Probably the ultimate significant point in hitherto commented chronology is a starting inclination to replace soft carbon pastes by materials of related character with respect to ease of modifying, but with more robust matrix.[20] Such a substrate has proved itself to be convenient for preparation of screen-printed electrodes (SPEs) that co-determine the newest trends in electrochemistry.[21]

The entire history of the electrochemistry with carbon paste-based electrodes is documented on approximately 1000 original papers when about 50 to 100 publications have arrived annually in the last 5 years.[22] In this article, the recent period of 1995 to 2000 was summarized with particular interest in order to cover the current trends in the topic since the last comprehensive review papers of similar focus had been published.[13,15]

II. CARBON PASTE AS ELECTRODE MATERIAL

A. Unmodified Carbon Pastes

Due to a rapid development of various types of modified carbon pastes, it was necessary to introduce a new adequate specification. Classically, all carbon pastes were binary mixtures prepared from carbon powder and organic liquid of nonelectrolytic character. Now, such mixtures are classified as bare ("virgin") or, more often, as unmodified carbon pastes.[13]

For long time, the choice of the main constituents for carbon pastes was rather monotonic and, in fact, there was no reason to seek new alternative materials. The properties of conventional paste mixtures from spectroscopic graphites and paraffin oils were found satisfactory for a majority of applications, including very popular modifications. Nevertheless, also in this area, the recent years have brought some interesting innovations.

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The proper electroactive moiety in carbon pastes is still graphite powder with micrometric particles of high purity and distribution uniformity. Such materials are now commonly available on the market as spectroscopic graphites and may be ordered from annual catalogues of renowned distributors such as *Aldrich, Sigma, Fluka,* or *Riedel-de-Haen*. These products absolutely prevail in the composition of carbon pastes used in recent years. According to the authors' own experience, especially suitable are "RW-B" or "Sigradur" graphites (Ref. 13 and refs. therein) offered by factories specialized in production of carbon materials. Usually, graphite powders are not pretreated further prior to use. Some procedures made in the past and concentrated on lowering undesirable absorption capabilities of some commercial graphites[23] seem to be too complicated compared to their benefit. From a present day's point of view, it is more effective to perform some test experiments with newly made pastes that reveal excessive absorptiveness of some graphites.[24] Then, it is better to choose some commercially available powders with specially pretreated surface exhibiting only negligible absorption capability.[25]

As nonelectrolytic binders, two trademark products of spectroscopic paraffin oils are predominantly used. Nujol® (*Aldrich*) and Uvasol® (*Merck*) figure in experimental sections of almost all recent papers (Refs. 13-15,17 and refs. therein). These non-polar pasting liquids fulfill all the important criteria; both are sufficiently chemically inert, insulating, nonvolatile, water-immiscible, and forming paste mixtures of fine consistency. However, there also are some less favorable characteristics of pastes made from both oils; for instance, their vulnerability in media with organic solvents.[6,11] In this respect, better experience has been gained with silicone oil-based carbon pastes that also represent quite common type of pasting liquid.[13,26] Another group of binders are some liquid organophosphates. Although these polar substances had formerly been used as carbon paste modifiers,[10,13] their use as binding liquids is relatively new.[27] Recent time has brought some interesting applications of these pastes in practical electroanalysis.[28-30] Their attractive property is a high ion-pairing ability. However, one has to be aware of their lesser stability and of rather atypical signal-to-noise characteristics requiring special pretreatments.

Numerous practical aspects concerning the preparation of carbon pastes, the choice of suitable components and their ratio, as well as some basic rules of using newly prepared CPEs have been reviewed more recently.[26] This review also illustrates that traditional manual procedures of homogenizing pastes in a mortar are still preferred despite the fact that ready-to-use carbon paste mixtures are commercially available (e.g., from *Metrohm*[31]). The popularity of laboratory preparation of carbon pastes can be explained simply — hand mixing of carbon pastes is advantageous because the analyst can by himself choose the individual components as well as their mutual ratio. This is particularly valid for the preparation of modified carbon pastes.

B. Modified Carbon Pastes

The base of modified carbon pastes is usually a mixture of powdered graphite and nonelectrolytic binder.[10,13,15] Another constituent in the mixture is then a modifier itself. Modifying agent is usually one substance, but the pastes can also be modified with two or even more components, which is the case of carbon paste-based biosensors containing enzyme (or its carrier) together with appropriate mediator (Ref. 17 and refs. therein) or CMCPEs with a mixture of two modifiers.[32] The amount of modifier in the paste usually varies between 10 to 30% (w/w), depending on the character of modifying agent and its capability of forming enough active sites in modified paste (e.g., functional groups immobilised at the electrode surface[28] or molecules of an extractant in the bulk[29,30]).

In general, the main reason to modify an electrode is to obtain qualitatively new sensor with desired, often predefined properties. Regarding this, carbon pastes undoubtedly represent one of the most convenient materials for the preparation of modified electrodes.[10] In contrast to relatively complicated modifications of solid substrates, the preparation of CMCPEs is very simple, typically by means of various alternative procedures. The modifier can be dissolved directly in the

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binder[13,32,33] or admixed mechanically to the paste during its homogenization.[13,34,35] It is also possible to soak graphite particles with a solution of a modifier, and after evaporating the solvent use the impregnated carbon powder.[9,36] Finally, already-prepared pastes can be modified *in situ*.[28] Whereas direct modifications obviously provide special sensors for one-purpose use, considerate *in situ* approaches offer a possibility to employ the same carbon paste for repetitive modifications with different agents.

Kalcher[10] has made a classification of four possible functions of modifiers that can be summarized in this way:

- preferential entrapment of desired species (e.g., preconcentration in stripping analysis)
- mediation of electrode reactions via immobilized molecules or their fragments
- acting in catalytic phenomena (catalytic electrochemical responses)
- alteration of the surface characteristics of a CPE

When considering these possibilities in combination with the above-mentioned flexibility of carbon pastes, it is not surprising that in the last decade a number and a diversity of substances used for the preparation of CMCPEs have grown in a geometric order. Among modifiers recently used one can find single compounds,[34] sophisticated chemical agents,[32,37-46] special inorganic materials and matrices,[47-62] or living organisms.[63-66] Typical modifiers can be divided into several groups.

- *Chemical Compounds and Analytical Reagents*. Powdered HgO (yellow form) as a modifier was successfully applied as renewable source of mercury film generated at the carbon paste in anodic stripping voltammetry of heavy metals.[34] Classic analytical reagents like dimethylglyoxime,[37] 8-hydroxyquinoline,[32,38,39] or derivatives of 2-naphthol[40,41] have been used as selective modifiers for adsorptive accumulation of selected ions, which is, regarding CPEs, a practice with long tradition.[10-15] Some compounds of this type contained in the paste may be slightly soluble in water and hence have to be stabilised against "bleeding" (dissolution) by fixing with an additional adhesion agent.[32]
- *Ion-Exchangers*. A group of substances with ion-pairing properties has always held a significant position among CMCPEs.[10-15] Recently, cetyltrimethylammonium bromide (CTAB) served again as a reliable modifier to preconcentrate and detect some less common metal species,[42-45] whereas chromatographic packing agent "Amberlite IRC-718" can be recommended for speciation analysis.[46]
- *Clay Minerals (Zeolites and Familiar Materials*[47-57]*)*. These substances of both natural and synthetic origin represent a group of hydrated crystalline aluminosilicates that are capable of acting as both ion-exchangers and "ion-traps" excluding ion species of inappropriate size. Moreover, zeolites[51,52] and related materials (e.g., montmorrilonite,[48,49,53] or vermicullite[47,50]) also exhibit adsorption and catalytic capabilities. Thanks to these synergistic effects, zeolites have become apparently the most frequently used modifiers of recent years as documented in Walcarius's review.[67] Carbon pastes with dispersed zeolites (up to 50% w/w) can be employed to study the behaviour of numerous inorganic ions in their natural environment when zeolite-modified CPEs are applicable to their speciation in real samples.
- *Humic Substances*.[55-59] Extremely voluminous molecules of humic acid and humates are also known as very effective ion-exchangers of natural origin. CPEs modified with humates have been shown to be very convenient to detect noble metal ions.
- *Silica and Silica-Containing Matrices*.[60-62] Current possibilities in production of new synthetic pure and grafted silicas are reflected in intensive development of CMCPEs containing these materials. Carbon pastes based on silica with immobilized inorganic films or organic functional groups permit one to carry out selective preconcentration of various species or their detection via catalytic response. Principles and applications of silica-modified electrodes, including carbon paste sensors,

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were outlined in a review compiled again by Walcarius.[68]

- *Substrates from Living Organisms*.[63-66] Sometimes, carbon pastes were also selected as convenient electrode material for modifying with biomass (Ref. 10-15 and refs. therein). Such trends still continue as can be seen on the use of peat moss[63] or algae[64] or, more recently, bacteria[65] and chitin (horny substance forming insect bodies[66]).

Carbon paste electroactive electrodes (CPEEs) can also be regarded as a special kind of modified sensors, although species contained in the paste do not play role of classic modifiers. The proper paste of CPEEs is formed by graphite particles bounded with a small portion of strong electrolyte (e.g., 2 *M* H_2SO_4[69] or KOH[70]). Newer approaches[35] tend to omit these traditionally used solutions as very aggressive, and attacking the substances admixed into the paste prior to the commencement of the electrochemistry as such.[8]

Finally, even robust ("solid phase") carbon pastes are more or less related to a family of modified electrodes because they have been also modified. One of the first pastes of this kind was prepared from fenanthrene[71] that was melted, mixed with graphite, and this mixture left to harden. Then, after packing in a holder, the paste was modified *in situ*. Such solid-like pastes represent a transient element between ordinary carbon paste mixtures and composite solid electrodes[15] and, as already mentioned, similar matrices seem to be perspective electrode material for screen-printed electrodes designing in the laboratory.

III. SOME TRENDS IN ELECTROCHEMICAL INVESTIGATIONS WITH CARBON PASTE ELECTRODES

A. Construction of Carbon Paste Electrodes

Typically soft carbon pastes have to be packed into suitable electrode bodies. Their construction, of course, depends on the type of electrode (e.g., whether a macro- or a microvariant is to be used) or after the character of measurement and the overall electrode cell arrangement (batch vs. flow systems).

In common experiments, carbon paste electrode holders did not undergo any dramatic development in their functioning and design[13,15] Still, the most popular bodies are various glass-, PVC tubes, and Teflon® rods whose end-hole can be easily refilled with a new portion of carbon paste (e.g.,[31,35,42-45,71]). Also, simple constructions equipped with a piston for extrusion of the paste[24,34,51] are frequently employed, including commercially available products from *Metrohm*.[13] For common CPEs, the actual diameter of the end-hole forming the proper carbon paste surface is being chosen from 2 to 10 mm, which is convenient for a majority of electrochemical measurements.[2,26] Both above-mentioned construction variants of CPEs for batch measurements allows to utilize fully one of the most valuable property of carbon pastes — easy and quick surface renewal, or, in necessary cases, even removal and renewing of a larger portion of the paste. Practically immediate surface renewal can be achieved by wiping some paste off using a wet filter paper. If being performed carefully,[24,26] this procedure provides surface reproducibility nearly comparable to that attained by rather time-consuming circle-like polishing of the electrode surface on a paper pad.[53]

More interesting designs of CPEs are usually reported in association with carbon paste-based flow cells,[72] electrochemical detectors,[73] coulometric,[74] amperometric,[75,76] and potentiometric[77] sensors, or some sensing devices for special measurements *in vivo*.[78,79] For instance, electrochemical investigations on modulation of the electrode response can be performed with periodically renewed carbon paste by means of a special cell with doubled carbon paste filling.[76] Among others, such a design with intimate surface renewal is very effective in analysis of organic and biological materials where the surface of an electrode may readily be poisoned either with matrix constituents or by electrode reaction products.[13,72]

A carbon paste electrode with unusually large surface diameter of 20 mm was reported to be convenient for coulometric measurements.[74] To the authors' knowledge, this is the largest active sur-

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face that has ever been reported for a CPE used in practical measurements. On the contrary, some authors have described single CPEs whose tip could be measured in micrometers.[79] These miniaturized sensors had been popular in the 1980s, being introduced again by Adams in brain electrochemistry *in vivo*.[80] Their recent applications are only occasional,[81-83] which is a fate quite similar to that of carbon paste-based ultramicroelectrodes (CP-UMEs[84]). CP-UMEs designed as a membrane with micrometric pores filled up with a carbon paste were found to exhibit sigmoidal I-E curves typical for microelectrode arrays. In contrast to this, ordinary CPE give rise to normally shaped cyclic voltammograms. This has revealed that whereas CP-UMEs offer an ensemble of isolated carbon active sites thanks to their separation in the membrane pores, the corresponding active sites around carbon particles in the reference carbon paste are merged in one large surface region behaving like that of common solid macroelectrodes.[84,85]

Today practically forgotten ensembles of CP-UMEs were, however, worth to mention because of their significant contribution to clarifying the behavior of carbon paste electrodes with insulating binder. Some newer insights into the important aspects of the characterization of CPEs are summarized below.

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B. Some Advances in Characterisation of Carbon Pastes

1. Physico-Chemical and Electrochemical Properties

The nature and behavior of common carbon pastes can be portrayed by means of the following physico-chemical characteristics:

- *heterogeneity* (composite character)
- *lipophility* (hydrophobicity)
- *low ohmic resistance* (high conductivity)
- *instability* in nonaqueous solutions (disintegration)
- *ageing* effects (limited life-time)

These properties are closely connected with a specific microstructure of carbon pastes. Recently, some newly made real images of the carbon paste microstructure have been presented based on scanning electron and optical microscopic observations.[25,31,34,86] The images have confirmed the conclusions of the previous studies (see review[25]) that carbon pastes represent mixtures with rather unconsolidated structure where the graphite particles are practically covered with a very thin film of the binder. Nevertheless, the individual graphite particles are apparently in some physical contact beneath the binder layer, which may explain a very low ohmic resistance of most carbon pastes (varying in ohms, max. in tens of ohms[24-26]). An alternative interpretation of their surprisingly high conductivity can be due to a "tunnel effect" similar to that known for semiconductors.[87]

The hydrophobicity is apparently the most frequently reported property of carbon paste-based electrodes.[11-15,17] The lipophilic character of both CPEs and CMCPEs results, among others, in specific reaction kinetics of many electrode reactions of organic redox systems. (Behind their moderated rates is the repelling effect of pasting liquid hindering the access of hydrophilic species involved in the electrode reactions toward the carbon paste surface.[13]) Reaction kinetics can also be affected by the quality of graphite itself similarly as with related carbon solid electrodes.[4] Finally, even the carbon-to-pasting liquid ratio can play a significant role in this respect. Detailed interpretation of these phenomena and its consequences is, however, out of the scope of this article and can be found in the fundamental report from Adams et al.[88] or in some newer papers.[24,87]

Carbon paste mixtures may undergo significant changes in time ("aging" of CPEs). This feature, in the literature being mentioned only rarely, has been found characteristic for carbon pastes made of some more volatile binders such as organo phosphates.[27] Such undesirable behavior has confirmed logical assumptions that aging of carbon pastes is associated solely with the properties of the binder. Until now, any similar role of graphite has not yet been reported.

2. Specifics of Carbon Pastes

Physico-chemical properties of carbon pastes are always mirrored in the overall electrochemi-

cal behaviour of CPEs, resulting in some special features and benefits:

- *very low background currents* (favorable signal-to-noise ratio),
- *individual polarizability* (with variable potential window),
- *specific reaction kinetics* (affected by both carbon paste constituents),
- *electrode activity at the carbon paste surface* as well as *in the carbon paste bulk,*
- variability in utilizing *various interactions and their synergistic effects* at both CPEs and CMCPEs (electrolysis, catalysis, adsorption, extraction, ion-pairing, and their combination)
- various alternative procedures for *pretreating, conditioning and regenerating* the electrode surface and carbon paste itself.

The individual specific features are discussed in all fundamental reviews devoted to carbon paste-based electrodes[10-15,17] or dealing exclusively with their characterization.[26,87] Herein, only selected aspects are noticed and commented in more detail.

3. Processes and Interactions at the Carbon Paste Surface and in the Carbon Paste Bulk

For a majority of substances the electrode processes connected with mass and charge transfer at CPEs are usually interpreted as interactions at the interface "binder layer | graphite particles | solution (electrolyte)", which applies also to the above-mentioned electrolytic activations. Interactions of this type can be monitored either as both faradayic and nonfaradayic current signals in voltammetry, coulometry, and amperometry, or by means of chemical equilibria in potentiometric measurements. Some models combine the principles of mass- and charge transfer with specific transport conditions at CPEs. This is the case of so-called "membrane model" assuming extraction (penetration) of some highly lipophilic molecules through the liquid binder layer.[89]

a. Electrolytic Phenomena at Carbon Pastes

Polarization of Bare Carbon Pastes. In voltammetry, the polarizability of carbon pastes was for a long time believed to depend on the functioning of graphite and the role of pasting liquid was considered as less significant, influencing positively only the background currents level. Recent studies on comparing several CPEs prepared from identical graphite and different liquids have shown that polarization limits of a CPE can be controlled effectively even via the choice of the binder. For example, tricresyl phosphate-based carbon paste was found to exhibit extreme polarization limits and could be polarized from –2 to +2 V in an ammonia buffer.[27] Such an interval was absolutely unattainable with CPEs from Nujol- and silicone oils and, it is atypically broad for any electrode in aqueous media. A very wide potential window, especially in the negative potential range, was obtained also with a carbon paste containing lipophilic phthalate.[27] Thus, it suggests that this property has some general validity and seems to be useful to employ these carbon pastes as the working electrodes for cathodic reductions. For this purpose, paraffin and silicone oil-based CPEs do not offer very good performance and are recommended rather for measurements within the anodic potential range.[2,3,11-15] Cathodic polarizations with common CPEs suffer, besides their higher background due to a limited hydrogen overpotential, from the unwanted response of oxygen contained in the paste.[2,3,13] Coincidentally, lipophilic esters-containing carbon pastes were found to exhibit — during cathodic polarization — atypically low signal for oxygen.[27] Its lowered content was attributed to a specific carbon paste structure.[25] Also, this observation has implied a suitability of such pastes for measurements at negative potentials.

Electrolytic Activation. Either anodic and cathodic polarizations performed at extreme potentials or anodic-cathodic cycling are still popular procedures to pretreate the surface of carbon electrodes, including CPEs.[90]

In the case of carbon pastes, processes and phenomena associated with activation at positive potentials (anodization) are mostly interpreted as

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a partial oxidation of the surface of graphite particles exposed to the solution. During their activation, various oxygen-containing functional groups are formed and instantaneously protonated (see Figure 1).

Owing to this, these fragments become markedly hydrophilic and repel hydrophobic molecules of the binder. Thus, anodization leads to a removal of the lipophilic layer of pasting liquid and results in the principal changes of surface conditions at CPEs. Their surface becomes hydrophilic and behaves, more or less, like that of solid graphites.[88] This is of principal importance in organic electrochemistry where the anodization procedures may significantly improve often unfavorable reaction kinetics at CPEs and remove the undesirable reaction products from the electrode surface. In addition, anodizations can also be a very effective way of enhancing the electrode sensitivity.[88,90]

Parent cathodic activations are much less frequent and available literature sources hide only a few notes about their eventual applicability. Despite this, the recent results confirm a high effectiveness of cathodisation, for instance, for suppressing undesirable background currents within the potential range of interest.[28,30]

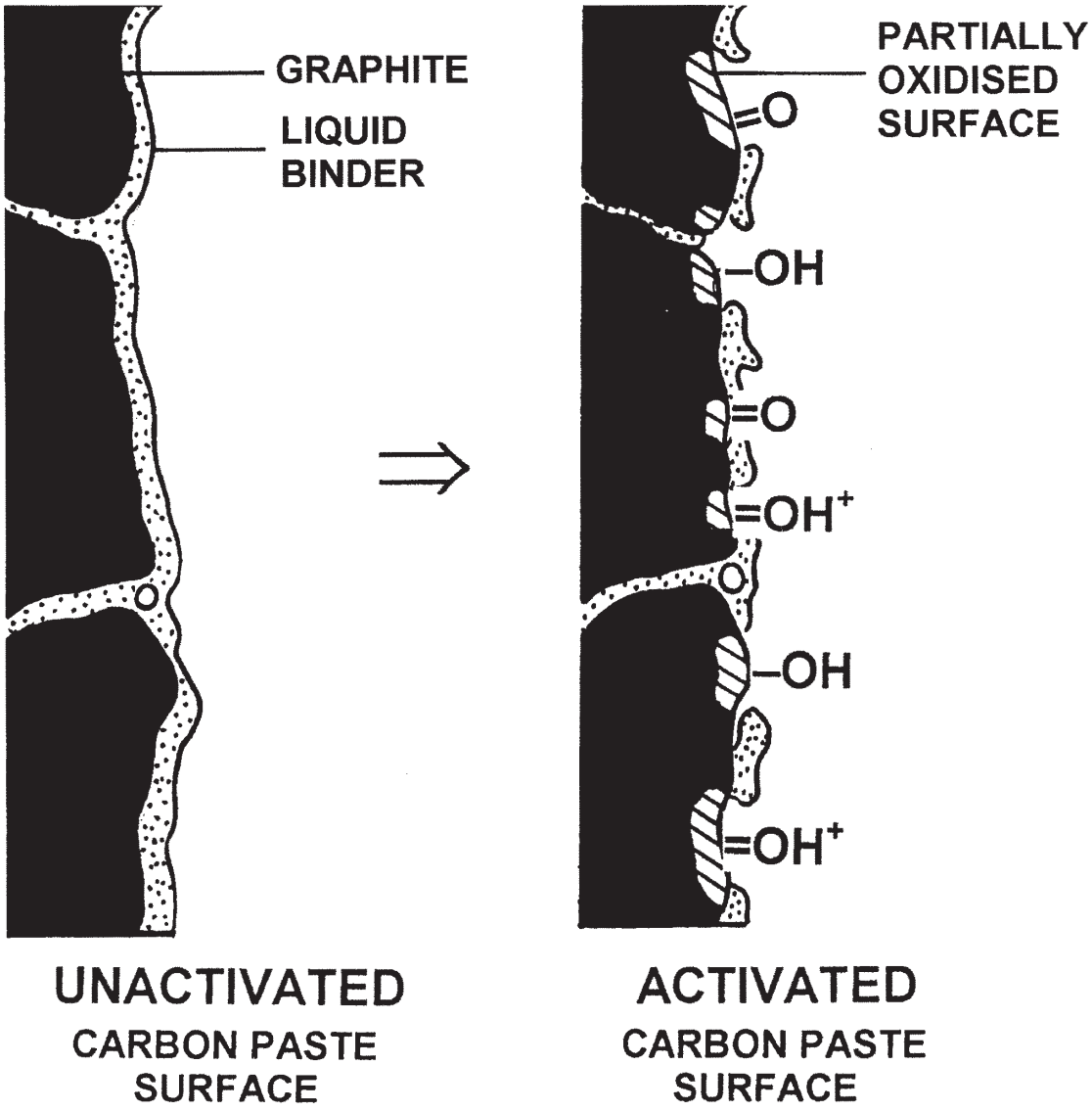

FIGURE 1. Anodic activation of the carbon paste surface. A schematic view.

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An alternative description of the electrochemical reactions at CPEs and their influencing by electrolytic activation is based on a pinhole mechanism.[91] The model postulates that the binder layer contains many small pinholes facilitating the charge and mass transfer. Their radius is practically independent of the carbon paste composition, but may vary in consequence of activation of the carbon paste surface. Some later experiments[75,76] showed that applicability of the pinhole mechanism is rather limited and it applies only to some highly hydrophilic species, whereas more hydrophobic substances tend to penetrate through the uniform layer of pasting liquid phase according to the above-mentioned membrane model.

Electrolytic Preconcentrations at Carbon Pastes. CPEs can also be utilized in stripping analysis for potentiostatic accumulation of selected heavy metals and metalloids. In these cases, it is advantageous to arrange carbon pastes as substrates (supports) plated with either Hg or Au films. At these electrodes, the corresponding metal ions are reduced and deposited in the elemental form either via effective amalgamation with mercury or thanks to the affinity towards gold surface. The proper detection of accumulated species is then carried out by their reoxidation in anodic voltammetric or potentiometric stripping mode. As documented in a recent review,[92] both Hg- and Au-film plated CPEs may provide a performance similar to that of other carbon or metallic electrodes commonly used for electrolytic accumulations (glassy carbon, mercury drop, platinum, or gold disk).

b. Interactions of Non-Electrolytic Nature

Adsorption, Extraction, Ion-Pairing, and Their Combination. Whereas electrolytic processes associated with charge transfer require, in principle, the presence of electroactive sites (i.e., carbon particles), nonelectrolytic interactions may proceed — independently on functioning of graphite — in pasting liquid phase or in contact with a special modifying agent.[13,87]

The role of the binder in nonelectrolytic phenomena is rather marginal as far as the adsorption interactions are concerned. At carbon paste surfaces, adsorption is facilitated mainly via modifiers or by a suitable carbon material.[10,13] Carbon pastes as such do not offer any special adsorption capabilities compared with other electrodes.

In contrast to this, extraction of nonpolar substances onto the electrode bulk is very typical and even unique property of CPEs if one does not consider some special constructions of membrane sensors.[89] Extraction processes at carbon pastes are governed by differences in solubility of extracted species in liquid binder and the respective aqueous phase (supporting electrolyte solution). The resulting distribution ratio then defines the overall effectiveness of extraction that can be controlled via the carbon paste composition, experimental conditions (e.g., pH of the electrolyte and its eventual exchange during measurements) or by chemical structure of the substance itself.[13,87]

Extractions at CPEs can be combined with adsorption and, more often, with ion-pair formation. Common paraffin and silicone oil containing carbon pastes possess only very limited ion-pairing capabilities. Above-mentioned carbon paste mixtures made from tricresyl phosphate (TCP-CPE) are much more convenient. In acidic media, its polar molecules are readily protonated and form ion-associates with various voluminous anions such as tetrachloroaurate[27] or iodide.[28-30] These relatively stable ion-aggregates are well extractable onto the TCP-CPE bulk, thus providing a way for their effective accumulation and the subsequent selective detection of the electroactive moiety.[27] Regarding CMCPEs, surfactants with long lipophilic chains were repeatedly recommended as particularly suitable modifying agents for accumulations based on ion-pair formation. Figure 2 depicts two typical variants of these modifications.

Cationic surfactant (Figure 2a) like cetyltrimethylammonium bromide thus may entrap various anions such as I^-, $Ti^{IV}O(C_2O_4)_2^{2-}$ or MoO_4^{2-} [29,42-45]), whereas, for example, sodium n-alkyl sulfonate (anionic surfactant, Figure 2b) binds effectively some organic cations[31] or Ag^+ ions.[28] Because both quarternary ammonium salts and alkyl sulfonates are soluble in water, it is necessary to apply *in situ* modification. The methods utilizing both ion-pairing and extraction at carbon paste-based electrodes can purposely be arranged

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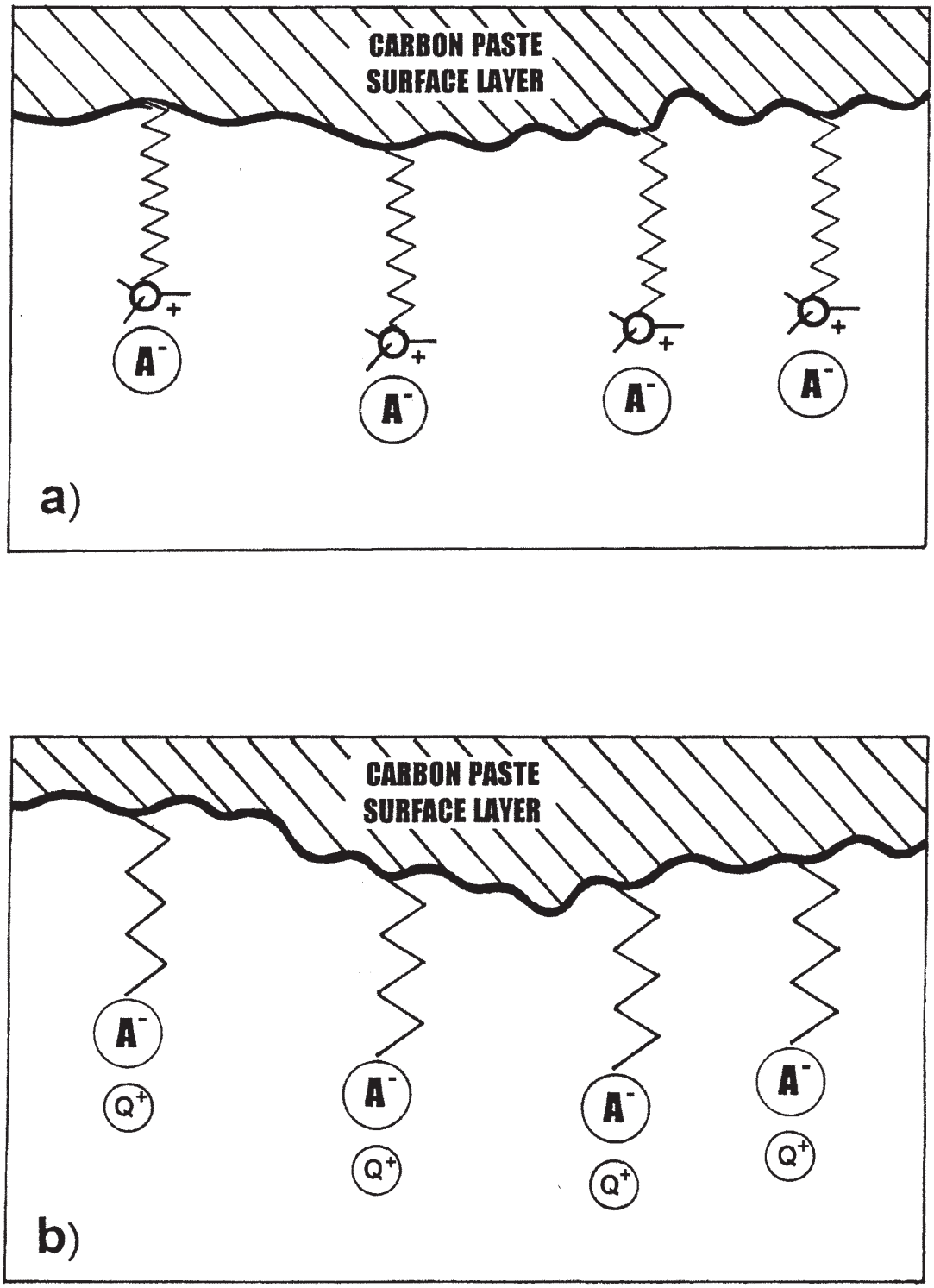

FIGURE 2. Carbon paste modified with cationic (a) or anionic (b) surfactant.

for voltammetric stripping analysis, measurements in flowing streams or for potentiometry (recently as automated titrations[15] or computerized stripping potentiometry[30]).

The variability of the processes and interactions at carbon pastes is very useful in both theoretical and applied electrochemistry as they allow performing some special measurements as well as highly selective and sophisticated analytical determinations. Their survey emphasizing the recent progress is given in the following sections.

C. Main Trends in Electrochemical Studies Employing Carbon Paste Electrodes

As the majority of electrochemical investigations have been carried out with modified carbon pastes, it is quite difficult to comprehend all the advances made recently. Studies with CMCPEs are focused rather individually, depending on the type of modifier, method of modification, and its purpose. Nevertheless, main trends of such a research can be illustrated.

Several research groups have achieved a great progress in the area of clay-modified carbon pastes.[47-57] Their detailed studies were, for example, dealing with defining the ion-exchanging capacity of various types of zeolite and zeolite-like materials, or mechanisms of ion-exchanging processes for different forms of one species to be analysed. At present, proposed methods are already being successfully applied in practical analysis.[67]

Numerous investigations were focused on the characterization of sensors modified with some "fashionable" materials such as fullerenes,[93] calixarenes,[94] metallothioneins,[95] or Ru-(bipyridyl)$_3^{2+}$-based systems.[96] Extensive research work has been done on carbon paste-based biosensors, covering now approx. 50% of all theoretical studies performed with carbon pastes.[22] In this field, a special review can be expected soon.

In solid state electrochemistry with CPEEs,[8] various studies on minerals and ores are of continuing interest; for example, pyrite pulps (with traces of Ag and Hg[97]), manganese ore,[98] galenite,[99] or sfalerite.[100] Defined electrochemical behavior may sometimes provide information useful for more effective exploitation and technological processing of strategically important ores.

Many attractive applications have resulted from electrochemical investigations of various organic substances such as environmental pollutants, surfactants, food additives, biologically important compounds, or numerous pharmaceutical formulas. The individual methods for their determination are surveyed in Section IV.

Finally, some modified carbon pastes can also be chosen as a substrate for rather unusual investigations. For instance, electrochemiluminescent reactions of persulfate in aqueous solutions could be studied with a CPE modified *in situ* with Ru-compound as catalyzer.[96] Another CPE with added chlorin-fullerene was capable of producing some photocurrent, thus serving as a novel type of solar cell.[93]

IV. ELECTROANALYTICAL APPLICATIONS OF UNMODIFIED AND MODIFIED CARBON PASTE ELECTRODES

A. Inorganic Analysis

Table 1 surveys the applications of both CPEs and CMCPEs in inorganic analysis reported within the period 1995 to 2000; earlier publications were included only exceptionally (e.g., [124] as hitherto unnoticed in the previous reviews).

The data summarized in Table 1 underline the individual trends and advances overviewed in the previous text. Among measuring techniques, modern variants of stripping voltammetry have prevailed; they are mostly performed with powerful computer-controlled analyzers. Their effective combination with carbon paste-based detection systems allows to propose analytical procedures with excellent detection capabilities. The values of detection limits cited in the table have rather informative character; nevertheless, they indicate roughly the performance of the corresponding methods. Typically, the detection limits were declared as an estimate for accumulation time varying from 1 to 15 min (except 120 min period reported in Ref. 28).

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TABLE 1
Selected Applications of Carbon Paste Electrodes in Inorganic Analysis

Analyte	Type of carbon paste electrode (modifier)	Principle(s) of the method	Measuring technique (specification)	Detection limit [sample]	Cit.
Au^{III}	CMCPE (humic acid + ethylendiamine)	ion-pair formation	CV, DPSV	1×10^{-8} M [model solutions]	56
	CMCPE (bacteria)	interaction at electrolytically pretreated surface	CSV		65
	CPE (containing TCP)	ion-pair formation combined with extraction	CCSA		101
Ag^{I}	CMCPE (containing TCP and modified by heptyl sulfonic acid *in situ*)	ion-pair formation at cathodically pretreated surface	DPASV	3×10^{-12} M [tap water]	28
	CMCPE (N-benzoyl-N',N'-diisobutylthiourea	complex formation followed by reaction with the surface groups	DPSV (open circuit)	1×10^{-7} M [model solutions]	102
	CPE (unmodified)	electrolytic preconcentration	SWASV	2×10^{-7} M [lake and river water]	103
	CMCPE (keratin)	accumulation via reaction with functional groups	DPCSV	2×10^{-8} M [photographic developer]	104
Hg^{I}, Hg^{II}	CMCPE (thiolic resin)	complex formation; controlled potential differentiation between both oxidation states		2-4 µg/L [aquatic samples]	105
	CMCPE (humic acid + immobilised functional groups)	accumulation via reaction with $-NH_2$ functional group	LSSV	5×10^{-8} M [model solutions]	57
	CPE (plated with Au-film *in situ*)	electrolytic preconcentration via affinity towards gold	DPASV	3×10^{-10} M [polluted tap water]	106
Hg^{II}	CMCPE (vermiculite)	ion-pair formation	SWASV	6×10^{-8} M [model solutions]	50

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TABLE 1 (continued)

Cu^{I}	CMCPE (rubeanic acid)	complex formation	DPCSV (open circuit)	8×10^{-5} M [reference material]	107
Cu^{I}, Cu^{II}	CMCPE) (Chelite P)	accumulation via reaction with -NH_2 functional group	DPSV	2×10^{-6} M [river water]	108
	CMCPE (alga *Anabaena* + Nafion film)	bioaccumulation effect	DPASV (open circuit)	8×10^{-5} M [model solutions]	64
	CMCPE (crown-ethers)	complexing + ion-exclusion effect	DPCSV	0.050 ppm [alcoholic beverages]	109
As^{III}, As^{V}	CPE (plated with Au-film *in situ*)	electrolytic preconcentration onto gold film; reduction intermediate step	DPASV	1 μg/L [spiked tap water]	86
Bi^{III}	CMCPE (Bismuthol II)	accumulation via reaction with –SH functional group	LSCSV (open circuit)	2×10^{-8} M [model solutions]	110
Pb^{II}	CMCPE (crown-ethers)	complexing + ion-exclusion effect	CSV	3×10^{-9} M [soil, plants, water, air]	111
	CMCPE (tributylphoshate + modification with pyrazolone derivative *in situ)*	complex formation	DPCSV	1×10^{-9} M [water, alloy]	112
Cd^{II}	CMCPE (tributylphoshate + modification with pyrazolone derivative *in situ)*	complex formation	DPCSV	5×10^{-8} M [waste water, human hair]	33
Zn^{II}	CPE (containing TCP; plated with Hg-film *in situ*)	electrolytic preconcentration via amalgamation on mercury film	DPASV	1×10^{-7} M [tap waters]	113

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Tl^{I}, Tl^{III}	CMCPE (8-hydroxyquinoline + glycerin)	electrolytic preconcentration; masking with EDTA	DPASV	5×10^{-9} M [model solutions]	38,39
Fe^{III}	CPE (unmodified)	electrolytic reduction	DPCSV	1ppm [solid 5-aminoisophthalic acid]	242
Ni^{II} (+ Co^{II})	CMCPE (aza-crown-ethers)	complexing + ion-exclusion effect	DPCSV (simultaneous d.)	4×10^{-8} M [model solutions]	114
Co^{II}	CMCPE (N-p-chlorofenylcinnamo-hydroxamic acid)	complex formation	DPASV	3×10^{-7} M [vitamin]	115
	CMCPE [1-(2-pyridyl-azo)-2-naphthol]		DPCSV	6×10^{-9} M [human hair, liver, spinach]	40
Mn^{II}	CMCPE [1-(2-pyridyl-azo)-2-naphthol]	complex formation	DPCSV (open circuit)	7×10^{-9} M [sea water]	41
Zr^{IV}	CMCPE (1-nitroso-2-naphthol)	complex formation equilibrium	potentiometry	1×10^{-6} M [ceramic glass]	116
Ti^{IV}	CMCPE (CTAB *in situ*)	ion-pair formation, micellar congregation; reduction intermediate step	DPASV	0.1 µg/L [mineral (stone-wool), building material]	42,43
V^{V}	CMCPE (CTAB; oxalate, *in situ*)	ion-pair formation, micellar congregation; reduction intermediate step	DPASV	0.07 µg/L [alloys]	43,44
Mo^{VI}	CMCPE (CTAB; oxalate, *in situ*)	ion-pair formation, micellar congregation; reduction intermediate step	DPASV	0.04 µg/L [alloys]	43,45
	CMCPE (chitin)	electrostatic interaction with functional groups of modifier; medium exchange	ASV	1×10^{-7} M [sea water]	66

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TABLE 1 (continued)

W^{VI}	CMCPE (8-mercaptoquinoline)	complex formation	ASV	1 μg/L [model solutions]	117
U^{VI}	CMCPE (propyl gallate)	complex formation	DPV (field analysis)	1 μg/L [ground water]	118
Pd^{II}	CMCPE (dimethylglyoxim)	complex formation	FIA	5×10^{-7} M [model solutions]	37
	CMCPE (sodium humate)	ion-pair formation	LSASV	5×10^{-7} M [environmental samples]	58
I^-	CMCPE (CTAB *in situ*)	ion-pair formation	DPSV	0.03 mg/L [table salts]	119
	CMCPE (cinchonine)			8×10^{-8} M [disifectant]	120
	CPE (containing TCP)	ion-pair formation, extraction (cathodisation pretreatment [30])	DPCSV, CCSA	$1\text{-}3 \times 10^{-7}$ M [iodinated and natural table salts]	29,30
	CMCPE (Septonex *in situ*)	ion-pair formation combined with extraction	DPCSV	2×10^{-7} M [mineral waters]	121
HPO_4^{2-}	CMCPE ($Hg_2HPO_4^-$)	ion-exchange equilibrium	potentiometry	- - [conc. phosphoric acid]	122
NO_2^-	CMCPE (Prussian Blue)	electrocatalytic effect	LSV	200 ppb [waste water]	123
N_3^-	CPE (unmodified)	electrolytic oxidation	LSV (combined with POL at DME)	50 $\mu g/m^3$ [air, lead azide (with or without dextrin)]	124

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ClO_4^-	CMCPE (Amberlite LA2 - admixed; $Tl^{III}Cl_4^-$ *in situ*)	ion-exchange; catalytic effect	DPV (open circuit)	50 µg/L [spiked tap water]	125
	CP-ISEs (containing TCP)	ion-pairing with counter-ion (CPyC as titrant)	potentiometry	$0.4\text{-}2..5 \times 10^{-6}$ M [explosives, rocket propellant extracts]	126
H_2O_2	CMCPE (Pd-powder)	electrocatalytic activity	LSV	50 µg/L [model solutions]	127
	CMCPE (MnO_2 as bulk- and film modifier)		FIA	45 µg/L [hair blonding booster, mouth wash; rainwater]	128, 129,243
	CMCPE (Me^{II}-phthalocyanines)		CV, DPV	22 ppb [model solutions]	130
NH_2OH	CMCPE (Pd-powder)	electrocatalytic activity	FIA	20 pg [river water]	131
N_2H_4	(immobilized tyrosinase)	inhibition of immobilized tyrosinase	AMP	$\sim 10^{-6}$ M [river, drinking water]	134
	(ST-NiTsPc) [mineral oil]	electrocatalytical N_2H_4 oxidation	CV	1×10^{-5} M [model samples]	135

In published determinations, CMCPEs have played a dominant role when representing about 90% of all applications. Especially those modifications enabling complex reactions with organic reagents (e.g.,[38-41,116,123]) or selective ion-exchange[42-45,119-122] were found attractive. Some other methods were based on measurements of electrocatalytical activity.[127-131]

Application of both CPEs and CMCPEs permit to analyze a wide spectrum of materials of diverse origin: from biological tissues,[33,40] via technological and commercial products,[43,104,109,128] up to various environmental samples of a solid,[111] liquid,[41,118,129] or gaseous[111] state. Using carbon paste electrodes, one can analyze either friendly materials like spinach[40] or extremely dangerous substance — unstabilized lead azide.[124]

Quick and inexpensive trace analysis of samples with complex matrix requiring only minimal pretreatment has been demonstrated using carbon paste electrodes coupled with computer-controlled stripping potentiometry.[30,101] So far, this is rather seldom application because stripping potentiometric stations are still preferably equipped with conventional solid electrodes and their employment in inorganic analysis is relatively limited (mostly on determinations of metal ions[132,133]). Thus, carbon paste electrodes can offer numerous alternative methods, including specific procedures based on synergistic nonelectrolytic accumulations or electrocatalytic effects.[30,101] Herein, a number of originally voltammetric methods can simply be adapted. And with respect to the fact that in analysis of real samples, potentiometric stripping analysis is often superior to stripping voltammetry,[132,133] one can expect even further improvement of so "novelized" methods.[30,136,137] It seems that such an approach may represent one of the future trends in using carbon paste-based electrodes.

It can be concluded that carbon paste electrodes still held a prominent position in modern electroanalysis of inorganic ions and molecules. In particular, the development in the area of CMCPEs have brought a number of new methods and interesting procedures such as speciation analysis with clay-modified carbon pastes for monitoring of heavy metals and their migration in the environment.[67] Practically endless number of reagents and materials usable as modifiers in inorganic analysis suggests that further expansion of various types of CMCPEs can be predicted even at the beginning of a new millennium.

B. Organic Analysis

Table 2 surveys the selected applications of both bare CPEs and CMCPEs use in organic analysis covering the period of last 5 years. As there are different approaches to compile a representative table for classifying published papers, the type of analyte was chosen as the main classifier. The other classification could be based on already mentioned bare CPEs or anyhow modified CPEs, which could be done either by using different modifiers of the carbon paste composition, different mediators of the electron transfer during redox reactions taking place in the solution, enzyme, tissue, or cells modifications or immobilization on CPEs, by using redox polymers covering, etc.

Behind the widespread use of carbon pastes in organic analysis several reasons can be identified. From the chemical point of view, it is mainly the wide freedom in choosing the composition of carbon paste allowing to tailor it for expected analytical use enabling either to highly increase the sensitivity of the determination or simply only to enable it or to suppress the interferences or to establish high selectivity of the determination. Nevertheless, also bare CPEs are still widely used in organic analysis, mainly for direct determination of oxidizable pharmaceuticals in different pharmaceutical formulations or some easily oxidizable phenolics, aromatic amino derivatives, or similar compounds. The limit of determination reached by direct analysis on bare CPEs is usually from 1×10^{-6} to 1×10^{-7} *M*; when accumulation of the analyte on the surface of the working electrode takes place, the limit of determination drops to the concentration of 1×10^{-8} *M*. By choosing appropriate analyte preconcentration techniques, the limit of determination can further be significantly lowered. This is the case of especially guanine or adenine oxidation-based determination of DNA or RNA using potentiometric stripping analysis with adsorptive accumulation where the reported limits of determination are actually at the

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TABLE 2
Selected Applications of Carbon Paste Electrodes in Organic Analysis

Analyte	Type of electrode (modifier) [liquid binder]	Principle(s) of the method	Measuring technique	Detection limit [sample]	Ref.
		Saccharides			
Glucose	(GOD , Os polymer mediator)	Os^{2+}/Os^{3+} redox mediating	AMP	2×10^{-3} M [model samples]	138
	(GOD , ubiquinone mediator) [paraffin oil]	ubiquinone e^- transfer mediating	AMP	2×10^{-4} M [model samples]	139
	(GOD, HRP, 1,1′-dimethylferrocene) [PEG]	reductive current measurement, bienzyme electrode	AMP	2×10^{-5} M [drinks]	140
	(GOD, methylene green)	anodic current measurement	FIA, AMP	~ 3×10^{-3} M [serum]	141
	(GOD, PEI and Os polymer)	Os^{2+}/Os^{3+} redox mediating	CV, AMP	2×10^{-3} M [senzor stabilization study]	142
	(Aspergillus niger cells cont. GOD and ferrocene) [paraffin oil]	glucose oxidation, microbial mediation	AMP	~ 1×10^{-3} M [fermentation batches]	143
Glucose (urate)	(peroxidase and ferrocene) Nafion membrane	electrocatalytic H_2O_2 reduction	FIA	200 fmol H_2O_2, 1.5 pmol Glucose, 2 pmol Urate [serum]	144
Fructose	(PQQ dehydrogenase, PEI)	nonmediated fructose oxidation	FIA, AMP	8×10^{-5} M [honey samples]	145
	(FDH and $Os(bpy)_2$ complex)	mediated fructose oxidation	FIA, AMP	4×10^{-5} M [food analysis]	146

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TABLE 2 (continued)

Carboxylic and Substituted Carboxylic Acids					
Lactate	(Co(II) octaethoxyphtalocyanine, LOd) [paraffin oil]	oxidative H_2O_2 sensing	AMP	1 x 10^{-6} M [sour milks and wines]	147
	(Rh, LOd immobil.)	Rh catalysis towards H_2O_2 or O_2	FIA	2 x 10^{-5} M	148
	(bienzyme modification, LOd, HRP, PEI) [silicone oil]	H_2O_2 detection	FIA, AMP	3 x 10^{-6} M [fermentation medium]	149
	(Co polypyridyl complexes mediators, LADH or LADH + LDH) [mineral oil]	mono- or bienzyme $FADH_2$ and/or NADH oxidation	CV	5 x 10^{-6} M [clinical samples]	150
D-, L-Lactate	(D-lactate dehydrogenase, L-lactate oxidase, HRP, PEI, redox polymer) [silicon or paraffin oil]	mediated NAD(+) reduction, HRP – H_2O_2 reduction	FIA	100 (10) x 10^{-6} M, resp. [fermentation broths]	151
Ascorbic acid	[diisooctylphtalate]	AA chemisorption on CPE	P	1 x 10^{-7} M [NaOH-NaCl medium]	152
	Co^{II}-phthalocyanine	catalysed oxidation	DPCSV	0.8 ppm [fruit juices]	244
	(methylene green)	catalytic AA oxidation	FIA	1 x 10^{-8} M [model samples]	153
Ascorbic acid, O_2	(lipid treated CPE) [silicone oil]	O_2 reduction, AA oxidation by sequence of pulses	DPV	10(AA) and 8(O_2) x 10^{-6} M [in vivo measurements]	154
Oxalic acid	(lead sulfate)	medium exchange, interfacial accumulation	SW ASV	0.3 mg.L^{-1} [orange juice]	155
Alcohols					
EtOH	(ADH, phenothiazine)	electrocatalytic oxidation of NADH	AMP	5 x 10^{-6} M [wine]	156
	(ADH, HRP, PEI, Os redox gel) [silicone oil]	direct and mediated e^- transfer	FIA, AMP	~ 10^{-6} M [model samples]	157
EtOH (Lactate)	PPD and PAP coating (ADH, LOd)	electrocatalytic NADH oxidation	AMP	8 x 10^{-10} M	158

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Glycerol	(GIDH and NAD(+)), PPD polymer	electrocatalytic NADH oxidation, adenine oxidation	AMP	4×10^{-7} M [plant extract syrup]	159
EtOH, NADH	zirconium phosphate MCPE (Nile blue, NMP mediator, ADH) [paraffin oil]	electrocatalytic NADH oxidation	AMP	2×10^{-6}(NADH) M, ~ 10^{-4} M (EtOH) [model samples]	160
NADH (EtOH, Glucose)	(methylene green) [nujol]	electrocatalytic NADH oxidation	CV, FIA, AMP	1 pmol [model samples]	161
		Amino Acids, Peptides, Heterocyclic Compounds			
Tryptophan	[solid paraffin]	CPE anodic pretreatment, anodic scan	AdSV	2 $ng.mL^{-1}$ [injection, synthetic serum]	162
Uric acid	(uricase, HRP)	enzymatic reduction of H_2O_2	FIA, AMP	3×10^{-6} M [serum]	163
	(PVP CPE) [mineral oil]	uric acid catalytic oxidation	SWV	2×10^{-7} M [human urine]	164
L-Prolin	(β-cyclodextrin) [paraffin oil]	enantioselective membrane construction	CHP	1×10^{-5} M [biological samples, food]	77
L-Phenyl-alanine	(salicylate hydroxylase, tyrosinase, L-Phenylalanine dehydrogenase)	enzymatic/electrochemical recycling of tyrosinase	AMP	5×10^{-6} M [human serum]	165
S containing amino acids	(crown ethers)	host-guest complex formation	V	2×10^{-8} M	166
Cysteine, Glutathione	(Ru(III)-DPDTC) [paraffin oil]	electrocatalytic analytes oxidation	AMP, CV	~ 3(Cys) and 6(Glu) $mg.L^{-1}$ [model samples]	167
Cysteine	Si-NiTsPc MCPE	electrocatalytic Cys oxidation			168
[Lys]8]]-vasopressin, Angiotensin II	[mineral oil]	tyrosine residue oxidation	PSA	~ 10^{-9} M [model samples]	169

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TABLE 2 (continued)

Human IgG	(alkaline phosphatase labeled IgG, 3-indoxyl phosphate)	anodic pretreatment, EIA, indigo detection	ACV	~ 10^{-10} M	170
Insulin, myoglobin	[mineral oil]	adsorptive accumulation on anodically pretreated CPE	PSA	2 x 10^{-9} M [model samples]	171
Bioactive peptides	[mineral oil]	oxidation of tryptophan and/or tyrosine	PSA	2 x 10^{-10} M [model samples]	172
IgG	(alkaline phosphatase label)	electrochemical EIA	CV, AMP	2.3 x 10^{-12} M	173
		DNA, RNA			
tRNA	[mineral oil]	CP anodic pretreatment, adsorptive accumulation	PSA	4 x 10^{-16} M [model samples]	174
DNA	[mineral oil]	guanine oxidation	PSA	15 ng.mL^{-1}	175
DNA, RNA	[mineral oil]	guanine oxidation	PSA	20 ng.mL^{-1} [model samples]	176
DNA (HIV-1) related	oligonucleotide immobil., $Co(phen)_3^{3+}$ indicator [mineral oil]	target hybridization	PSA	4 x 10^{-9} M [model samples]	177
DNA, RNA	[mineral oil]	guanine oxidation	FIA, AMP	460 pg [model samples]	178
Adenin	[paraffin oil]	oxidative pretreatment of CPE, medium exchange	SWV	2 x 10^{-7} M [model samples]	179
PNA	[mineral oil]	adsorptive preconcentration	PSA	~ ng.mL^{-1} [model samples]	180
DNA	immob. of inosine probe on CPE	detection of duplex formation by appearance of guanine peak	CHP	120 ng.mL^{-1} [hybridization sensing]	181
		Pesticides			
Thiram (T) and Disulfiram (D)	Cobalt phtalocyanine mediator	adsorptive accumulation, analyte oxidation	DPV, AdSV	7 (T) and 2 (D) x 10^{-8} M [strawberries]	182

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Ioxynil (I), 2-Me-3-nitro-anilin (M)	(C 18)	electrochemical oxidation	AdSV	1 (I] and 3 (M) x 10^{-7} $g.mL^{-1}$ [drinking water]	183
Matamitron	(silica)	electrochemical reduction	AdSV, SWV	4 x 10^{-10} M [soils, natural waters]	184, 185
Phosalone, Carbophos	(Co(II)2,2′-dipyridylate)	mixed Co(II)-ligand complexes formation	V	5 and 1 x 10^{-9} M, resp. [alkaline hydrolyzates]	186
Karbation related compounds	(crown ethers)	host-guest complexes formation, electrochemical oxidation	AdSV	4 x 10^{-9} M	187
Phenytoin, Phenobarbital	(Nafion)	ferroceneammonium and cobaltocenium ion redox label determination	SWV	2 x 10^{-7} M [dual immunoassay]	188, 189
		Phenolics			
Hydroquinone derivatives	[paraffin oil]	analyte oxidation adsorptive preconcentration	DPV	0.07 $mg.L^{-1}$ [cosmetics]	190
Phenols	(tyrosinase)	on line SPE, biosensing	AMP	~ 1 x 10^{-6} $g.L^{-1}$ [river water]	191
	(tyrosinase)	biocatalytic accumulation	CHA	2 x 10^{-8} M [environmental samples]	192
	(HRP, H_2O_2,lactitol) [paraffin oil]	phenoxy radicals electrochemical reduction	FIA, AMP	~ 10^{-6} M [river water]	193
	(solid paraffin)	adsorption on anodically pretreated CPE	ASV	5 x 10^{-8} M [tap, waste water]	194
	(C10 to C14 , tyrosinase]	extractive accumulation	FIA	6 x 10^{-9} M [river water]	195
Flavonoids	[nujol]	electrochemical oxidation	AdSV	~ 10^{-8} M [multivitamin preparations]	196
Flavanols	(polyphenol oxidase) [nujol]	plant tissue biosensors	AMP	[beers, lagers]	197

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TABLE 2 (continued)

Flavonoids	[nujol or diphenylether]	direct and medium-cxchange determination	AdSV, FIA	~ 10^{-8} M [multivitamin preparation]	198
2-Nitrophenol	(bentonite)	electrochemical reduction	FIA, DPV	0.2 mg.L^{-1} [sea water]	199, 200
2-Methyl-4,6-dinitrophenol	(hidepowder)	reduction of nitro group	CV, DPV	3.2 x 10^{-6} M	201
Salmonella cells	alkaline phosphatase-labeled antibody conjugation [paraffin oil]	EIA, based on measuring phenol oxidation peak	DPV	5 x 10^{3} cells.mL^{-1} [models for food analysis]	202
Catechin and acridine deriv.	(DNA) [pharmaceutical vaseline]	analytes intercalation to DNA	DPV	~ 10^{-9} M [model samples]	203
Catechol-amines	solid CMCPE (tyrosinase)	electrochemical oxidation	HPLC-ECD	290 pg [model samples]	245
Dopamine	(potato tissue polyphenol oxidase)	nonmediated biosensing	AMP	3 x 10^{-6} M	204
Dopamine (phenols)	(tyrosinase) [solid paraffin]	quinone sensing	FIA	5 x 10^{-8} M [senzor stability study]	205
Dopamine (uric acid)	[clay] (Nafion)	preanodization, charge-inclusion	SWV	3 x 10^{-9} M (2 x 10^{-7} M) [human urine]	206
		Pharmaceuticals			
Cephalosporin antibiotics	(fatty acid)	electrochemical analyte oxidation	DC SV	~ 10^{-8} M [urine, serum]	207
Aceclofenac	(hydrophobic substances as fatty acids, surfactants) [nujol]	electrochemical analyte oxidation	AdSV	2 x 10^{-8} M [formulations]	208
Phenylephrine	(cation exchange resin) [paste Metrohm 62801000]	electrochemical analyte oxidation	ASV, LSV	2 x 10^{-6} M [urine]	209
Phenothiazine drugs	(DNA) [mineral oil]	DNA-phenothiazine intercalation	CHP	5 x 10^{-9} M [model samples]	210
Clenbuterol	(Nafion)	electrochemical oxidation	DPV	1 x 10^{-9} M [bovine urine]	211

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Phenytoin	1-octanol, Nafion loaded CPE	competitive EIA	SWV	5×10^{-9} M [serum]	212
Doxazosin	bare CPE, Tenax MCPE	electrochemical reduction	AdSV, SWV	4×10^{-11} M [urine, formulations]	213
	(C8)	doxazosin oxidation	DPV, SWV, AdSV	7.4×10^{-10} M [urine, formulations]	214
Imipramine	(fatty acid)	electrochemical oxidation	V	1×10^{-9} M [pharmaceuticals, biol. s.]	215
Imipramine (I), Trimipramine Thioridazine	(β-cyclodextrine) [pharmaceutical vaseline]	inclusion complexes formation	CV, DPV, AdSV	7×10^{-9} M Thioridazine 2×10^{-8} M I and Trimipramine [tablets]	216
Daunomycin	(DNA)	daunomycin-DNA intercalation	CV, PSA	DNA-drug interactions	217
Nifuroxazide	(polystyren/DVB)	electrochemical NO_2 group reduction	AdSV	10×10^{-9} g.mL^{-1} [urine]	218
Aztreonam	(gelatin)		DPV, SWV	8×10^{-8} M [urine]	219
Indomethacin	[nujol or silicone or castor oil]	electrochemical oxidation, extractive accum., medium exchange	V	3×10^{-8} M [urine]	220
Prazosin	(Nafion)	accumulation at 750 mV followed by cathodic sweep	AdSV	3×10^{-11} M [tablets, urine]	221
	(C8)	oxidation of Prazosin	AdSV, DPV, SWv	8×10^{-10} M [urine, formulations]	222
Buprenorphine	[paraffin oil]	electrochemical analyte oxidation	CV, DPV, FIA	1×10^{-8} M [pharmaceuticals, urine]	223
Azepine, Phenothiazines	[DNA]	drug-DNA intercalation	DPV	~ 10^{-9} M	224

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TABLE 2 (continued)

		Peroxide Determination for Organic Analysis			
H_2O_2	(asparagus tissue and ferrocene) [mineral oil]	generated ferricinium ion reduction	FIA, AMP	4×10^{-7} M [milk]	225
	(HRP immobil. in silica sol-gel)	hexacyanoferrate(II) mediation	FIA, AMP	2×10^{-5} M [glucose senzor]	226
H_2O_2, 2-BP	(HRP or fungal peroxidase) [paraffin oil, lactitol]	peroxide detection	FIA	$2(H_2O_2)$ and 100×10^{-7} M [model samples]	227
H_2O_2	TEMPO loaded CPE [silicon oil]	electrocatalytic oxidation of H_2O_2	AMP	5×10^{-8} M [model samples]	228
	(Meldola Blue, fumed silica, HRP) [paraffin oil]	H_2O_2 bioelectrocatalytic reduction	CV, FIA, AMP	1×10^{-7} M [glucose, lactate etc]	229
	(zucchini peroxidase)	oxidation of guaiacol	FIA, SPFT	2×10^{-6} M [pharmaceuticals, water]	230
	HRP-ferrocene MCPE coated by PAP	H_2O_2 detection	FIA, AMP	9×10^{-9} M [milk]	231
	(HRP and 3,3′,5,5′-tetramethylbenzidine , GOD)	H_2O_2 detection	AMP	10^{-8} M [Glucose determination]	232
		Other substances			
Estrogens	[oleic acid]	analyte electrochemical oxidation	AdSV	4×10^{-7} M [pharmaceuticals]	233
Ephedrine	sepiolite	adsorptive preconcentration	SWV	3×10^{-6} g.L^{-1}	234
Cocaine	[paraffin oil]	analyte oxidation	FIA, AMP	2×10^{-7} M [confiscated goods]	235
Cholesterol	(hydroxymethyl ferrocene, HRP)	direct determination	CV, CHA	1×10^{-6} M [serum]	236
Nicotinic acid	(bacterial Pf cells, p-benzoquinone)	electrocatalytic hydroxylation of nicotinic acid	AMP	5×10^{-6} M [model samples]	237

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Surfactants	CPE-ISEs	ion pair formation equilibrium	potentiometric titrations	1×10^{-5} M	246
Anionic surfactants	(NPOE, ferrocenyl surfactant)	indirectly, from ferrocenyl oxidation wave	AdSV	1×10^{-7} M [model samples]	238
Creatinine, Creatine	ferrocene-embedded CPE with entrapped peroxidase	H_2O_2 determination	AMP	1×10^{-8} M [serum, urine]	239
Roxarsone	(Amberlite LA2) [paraffin oil]	analyte reduction, extractive accumulation using cation exchanger	DPV	1×10^{-7} M [drinks, tablets]	240
NAD(P)H	(peroxidase and ferrocene MCPE , 1-methoxyphenazine methosulfate)	mediated NAD(P)H oxidation with H_2O_2 mediated detection	AMP	4×10^{-8} M [serum, enzyme activity]	241

10^{-16} *M* concentration level for model samples.[174] The same is valid for the analyses of peptides[170,172] which are usually based on the oxidation of tryptophan, tyrosine, or cysteine. Such an extraordinary sensitivity is very promising, for example, for the construction of disposable senzors for monitoring nucleic acid damage, although problems connected with overcoming the interferences signals, lower reproducibility, or stability of the signal still persist. The limit of determination for amino acids in human serum, clinical samples or food samples, is much higher, typically around 10^{-6} to 10^{-7} *M*.[77,165] The relatively straightforward use of bare CPEs in organic analysis is justified especially in the field of pharmaceutical analysis for checking the content of drugs in tablets, injections, or other formulations where the lower selectivity of electrochemical methods is not so prohibitive due to the strict rules for the composition of these formulations and the content of the above-mentioned specimen. Also, the determination of drugs or drug metabolites in urine is well suited for bare CPEs because the matrix is not too complicated and the analyst is usually looking for the presence of a certain substance at appropriate potential interval. Also, the products of metabolic drug transformations in human body are often oxidizable allowing to look for either the original drug, or for its metabolite.

The highest number of papers is connected with utilization of different enzymes. From earlier immobilization of enzymes on the surface of carbon pastes, nowadays direct enzyme admixing into the paste is prevalent and quite frequent. Among the enzymes, especially dehydrogenases like lactate dehydrogenase, alcohol dehydrogenase, etc., then oxidases like glucose or lactate oxidase and peroxidases like horseradish peroxidase are used most often. Selected applications in Table 2 illustrate the main trends in this field. In saccharides analysis by far the greatest number of papers deal with determination of glucose,[138-144] mainly in food samples or serum. Although many attempts have been made to decrease the limit of determination of glucose either by choosing different mediators for shuttling the electrons from the reduced form of the enzyme to the electrode, or by bulk modification of the paste or by immobilization of cells containing glucose oxidase, the lowest reported limit of determination is around 2×10^{-5} *M*. The glucose determination is mainly based on glucose oxidase using molecular oxygen as the reoxidation agent in the catalytic cycle with either water or hydrogen peroxide as the final product. The electron transfer mediators vary widely with still no universal mediator for glucose oxidase (see Table 2). Very low detection limit of 1.5 pmol is reported for glucose (and urate) in recent paper,[144] dealing with peroxidase and ferrocene-embedded CPE with bioelectrocatalytic hydrogen peroxide reduction at 100 mV vs. Ag/AgCl/sat. KCl electrode, where hydrogen peroxide was formed by the action of the corresponding oxidase. Papers on fructose determination[145,146] report in food analysis the limits of determination to be around 5×10^{-5} *M,* which are similar to typical previous glucose determinations. Fructose oxidizing enzymes involve either fructose dehydrogenase[146] or pyrrolo quinoline quinone dehydrogenase,[145] the latter not requiring electron transfer mediating.

Another group of organic analytes frequently challenged by CPE are carboxylic acids.[147-155] Here lactate is the most frequently studied analyte whose determination is important in food analysis when looking into fermentation processes[149,151] or in clinical analysis.[150] Simultaneous determination of D- and L-lactate was enabled by D-lactate dehydrogenase coimmobilized with a redox mediator to a polymer backbone and the cofactor NAD(+) and L-lactate oxidase and horseradish peroxidase coadsorbed on graphite. Under flow injection conditions up to 40 samples per hour can be determined, although the limits of determination are in the range of (1 to 10) $\times 10^{-5}$ *M*.[151] The lowest limit of determination of 1×10^{-8} *M* was reported for ascorbic acid[153] in model samples. Methylene green modified CPE[153] showed high catalytic activity toward the oxidation of the acid reducing the oxidation overpotential by 400 mV. Again, in practical *in vivo* measurements the limit of determination for ascorbic acid determination was about 1×10^{-5} *M*.[154] In the group of alcohols[156-161] the dominant role plays ethanol, which is being determined in different beverages. Although for ethanol the limit of determination of 8×10^{-10} *M*[158] is reported, practical samples again show several orders of magnitude higher limits of determination. The principle of these determinations is mainly connected with

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electrocatalytic NADH oxidation. When evaluating the papers on amino acids, peptides, and hetorocyclic compounds in Table 2, then it is clear that the best results have been reported on peptides.[169-173] The principle of the determination of immunoglobulin G[173] is in the attachment of the analyte to a carbon paste with an enzyme label of alkaline phosphatase linked to the antibody. α-Naphthol, as the easily oxidizable enzymatic product, enabled this extremely sensitive determination with LOD of 2×10^{-12} *M* and the development of two immunoelectrochemical devices.

Papers dealing with the determination of either DNA or RNA[174-181] almost all show high sensitivity even on bare CPEs and most of the results were obtained using potentiometric stripping analysis following adsorption of the analyte on CPE and origin of the signal is based on guanine oxidation. The CPE pretreatment is also very important and sometimes plays a crucial role.[176] In comparison with either DPV or SWV,[179] the sensitivity of PSA is higher by several orders of magnitude.[174-176,180] It is the high sensitivity of PSA connected with strong adsorption of these analytes on CPE as a preconcentration step that is very promising for the future quantitation of nucleic acids and their analogs in diagnostic and biological applications.[180] Such a DNA hybridization biosensor has already been constructed,[181] and it is based on inosine-substituted (guanine free) probe onto the CP transducer where the duplex formation is monitored by the appearance of the guanine oxidation peak of the target. Quite good reproducibility (R.S.D. of 2 to 3%) is reported for the determination of very low concentrations of nucleic acids[178] using flow injection amperometry. Such a very good reproducibility is really quite unusual, taking into account the reported picogram quantities and the electrode material used.

The performance of CPEs is quite good when looking into analyses of pesticides.[182-189] The increase in sensitivity was enabled by adsorptive accumulation of the analyte on silica modified CPE[182-185] or by formation of host-guest complexes.[186-187] These complexes enabled the determination of selected pesticides even in practical samples like soil or natural waters with limits of determination in the concentration range of 10^{-9} *M* or even lower.

Phenolics and biogenic amines[190-206] are also of continuing interest when working with CPEs. The reported limits of determination based on quinone sensing are quite good (5×10^{-8} *M*). Copper containing enzyme tyrosinase is used most often for determination of phenols, resulting in formation of ortho-quinone derivatives. The enzymatic activity of tyrosinase toward phenolics enables the determination of different monophenolic compounds but also means low selectivity of tyrosinase-based CPE. When properly tailored methods of accumulation are used, like biocatalytic accumulation,[192] extractive accumulation,[195] or medium exchange strategy,[198] they result in quite low limits of determination even in environmental, clinical, or food samples.

The group of pharmaceuticals is very well suited for analysis using CPE.[207-224] The reason for it is in quite strict demands on the content of different kinds of pharmaceutical formulations where rarely anything else than the active ingredient is electrochemically active. This is not only an advantage for analysis of pharmaceutical formulations but also for the analysis of pharmaceuticals or their metabolites in body fluids, mainly in urine or serum. The most sensitive methods reported were on Clenbuterol,[211] Doxazosin,[213,214] Imipramine,[215] and Prazosin,[221,222] all of them being evaluated on practical biological samples. Clenbuterol determination in bovine serum[211] was performed following the accumulation on Nafion-modified CPE when the two-step clean-up procedure included liquid-liquid extraction and solid phase extraction. Tenax-modified CPE enabled the accumulation of Doxazosin[213] on the surface of a CPE. Three minute accumulation followed by redissolution technique as DPV and SWV allowed to quantify Doxazosine in very low amounts in human urine. Sensitive Prazosine determination in urine and formulation is connected with C-8 modification of CPE, which allowed a more efficient accumulation of the analyte, the final measurements being based on the oxidation of the amine group of Prazosine.

Determination of peroxides[225-232] is included mainly for illustration purposes. Although in this case inorganic substance is being determined by CPEs, hydrogen peroxide is the end product of horseradish peroxidase connected methods where

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the analyte of interest is glucose[226, 229,232] or lactate.[229]

In Table 2 part dealing with "other substances", some interesting applications of the use of CPE in organic analysis are summarized. Among them, anionic surfactants[238] show reasonable limits of determinations, the determination of cocaine[235] is quite straightforward with a low limit of determination. The determination of growth regulator Roxarsone[240] is based on the reduction of the nitro group of the analyte, although the determination based on the oxidation of Roxarsone is also possible but less sensitive.

Generally, the possibility of using CPEs for following both oxidation and reduction of organic compounds is advantageous, although, up to now, not fully exploited. This is somewhat surprising when considering that CPEs offer favorable signal-to-noise characteristics, especially when being polarized anodically. Thanks to very low background currents over the whole anodic range, the bare carbon paste represents one of the most convenient electrode materials for anodic oxidations of organic compounds.[4,13] This statement seems to apply also in today's electrochemistry that is characterized by myriad electrodes and sensors that are being used. The feature of very fine anodic polarizability of CPEs was repeatedly emphasized already during Adams's era when numerous organic compounds like aromatic amines, phenols, or some nitroderivatives had underwent systematic electrochemical investigations (see articles[2-4] and references therein). The results of such studies can be useful also in the present's day electrochemistry, for instance, as an inspiration in the development of novel methods to determine some organic substances[240] and pollutants.[184,185]

As can be seen from the selected and commented applications of CPEs, their employment in organic electrochemistry offers many diverse possibilities and approaches. Bare carbon pastes are simply usable for the above-commented oxidations and reductions, but one can also choose them for unique extraction accumulations.[220,240] If the surface of a CPE is activated electrolytically,[171,179,206] one can aim significant improvements of its kinetic characteristics via lowering the overpotential of some electrode reactions.[150,243,156] Special carbon paste mixtures can be operated even in media containing organic solvents.[13,26]

Such approaches then markedly widen a spectrum of compounds that can be studied using CPEs. However, analogously to inorganic applications of CPEs, an unflagging optimism is displayed mainly in association with chemically and biologically modified carbon pastes, namely, with a choice of new modifiers, electron transfer mediators, and enzymes. Suitably selected modifying agents may catalyze[153,159-161] or inhibit[134] some reactions. Modifiers can also participate in some selective accumulations via adsorption[182,190] or ion-pairing.[246,247] Finally, the use of both CPEs and CMCPEs may result in very sensitive and promising analytical methods[173,174] that would show some future trends in applications of carbon paste-based electrodes, including a way of how to move a procedure from model to practical samples.

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