

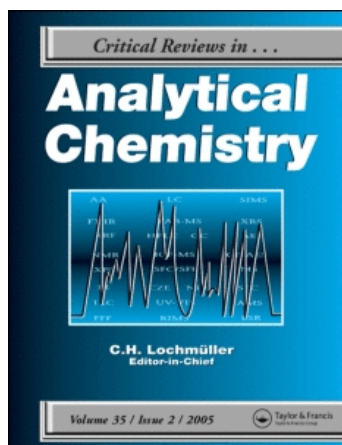
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Recent Advances in Electroanalysis of Organic Compounds at Carbon Paste Electrodes

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In this review (with 223 refs), electroanalysis of organic compounds with carbon paste-based electrodes, sensors, and detectors is discussed. The individual methods, covering the period of 2004–2008, are summarized in tables with accompanying commentaries, attention being paid to environmental pollutants, pharmaceutical formulations and drugs, as well as other biologically active organic compounds. Recent achievements and trends are discussed, critically evaluated, and some future prospects are outlined.

Keywords Carbon paste electrodes, electroanalysis, sensors, organic pollutants, pharmaceuticals, drugs, biologically active compounds, review

INTRODUCTION

In 2009, we commemorate the 50th anniversary of the Nobel Prize for polarography (1) and, coincidentally, last year we celebrated the 50th anniversary of the introduction of carbon paste electrodes (CPEs) (2). Polarography with the dropping mercury electrode (DME) and electroanalysis with CPEs also share similar fates with respect to their more-or-less accidental discovery and later-achieved position. Whereas direct current polarography (DCP) was invented during investigations of electrocapillary phenomena at DME, carbon paste was a “side-product,” coming from Ralph Adams with unsuccessful experiments with the so-called dropping carbon electrode [DCE (3,4)]. Both DME and CPE spread over the globe and touched almost every area of theoretical and applied electrochemistry. Since their introduction, CPEs underwent a lengthy and impressive development (5–13). In this paper we pay attention to the period of 2004–2008, not covered by the most up-dated review (8). Because a full overview of electroanalysis with CPEs was beyond the scope of this dedicated issue, it was decided to focus on electroanalysis of organic compounds taking into account recently prepared extensive review on inorganic compounds (13). Last,

but not least, an “organic” orientation of this paper reflects the legacy of Heyrovský’s polarography, which is now more frequently used in organic electrochemistry.

The following general trends concerning CPEs can be observed:

1. New types of carbon paste mixtures are developed, tested, and applied. Traditional CPEs are being replaced by alternate materials. Classical forms of graphite moiety are replaced by new carbon materials like fullerenes “C-60,” hollow carbon fibers, or carbon nanotubes (12) and traditional pasting liquids are substituted by room-temperature ionic liquids (RTILs) or other recently synthesized organic liquids (13).
2. New approaches to chemical and biological modification of CPEs are investigated.
3. Methodologies based on the use of various nanoparticles (e.g., nanosized metals, synthetic zeolites and silicas, inorganic/organic hybrids of Dawson type) or newly synthesized polymers (with immobilized functional active groups or encapsulating some enzymes and mediators) are extensively tested.

Research in the field of organic compounds can be divided into the four following categories:

1. Qualitative and quantitative analysis of organic substances with particular emphasis on environmental pollutants such as electroactive derivatives of polyaromatic hydrocarbons (PAHs), various pesticides, organic dyes, or industrial

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

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- surfactants (8). Typically, the respective electrochemical characterization has to precede the proper determination;
- Carbon paste biosensors utilizing advantageous properties of carbon paste for its modification with various enzymes or enzyme-containing tissues, together with the corresponding mediators (9);
 - Pharmaceutical and clinical analysis with CPEs is represented by hundreds of papers resulting in methodical procedures for more than 150 different pharmaceuticals and drugs in real samples (2,8);
 - Qualitative and quantitative analysis of biologically active compounds (BAC) such as purines, amino acids, peptides lipids, enzymes, hormones, biological co-factors, neurotransmitters (catechols and dopamin), nucleic acids (DNA, RNA), sugars, vitamins, antioxidants, or even some microorganisms like bacteria and viruses. Most of these substances can be analyzed with CP biosensors, but not necessarily because there are other carbon paste-based configurations available for these purposes (8).

Both unmodified and modified CPEs are both widely applicable in organic analysis, whereas in inorganic analysis bare CPEs are only rarely used (13). Unmodified CPEs are still very popular in pharmaceutical analysis, where a hydrophobic binder acts as a certain type of modifier that attracts highly lipophilic molecules of pharmaceuticals and drugs. Due to a complex character of many organic samples, a pre-separation step (HPLC, CZE, SPE, LLE, etc.) is often required prior to electrochemical detection.

RECENT TRENDS IN ANALYSIS OF ORGANIC SUBSTANCES

Modern electroanalytical methods using classical three electrode systems critically depend on the working electrode as the choice of a reference and an auxiliary electrode is usually just a routine task. Therefore, there is an effort to prepare tailor-made so-called "designer CPEs," with lower overpotential of the redox reaction, better selectivity, or higher sensitivity (e.g., via the appearance of the catalytic currents). But it is necessary to keep in mind that the broad range of various CPEs could be disadvantageous, too. There are so many papers on glucose determination (14–30), hydrogen peroxide (31–46), or NADH (47–51), with each author stressing the advantages of a new electrode or new electrode material; even for scientists working in the field of electroanalysis utilizing paste electrode it is quite difficult to choose the best electrode type for the problem to be solved. Moreover, amperometric or voltamperometric methods are linked with an inherent problem of electrode passivation or fouling which limits the practical applications.

The promising properties of RTILs (thermal stability, non-volatility, designability, ion conductivity, composition variability, polarity adjustability, etc.) have not yet been fully utilized in the world of CPEs. High ion density and ion conductivity seems to be an especially limited factor. We can see an increasing number of papers dealing with DNA, protein, or gene sequence

analysis (52–66). The use of polymerase chain reactions (PCR) in DNA hybridization and the study of dsDNA-modified CP sensors or biosensors are very promising and, due to the involved PCR, also extremely sensitive. A bright future could be forecast for specific DNA or protein biosensors coupled with PCR.

The development of new methods of using bare CPEs is justified, especially in the field of pharmaceutical analysis of relatively simple matrices (tablets, injections, syrups) where the new methods are usually very simple, fast, non-expensive, and present an independent alternative for more frequently used spectrophotometric or separation methods. Any type of modification of the CPEs composition is connected with a desirable increase in either selectivity or sensitivity. The gains must prevail over the more complicated and labor-intensive preparation of the electrode, easier passivation, or electrode fouling, and usually more fixed electrochemical protocol.

DETERMINATION OF ORGANIC COMPOUNDS USING CARBON PASTE ELECTRODES

CPEs can be used as classical working electrodes in batch methods or in flowing systems (HPLC-ED, CZE-ED, FIA-ED). A simple configuration of the carbon paste based wall-jet type detector is depicted in Figure 1. Batch methods are usually very sensitive because of the possibility to accumulate the analyte from the solution on the surface of the working electrode. On the other hand, the adsorption, co-reduction, or co-oxidation of interferences can obscure the electrode process under study or passivate the electrode so that either relatively simple matrices or a preliminary separation is necessary. Therefore, voltammetry at CPEs is suited for analysis of various pharmaceutical products because the analyzed matrices are relatively simple with usually only one electrochemically active analyte present, while other substances present are usually electrochemically inactive. Surprisingly, the developed batch methods are often also usable on biological fluids like human serum or urine where the concentration of the pharmaceutical or its metabolite is markedly higher than of other components. Table 1 surveys recent selected applications of bare, chemically modified, and biologically modified CPEs in the analysis of organic compounds important from the point of view of human health and environmental protection. The type of analyte was chosen as the main classifier and the analytes are arranged in an alphabetical order although it must be kept in mind that the analyzed species, in fact, could be different. The claimed linear dynamic range consists sometimes from two linear parts, typically in a higher concentration range for, e.g., DPV or SWV, and in the lower concentration range for AdSV. The widespread use of CPEs in this field is connected with the ease of their modification and thus with the ease of tailoring their properties with regard to selectivity and sensitivity. Nevertheless, bare CPEs are still frequently used in this field, constituting up to about 20% of the published papers. Without analyte accumulation on the surface of the working electrode, LOD is usually around 1×10^{-7} to 1×10^{-6} M; AdSV typically

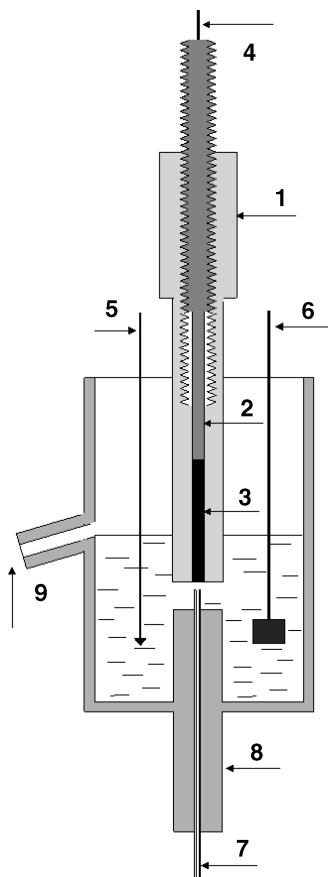


FIG. 1. Scheme of the CPE wall-jet type detector. 1—Teflon body, 2—stainless steel piston, 3—carbon paste working electrode, 4—electric contact, 5—reference electrode, 6—auxiliary electrode, 7—inlet capillary, 8—glass vessel, 9—mobile phase overflow.

decreases LOD to 1×10^{-8} – 1×10^{-9} M. LOD can be further decreased with either special techniques like electrode transfer to different supporting electrolyte, following the accumulation in another electrolyte, analyte multiplication reactions, use of catalytic reactions, or new modifiers with special properties as will be discussed below.

Recently published methods are frequently based on the oxidation of amino group (67–83, 85–87, 89–94) or hydroxy group (69, 75, 80, 81, 89, 95–128) on aromatic, heteroaromatic, or heterocyclic rings. LOD are typically around $(0.1\text{--}10) \times 10^{-7}$ M (68, 71, 72, 75, 80, 81, 88, 112, 122, 126, 129–131). LOD of the anti-arrhythmic agent amiodarone (132) on bare CPE below 10^{-9} M is enabled by a catalytic wave in the presence of potassium peroxodisulphate oxidation agent and enhancing surfactant Triton X-100. The catalytic peak also enabled determination of anthraquinone derivative emodin (109) using the dissolved oxygen as oxidizing agent. AdSV of another anthraquinone derivative physcion (116) on bare CPE based on catalytic principle with re-oxidation by dissolved oxygen gives LOD 8×10^{-11} M. Reactivation of CPE surface by scanning the potential between

0.4 and 1.3 V enabled the determination of sub-nanomolar concentrations of tamoxifen (133).

Modification of the CPE involves nanomaterials like single or multiple wall carbon nanotubes or metals like silver, gold, platinum, or palladium, or nanocrystalline metal oxides or formation of bismuth or platinum films on the electrode surface. These nanomaterials play an important role as either catalysts or homogenizing components for other paste components. Inorganic modifiers such as montmorillonite, sepiolite, fluoroapatite, hydroxyapatite, and zeolites serve for selective accumulation of the analyte on the electrode surface which is reflected by peak current increase and lower limits of detection. The well known catalytic properties of carbon nanotubes can substantially decrease LOD (74, 89, 94, 97, 119–121, 134–139). Nevertheless, nanomolar LOD was reported only for easily oxidizable flavonoid quercetin (121) or easily reducible methylparathion (87) for which catalytic properties of single wall carbon nanotubes (SWCNT) were supported by the use of RTIL 1-butyl-3-methylimidazolium hexafluorophosphate, which reportedly enhances the adsorption of methylparathion on the electrode surface. RTILs were recently tested as modifiers or substitutes of pasting liquids with some encouraging results already published. However, according to our opinion, the disadvantages connected with too high conductivity and very different properties coming from their structural differences makes RTILs application rather complicated. When using paraffin, mineral, or silicone oil together with “any type” of carbon powder, the prepared CPE usually works very well, which is not the case with “any type” of ionic liquid. In some papers, the beneficial contribution of RTILs is clearly cited (69, 87, 101, 102, 105, 114, 139), but it may be difficult to distinguish whether the beneficial effect comes from carbon nanotubes or from RTIL (87, 139). CPE can be used for determination of both oxidizable and reducible group in the same analyte (75), which increases the reliability of the determination.

A very useful combination is CPEs combined with high separation power of either CZE (140–143) or HPLC (93, 126, 144). The resulting methods are then not only highly sensitive but could be used for complicated matrices (biological fluids, food and drinks, environmental samples) (Fig. 2). Cu(I) cations (supported by multi wall carbon nanotubes [MWCNT]) (140) play an important role in capillary zone electrophoresis with electrochemical detection (CZE-ED) of several amino acids; the same is valid for the determination of glucose, sucrose, fructose, and ascorbic acid [Cu(I) cations supported by PEG] (141). Nineteen essential amino acids gave oxidation peaks at CPE (140). Carbohydrate or AA can be adsorbed at CPE modified by PEG, the oxidation is then triggered by the deprotonation of the analyte and its isomerization to enediol form followed with the oxidation by Cu(I), Cu(II), and Cu(III) surface states (141). Nano-nickel oxide was utilized to catalyze the oxidation of glucose, sucrose, and fructose (143). The role of nNiO laid the facilitation of the carbohydrate dehydrogenation/oxidation which is reflected in better reproducibility and sensitivity of the CZE-ED in honey samples.

TABLE 1
Determination of organic compounds using carbon paste electrodes

Analyte	Type of CPE	Technique	LDR (LOD)	Remarks	Ref(s)
<i>N</i> -Acetylcysteine	CNT, CoSal	CV, DPV	1×10^{-7} – 1×10^{-4} M (5×10^{-8} M)	0.1 M PhB pH 7, pharmaceutical and clinical samples	(150)
Amino acids	MWCNT, Cu ₂ O	CZE-AMP +0.75 V vs. SCE	1×10^{-4} – 5×10^{-6} M (1×10^{-8} – 1×10^{-7} M)	Alkaline buffers pH 12.5, t_{anal} 20 min	(140)
p-Aminobenzoic acid	Crown ethers	DPV	0.4–500 $\mu\text{g/mL}$ (0.1 $\mu\text{g/mL}$)	BRB pH 2, pharmaceuticals, yeast	(67)
3-Amino-fluoranthene	Bare	AdSDPV	2×10^{-8} – 1×10^{-4} M (2×10^{-8} M)	0.04 M BRB pH 4, model samples	(68)
p-Aminophenol	IL	CV, DPV	2×10^{-6} – 3×10^{-4} M (6×10^{-7} M)	0.1 M PhB pH 7, model waste waters	(69)
Aminophylline	Pt film	CV, DPV	8–40 mg/L (1 mg/L)	0.1 M PhB pH 3.2–6.6, cosmetic creams	(70)
8-Aminoquinoline	Bare	AdSDPV	2×10^{-7} – 1×10^{-4} M (2×10^{-7} M)	0.1 M NaOH, model quinolines mixtures	(71)
Aminoquinolines	Bare	DPV, AdSDPV	1×10^{-7} – 1×10^{-4} M (1×10^{-7} M)	0.1 M H ₃ PO ₄ , model samples	(72)
Amiodarone	Bare	AdSV	2×10^{-10} – 2.3×10^{-8} M (1.5×10^{-10} M)	0.2 M AcB pH 5.3. K ₂ S ₂ O ₈ , Triton X-100, t_{acc} 30 s	(132)
Amitrole	MWCNT	AdSV	0.8–7 μM (0.6 μM)	0.05 M PhB pH 7.4, t_{acc} 5 min, spiked river water	(73)
Amoxicillin	VO(Salen)	CV, DPV, SWV, LSW	(8.5 μM for SWV)	tablets	(95)
Ascorbic acid, sugars	PEG, Cu ₂ O	CZE-AMP +0.3 to +0.6 V vs. SCE	1×10^{-6} – 5×10^{-5} M ($\sim 5 \times 10^{-7}$ M)	30 mM NaOH, t_{anal} 22 min, simultaneous determ. in beverages	(141)
Ascorbic acid	Fe(III) Y zeolite	SWV	4×10^{-7} – 1.2×10^{-3} M (2×10^{-8} M)	PhB pH 5, citrus fruits samples	(96)
Avidin, biotin	Avidin	AdSSWV, FIA	(3×10^{-15} M)	0.1 M AcB pH 4, transgenic maize extract, pharmaceuticals	(146)
Azobenzene dyes	Bare	AdSDPV	1×10^{-4} – 2×10^{-7} M (2×10^{-8} M)	BRB pH 3 and 4, model mixtures	(75)
Benorilate	nAg	DPV	1×10^{-7} – 2.5×10^{-4} M (1×10^{-8} M)	0.001 M PhB pH 6.88, pharmaceuticals	(76)
Bergenin	MWCNT	CV, DPV	6×10^{-7} – 1×10^{-5} M (7×10^{-8} M)	PhB pH 7, tablets	(97)
Bisphenol A	CTAB	VOL	2.5×10^{-8} – 1×10^{-6} M (7.5×10^{-9} M)	Waste plastic samples	(98)
Bromadiolone	Bare	DPV	(0.5 ng/mL)	0.2 M AcB pH 4.2, animal tissue	(77)
Caffeine	Q	CV, SWV	0.3×10^{-6} – 8×10^{-3} (0.3×10^{-6} M)	PhB pH 6, coffee samples	(151)
Carbamates	Polyamide	CZE-AMP +1 V vs. SCE	1×10^{-7} – 2×10^{-5} M (3×10^{-8} M)	Borate buffer pH 11, t_{anal} 23 min, sprayed vegetables samples	(142)
Carbidopa	PbO ₂ , resin	DPV	4.2×10^{-5} – 1.5×10^{-4} M (3.7×10^{-6} M)	0.1 M HClO ₄ , pharmaceuticals, simult. with L-dopa	(99)

(Continued on next page)

TABLE 1
Determination of organic compounds using carbon paste electrodes (Continued)

Analyte	Type of CPE	Technique	LDR (LOD)	Remarks	Ref(s)
Carbohydrates	nNiO	CZE-AMP +0.55 V vs. SCE	1×10^{-6} – 1×10^{-3} M (3×10^{-7} M)	0.05 M NaOH, t_{anal} 20 min, honey samples	(143)
Catechin	β -CD	SWV	2–70 $\mu\text{g/mL}$ (1.34 $\mu\text{g/mL}$)	0.05 M PhB pH 7, tea samples	(100)
Catechol	IL	CV	1×10^{-6} – 8×10^{-4} M (6×10^{-7} M)	PhB pH 3, synthetic samples	(101)
Catecholamines	IL	CV	$\sim 3 \times 10^{-7}$ – 1×10^{-4} M ($\sim 1 \times 10^{-7}$ M)	0.1 M H_2SO_4 + 0.01 M KCl, pharmaceuticals	(102)
Cephalosporins	Co(Salophen)	DPV	1×10^{-5} – 1×10^{-3} M (1×10^{-6} M)	0.1 M PhB pH 3, human synthetic serum	(152)
Chlorophenol	Montmorillonite, CTAB	SWV	5×10^{-8} – 1×10^{-5} M (2×10^{-8} M)	0.1 M PhB pH 8, t_{acc} 2 min, water samples	(103)
Chloroquine	dsDNA	CV, DPV	1×10^{-7} – 1×10^{-5} M (3×10^{-8} M)	0.02 M AcB, pH 4, serum	(74)
Chlorpyrifos	Sepiolite	AdSDPV	0.0001–2 ppm (8×10^{-5} ppm)	BRB pH 2, t_{acc} 80 s, water, juice, soil samples	(153)
Ciprofloxacin	SDBS	VOL	8×10^{-8} – 5×10^{-6} M (2×10^{-8} M)	PhB pH 4, t_{acc} 2 min, drugs	(154)
Ciprofloxacin	CTAB	CV, DPV, LSV	1×10^{-7} – 2×10^{-5} M (5×10^{-8} M)	0.1 M PhB pH 7, t_{acc} 3 min, drugs	(155)
Cisapride	CNT	AdSDPV	4×10^{-8} – 2×10^{-5} M (1×10^{-8} M)	BRB pH 6.1, tablets	(78)
Clozapine	dsDNA	AdSDPV	7×10^{-9} – 1.2×10^{-6} M (1.5×10^{-9} M)	0.5 M AcB pH 4.3, t_{acc} 3 min, human serum	(79)
Coumarins, psoralens	Bare	VOL	(0.06 and 0.20 mg/L, resp.)	PhB pH 2 and 7, citrus oils	(156)
L-Cysteine	FDCM	CV, DPV	1.5×10^{-5} – 3.2×10^{-3} M (1.4×10^{-6} M)	0.1 M PhB pH 8, plasma, pharmaceuticals	(157)
Cysteine	Bi powder	SWCSV	1×10^{-6} – 5×10^{-5} M (3×10^{-7} M)	0.1 M AcB pH 4.7, t_{acc} 100–600 s	(158)
Dipyridamole	CTAB	EIS, DPV	0.03–12 $\mu\text{g/mL}$ (0.01 $\mu\text{g/mL}$)	0.5 M PhB pH 8, t_{acc} 2 min, tablets	(159)
Dipyrrone	VO(Salen)	CV	9.9×10^{-6} – 2.8×10^{-3} M (7.2×10^{-6} M)	0.1 M KCl pH 5–8, pharmaceuticals	(160)
Diquat	Fluoroapatite	CV, SWV	3.1×10^{-8} M	0.1 M K_2SO_4 , river water	(161)
Dobesilate	$\text{La}(\text{OH})_3$ nanowires	LSV	3×10^{-10} – 1×10^{-8} M (5×10^{-11} M)	model samples	(104)
Dobesilate	IL	DPV	8×10^{-7} – 1×10^{-4} M (4×10^{-7} M)	0.5 M H_2SO_4 , capsules, urine	(105)
Dopamine	Ti phosphate, SiO_2	DPV	2×10^{-7} – 5×10^{-5} M (4.3×10^{-8} M)	0.1 M PhB pH 7.5, injections	(106)
Dopamine	SDBS	CV, DPV	5×10^{-7} – 8×10^{-4} M (5×10^{-8} M)	0.1 M PhB pH 7.4, injections, model biol. samples	(107)
Dopamine	SDS	DPV	0.01–0.2 mM (5 μM)	0.1 M NaCl, AA masking, pharmaceuticals	(108)
Emodin	Bare	AdSV	3×10^{-10} – 4×10^{-8} M (1×10^{-10} M)	AmB pH 8.2, t_{acc} 30 and 90 s, plant	(109)
Endosulfan	C18 modifier, Cu(II)	DPASV	0.001–0.011 mg/L (40 ng/L)	0.2 M BRB pH 4, model samples	(162)

TABLE 1
Determination of organic compounds using carbon paste electrodes (Continued)

Analyte	Type of CPE	Technique	LDR (LOD)	Remarks	Ref(s)
Estrone	CTAB	VOL	9×10^{-8} – 8×10^{-6} M (4×10^{-8} M)	t_{acc} 3 min, tablets	(110)
Ethinylestradiol	CPB	LSV	5×10^{-8} – 2×10^{-5} M (3×10^{-8} M)	0.07 M PhB pH 8, t_{acc} 3 min, tablets	(111)
Etoposide	Bare	CV, LSV, DPV	2.5×10^{-7} – 2.5×10^{-5} M (1×10^{-7} M)	0.04 M BRB pH 3, human serum	(112)
Flavonoids	Bare	SWV	0.15–5 (200) μ M (in nM region)	0.1 M PhB pH 7, body liquids	(129)
Flavonols	diphenylether	AdSV	30–1000 μ g/L (9 μ g/L)	0.04 M BRB pH 5, food products	(113)
Fluoren-9-ol, ac-etamidofluorene	Bare	SWV, AdSDPV	0.01–300 μ M (1 μ M and 0.04 μ M, resp.)	0.1 M H ₂ SO ₄ and BRB pH 7, resp.	(80)
Fluoroquinolones	Bare	CV, AdSDPV	2×10^{-7} – 6×10^{-5} M ($\sim 4 \times 10^{-7}$ M)	0.05 M AcB pH 5, urine, dosage forms	(130)
Fluoroquinolones	CD	DPV	3.2×10^{-8} – 2×10^{-5} M (2.4×10^{-8} M)	0.04 M BRB pH 4, t_{acc} 160 s, pharmaceuticals, urine	(163)
Guanine	Montmorillonite	CV, DPV	5×10^{-8} – 2×10^{-5} M (2×10^{-8} M)	0.1 M PhB pH 7, t_{acc} 4 min, urine samples	(164)
Guanine	ssDNA	SWV	0.025–100 μ M (12.5 nM)	PhB pH 7.4, oligonucleotides analysis	(165)
Heroin	Ru complex, zeolite	ECL	2–80 μ M (1.1 μ M)	0.1 M PhB pH 6.3	(147)
Homocysteine et al.	nAu, cysteamine	CV, HPLC-AMP, +0.8 V	0.1–1 μ M (30 nM)	AcN – 0.05 M PhB pH 2, serum samples	(144)
Hydroquinone	IL	CV	5×10^{-6} – 5×10^{-3} M (2.5×10^{-6} M)	PhB pH 2.5, waste waters	(114)
Inosine	La(OH) ₃ nanowires	LSV	4×10^{-9} – 2×10^{-8} M (8.3×10^{-10} M)	0.1 M PhB + 6×10^{-6} M Cu(II) + 6×10^{-6} M K ₂ S ₂ O ₈ , pharmaceuticals, human serum	(145)
Isoniazid	MWCNT	CV, DPV	1×10^{-6} – 1×10^{-3} M (5×10^{-7} M)	0.1 M AcB pH 4, clinical, pharmaceutical samples	(134)
Leucoindigo	Bare	CV, ACV, AdSV	1×10^{-6} – 7.5×10^{-9} M (7.4 nM)	0.1 M Tris-HCl pH 7.2, t_{acc} 2 min	(81)
Malachite green	SDBS	CV, DPV	8×10^{-9} – 5×10^{-7} M (4×10^{-9} M)	0.1 M PhB pH 6.5, t_{acc} 5 min, fish samples	(82)
Mefenamic acid	La(OH) ₃ nanowires	LSV	2×10^{-11} – 4×10^{-9} M (6×10^{-12} M)	0.1 M PhB pH 5.8, drug samples	(83)
Metamitron	Bi film	SWV, DPamp	10–200 μ M (2 μ M)	0.1 M AcB pH 4.5, model samples	(84)
Metformine	Cu(II) complex wires, MWCNT	LSV	9×10^{-7} – 5×10^{-5} M (6.5×10^{-7})	0.04 M BRB pH 7.2, tablets	(135)
Metformine	Cu(II), MWCNT	CV, SWV	2×10^{-7} – 1×10^{-5} M (6.7×10^{-8} M)	0.1 M AmB pH 8.9, pharmaceuticals	(136)
Methimazole	Co complex	CV, DPV	1×10^{-6} – 1×10^{-4} M (5×10^{-7} M)	0.1 M PhB pH 7, pharmaceutical and clinical samples (serum)	(166)

(Continued on next page)

TABLE 1
Determination of organic compounds using carbon paste electrodes (Continued)

Analyte	Type of CPE	Technique	LDR (LOD)	Remarks	Ref(s)
Methotrexate	CD	CV, SWV	(~1.3 ng/mL), 0.1% D-Mtx (m/m in LMtx)	0.05 M PhB pH 6.4, enantioseparation, tablets, injections	(85)
Metoclopramide	Bare	CV, SWASV	0.07–0.34 ng/mL (0.007 ng/mL)	0.4 M AcB pH 6 + 0.2 M KCl, t_{acc} 1 to 1.5 min, pharmaceuticals, spiked urine	(86)
Methylparathion	IL, SWCNT	CV, LSV	2×10^{-9} – 4×10^{-6} M (1×10^{-9} M)	0.1 M PhB pH 7, t_{acc} 3 min, lake water, fruit samples	(87)
MPCA	MnO ₂	CV, AMP +0.1 V vs. SCE	3.8×10^{-6} – 1×10^{-5} M (0.2 ppm)	0.1 M KCl, commercial product	(167)
Naphthoquinones	Bare	DPV, FIA	1–50 μ g/mL, (to ng/mL)	0.2 M PhB, biological samples	(168)
Natamycin	Bare	CV, DPV	2×10^{-6} – 8×10^{-5} M (1.5×10^{-6} M)	0.5 M H ₂ SO ₄ pH 1.8, capsules	(169)
Nicotinamide	Crown ethers	CV, DPV	0.1–500 μ g/mL (0.03 μ g/mL)	0.001 M CH ₃ COOH, pharmaceuticals	(170)
Oxalic acid	nPd	DCV, CV	1×10^{-2} – 2×10^{-5} M (2×10^{-5} M)	0.01 M H ₂ SO ₄ , model solutions	(171)
Paraquat	Phosphate	SWV	2.3×10^{-8} – 3×10^{-6} M (7.8×10^{-10} M)	0.1 M K ₂ SO ₄ , water samples	(172)
Paraquat	Hydroxyapatite	SWV	8×10^{-8} – 2×10^{-5} M (1.8×10^{-8} M)	0.1 M K ₂ SO ₄ , river waters	(173)
Paraquat	Fluoroapatite	SWV	5×10^{-8} – 7×10^{-5} M (3.5×10^{-9} M)	0.1 M K ₂ SO ₄ , model spiked food samples	(174)
Pefloxacin	dsDNA	AdSDPV	1×10^{-7} – 1×10^{-5} M (3×10^{-8} M)	0.02 M AcB pH 5, urine samples	(175)
D-Penicillamine	FDCA	CV, DPV	6.5×10^{-1} – 1×10^{-4} M (6×10^{-6} M)	0.1 M PhB pH 7, capsules	(176)
D-Penicillamine	FEPE	CV, DPV	7×10^{-6} – 2.3×10^{-4} M (3.9×10^{-6} M)	0.1 M PhB pH 7, capsules, human serum	(177)
Phenazopyridine	Bare	SWV	2.5×10^{-8} – 2.5×10^{-6} M (7.5×10^{-9} M)	0.5 M H ₂ SO ₄ , urine, tablets	(88)
Piroxicam	MWCNT	CV, DPV	0.15–5 μ g/mL (0.1 μ g/mL)	0.1 M AcB pH 6, t_{acc} 5 min, dosage forms	(89)
Phenol	Ppy, PVP	CV, ASV	1×10^{-6} – 1×10^{-3} M (1×10^{-7} M)	PhB pH 10, t_{acc} 10 min, waste waters	(115)
Physcion	Bare	AdSV	2×10^{-10} – 2×10^{-8} M (8×10^{-11} M)	0.4 M AmB pH 10.5, t_{acc} 1–2 min, catalytic current, plant extract	(116)
Propylthiouracil	CoClSal	CV, DPV	7.6×10^{-6} – 7.5×10^{-4} M (2×10^{-6} M)	0.1 M AcB pH 4, pharmaceutical, clinical preparations	(90)
Pyridoxine	Crown ethers	CV, DPV	0.6–100 μ M (0.2 μ M)	0.05 M Tris pH 10.3, multivitamin pharmaceuticals	(117)
Quercetin	Bare	SWASV	68–338 ppb (6.8 ppb)	0.04 M PhB pH 4 + 0.1 M KCl, t_{acc} 15 s, spiked urine	(118)
Quercetin	CNT	AdSV, ChP	0.1–1 μ M (3×10^{-8} M)	AcB pH 5.5, flavonoids samples	(119)

(Continued on next page)

TABLE 1
Determination of organic compounds using carbon paste electrodes (Continued)

Analyte	Type of CPE	Technique	LDR (LOD)	Remarks	Ref(s)
Quercetin, rutin	MWCNT	CV, DPV, RDPV	0.05–5 μM and 0.1–10 μM , resp. (2×10^{-8} M and 4×10^{-8} M, resp.)	0.04 M BRB pH 7, plant, serum samples	(120)
Quercetin	MWCNT	CV, COU	2×10^{-9} – 2×10^{-5} M ($\sim 1 \times 10^{-9}$ M)	0.1 M PhB pH 4, rutin hydrolysates	(121)
Repaglinide	Bare	DPV	8×10^{-7} – 3.2×10^{-6} M (1.3×10^{-7} M)	0.04 M BRB, tablets, human serum	(131)
Resveratrol	Bare	CV, SWV	5×10^{-9} – 1.6×10^{-7} M (in nM)	0.001 M KCl + 0.1 M HNO_3 pH 1, urine, pharmaceuticals dosage forms	(122)
Riboflavin	Crown ethers	CV, DPV, SWASV	0.5 ng/mL–70 $\mu\text{g/mL}$ (0.2 ng/mL)	0.04 M BRB pH 1.5, pharmaceuticals, food	(91)
Rutin	PVP	CV, LSV	3.9×10^{-7} – 1.3×10^{-5} M (1.5×10^{-7} M)	0.1 M PhB pH 6, t_{acc} 10 min, pharmaceuticals	(123)
Streptavidin	Bare	SWV	3–60 zmol/5 μl (0.3 aM)	0.2 M AcB pH 4, t_{acc} 10 min, electrode transfer	(92)
SDBS	Butylrhodamine B	ECL	2×10^{-6} – 8×10^{-3} M (5×10^{-7} M)	0.1 M NaOH	(148)
Sudan I	Montmorillonite	CV, SWV	2×10^{-7} – 4×10^{-6} M (8×10^{-8} M)	0.1 M PhB pH 7, t_{acc} 2 min, food samples	(124)
Tamoxifen	Bare	LSV	7×10^{-10} – 3×10^{-8} M (1×10^{-10} M)	AcB pH 4.1, tablets	(133)
Tanshinone II A	Bare	VOL	1.2×10^{-8} – 2.1×10^{-6} M (4.1×10^{-9} M)	0.2 M BRB pH 2.4 + EtOH, tablets	(178)
TEA, TPrA	Bare, heating 39°C	CZE, ECL, Ru complex	~ 0.01 – 40 μM (0.002 μM)	0.02 M PhB pH 8, model mixtures	(149)
Tetracycline et al.	Cu(II), dsDNA	VOL	1×10^{-9} M	0.2 M AcB + 0.02 M NaCl pH 4.7	(125)
Theophylline	K_2PtCl_6	HPLC-AMP	50–3200 ng/mL (1.1 ng/mL)	MeOH-PhB pH 5.5, serum, purines detection	(93)
Thymol	Bare	HPLC-AMP, +1.1 V vs. Ag/AgCl	2×10^{-7} – 1×10^{-7} M (2.9×10^{-7} M)	0.004 M BRB pH 7 – MeOH (1:9), pharmaceuticals	(126)
Tocopherol	CNT, dsDNA	CV, SWV	0.5–160 $\mu\text{g/L}$ (1.3×10^{-10} M)	0.1 M PhB, food, pharmaceuticals	(127)
Troponin I	Molecular sieve	ASV	0.8–5.0 ng/mL (0.5 ng/mL)	0.1 M HNO_3 , real myocardial samples, immunoreaction	(179)
Troponin I	Molecular sieve	ASV	0.5–5.0 ng/mL (0.2 ng/mL)	0.1 M HNO_3 , real myocardial samples, immunoreaction	(180)
Troxerutin	PVP	CV, COU	1×10^{-4} – 1×10^{-8} M (5×10^{-9} M)	0.1 M KCl, t_{acc} 5 min, pharmaceuticals	(128)
Tryptophan	MWCNT, CoSal	CV, DPV	5×10^{-5} – 5×10^{-7} M (1×10^{-7} M)	0.1 M AcB pH 4, pharmaceutical, clinical preparations	(137)
Tryptophan	FEPE	CV, ChrADPV	8.5×10^{-7} – 6.3×10^{-6} M (5.6×10^{-7} M)	0.1 M PhB pH 7, human serum	(181)
Urapidil	MWCNT	CV, DPV	5×10^{-8} – 2×10^{-6} M (3.8×10^{-8} M)	0.04 M BRB pH 6.8, t_{acc} 1 min, tablets	(94)
Uric acid, ascorbic acid	MWCNT, CoNSal, nafion	CV, DPV	1×10^{-7} – 1×10^{-4} M ($\sim 6 \times 10^{-8}$ M)	0.1 M AcB pH 4, model AA and UA samples	(138)

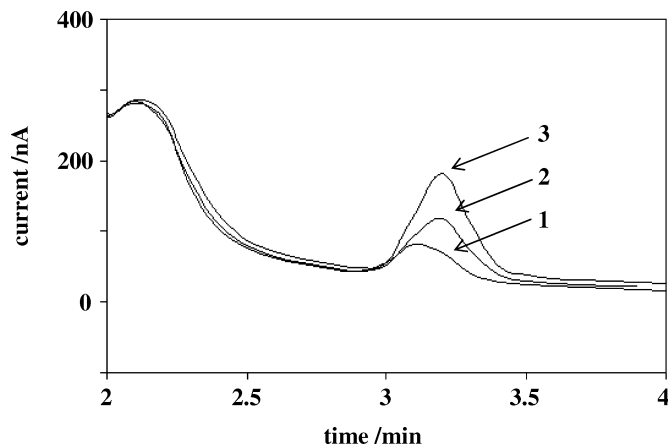


FIG. 2. The details of the chromatograms of thymol determination in thyme syrup (0.5 mL syrup diluted to 10 mL by 90% methanol in water), amperometric detection at CPE at +1, 1 V vs. Ag/AgCl reference electrode, mobile phase Britton-Robinson buffer pH 7 - methanol 1:9 (V/V), 0.5 mL/min, column Lichrospher® RP - 18, 100 - 5 μ m, 125 $\times$ 4 mm, injected 20 μ L, 1—thymol peak in the syrup, 2—added 100 μ L of 1×10^{-3} mol/L thymol in methanol, 3—added 200 μ L of 1×10^{-3} mol/L thymol in methanol.

Elemental gold (144) and platinum (93) nanoparticles were used for HPLC-ED of homocysteine (144) and theophylline (93) based on enhanced electron transfer connected with gold nanoparticles or with electrocatalytic activity of platinum nanoparticles towards the oxidation of the purine ring in theophylline and its metabolites. Taking into account that the CPE prepared from spherical microparticles of glassy carbon can be successfully used even in media with a high content of organic mobile phase modifiers like methanol or acetonitrile (126) it is possible to state that separation methods with detection at CPEs have a bright future.

The most sensitive recently published methods are based either on modification of CPE by lanthanum hydroxide nanowires (83, 104, 145) or on electrode transfer after a long time of analyte accumulation (92, 146). To get the inosine oxidation peak, the presence of Cu(II) ions and potassium disulphate was needed (145). The high sensitivity of the lanthanum hydroxide nanowires-modified CPE is reportedly connected with the formation of "porous layer" on the surface of CPE, thus markedly increasing its surface. The approach chosen for the determination of avidin and biotin (146) or streptavidin (92) is different. Here, the method is based on the oxidative signal resulting from the presence of tryptophan and tyrosine in the avidin protein molecule and very strong binding of avidin on the surface of the electrode so that transfer of the electrode to the washing solution and proper electrolyte is enabled. When streptavidin is used instead of avidin, the sensitivity of adsorptive transfer stripping voltammetry (AdTSV) is about one hundred times higher when working with only 5 μ L drops (92).

Last but not least, sensitive electroluminescent methods at CPEs (147–149) should also be mentioned. LOD of heroine (147) (based on electrocatalytic response of ruthenium complex) and of sodium dodecylbenzene sulphonate (based on oxidation of butyl-rhodamine B) (148) is around 1 μ M. LOD around 2 nM were reported for TEA and TPrA determination (149) with electrical heating of the CPE by 100 kHz alternating current. Here, tris(2,2'-bipyridyl)ruthenium(II) complex was added to the separation buffer for CZE. Surprisingly, the temperature elevation did not worsen the CPE performance but improved the peak shape, increased its reproducibility, and lowered the detectability of TEA and TPrA.

CARBON PASTE-BASED SENSORS AND BIOSENSORS

Fascinating possibilities of CPEs in this field are documented in Table 2. CPEs-based sensors or biosensors are typically used in the analysis of biogenic amines where electrochemistry successfully competes with separation methods. All published papers (182–185) utilize enzyme modification of CPE either by polyphenol oxidase (183–185) or horseradish peroxidase (182). Mainly, amperometry is used with quite low detection potentials. Ascorbic acid (AA) (186, 187) and uric acid (UA) (187–189) are also frequently targeted analytes. The method (187) utilizing incorporated thionone-nafion ion pair system as an electron mediator is able to simultaneously determine 500 nM AA and 50 nM UA, even in complex biological and clinical matrices. Even nanomolar limits of detection are reported for UA determination (188), with paste comprising multi-walled carbon nanotubes and ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. No enzyme was needed in contrast to similarly sensitive methods (189) where uricase together with electron transfer mediator tetracyanoquinodimethane were used. Amperometric sensors for D-lactic acid (190) depends on the biorecognition element of D-lactate cytochrome c oxidoreductase bound by glutaraldehyde in combination with methosulphate—Reinecke's salt as mediator. A similar principle was used for detection of D-amino acids (191) when fatty acid modification of flavin adenin dinucleotide redox cofactor was employed.

CP sensors are quite often also used for phenols (43, 192–204), which is based on their easy oxidation and/or easy enzymatic reactions. The use of immobilized bacteria or microbial cells expressing hydrolases and degrading organophosphorous (194), of tyrosinase (202, 203), and of either magnetic particles (202) or gold nanoparticles (203) was described. By far, the largest number of papers is devoted to the analysis of sugars (14–30, 205), glucose being the favorite analyte (14–30). The majority of methods utilizes glucose oxidase together with a broad range of metal complexes, metal nanomaterials, polymers, ionic liquids, etc. A very sensitive method for simultaneous determination of glucose and insulin (30) is based on a needle type of an integrated chemically and biologically modified carbon paste where the glucose signal relies on the catalytic activity of glucose oxidase and the insulin signal relies on the electrocatalytic activity of ruthenium oxide. The glucose sensor

TABLE 2
Determination of organic compounds using carbon paste electrode-based sensors

Analyte	Type of CPE	Technique	LDR (LOD)	Remarks	Ref(s)
D-Amino acids	DAAOX, ferrocene, modified FAD	AMP, +0.7 V vs. Ag/AgCl	3×10^{-3} – 1×10^{-4} M (1×10^{-4} M)	0.05 M PhB, pH 9.2	(191)
Ascorbic acid	FePC	POT	1×10^{-2} – 1×10^{-6} M (5×10^{-7} M)	0.05 M PhB, pH 6, catalytic AA oxidation, response time <10 s, vitamin preparations	(186)
Ascorbic acid, uric acid	Thionine, nafion	DPV, CV	1×10^{-4} – 1×10^{-6} M (5×10^{-7} M AA, 5×10^{-8} M UA)	0.1 M AcB, pH 5, ion pairing, pharmaceuticals, urine, serum	(187)
Benzoyl peroxide	CuTerpy	AMP, –0.05 V vs. SCE	0.9–5 μ g/mL (0.2 μ g/mL)	0.1 M PhB, pH 7, pharmaceuticals, RT 0.5 s	(208)
Biogenic amines	HRP	AMP, –50 mV vs. SCE	40–470 ng/mL, (17 ng/mL)	0.1 M PhB, pH 7, 10 μ M H ₂ O ₂ , blood samples, RT 0.5 s	(182)
*CA125	nAu, thionine, anti-CA125	AMP, DPV, EIA	10–30 U/mL (1.8 U/mL)	AcB, pH 7, human serum immunosensor	(57)
*CA19-9	nAu, HRP, CA19-9 antibody	DPV, CV, EIA	2–30 U/mL (1.37 U/mL)	PhB, pH 7, immunosensor	(58)
*CEA	nAg and nFe ₃ O ₄	CV, POT, ACI, EIA	1.5–200 ng/mL (0.5 ng/mL)	PhB pH 7.4, CEA antigen attachment, immunosensor	(59)
*CEA	nAu, thionine, nFe ₃ O ₄	DPV	1.5–60 ng/mL (0.3 ng/mL)	AcB, pH 6.8, immunoassay system	(60)
*CEA	nAu, nFe ₃ O ₄ , HRP, MPTMS	DPV	1–55 ng/mL (0.13 ng/mL)	PhB, pH 7, 1.3 mM OPD, 0.8 nM H ₂ O ₂ , immunosensor, protein diagnostics	(61)
Clozapine	HRP, MMPs, GA	AMP, 0.0 V vs. Ag/AgCl	2×10^{-4} – 3×10^{-5} M (5 μ M)	PhB pH 7.4, 0.1 mM H ₂ O ₂ , batch samples	(209)
Clozapine, thiols	HRP, MMPs	CV, AMP, 0.0 V vs. Ag/AgCl	10–220 μ M GSH (5 μ M)	PhB pH 7.4, 0.1 mM H ₂ O ₂	(210)
Cysteine, GSH	Tyrosinase	AMP, FIA, –0.05 V vs. Ag/AgCl	1–8 μ M, (0.1 μ M AMP, 1 μ M FIA)	pH 6.5, minimum AA and UA interferences	(211)
Cysteine	CoSal	AMP, POT, DPV	2×10^{-6} – 1×10^{-2} M (1×10^{-6} M)	0.05 M PhB or AcB, catalytic cysteine oxidation	(212)
Cysteine	(VO)O-Salen	CV, AMP, 0.65 V vs. SCE	2.4×10^{-4} – 2.3×10^{-3} M (1.7×10^{-4} M)	0.1 M KCl, pH 5, possibly pharmaceuticals	(213)
Cysteine	NPN	AMP, +0.33 V vs. Ag/AgCl	0.8×10^{-6} – 13.2×10^{-6} M (2.5×10^{-7} M)	0.1 M PhB, pH 7, food samples	(214)
*DNA sequence	Chitosan, MB	DPV	1.5×10^{-9} – 1.5×10^{-7} M (3×10^{-10} M)	20 mM TRIS, pH 7, PCR, hepatitis B virus sequences, MB peak decrease measurement	(52)
*DNA sequence	HRP, ssDNA, nAu	DPV	9.5×10^{-9} – 1.5×10^{-10} M (5×10^{-11} M)	0.1 M PhB pH 7, 0.5 M H ₂ O ₂ , test DNA samples, HRP inhibition by dsDNA	(53)
*DNA sequence	PP, ssDNA, EB, MWCNT	DPV	1×10^{-8} – 1×10^{-10} M (8.5×10^{-11} M)	0.1 M PhB pH 7, differential EB current measurements	(54)
*DNA	IL, ssDNA	CV	10–110 μ g/mL (1.5 μ g/mL)	PhB, pH 7, t_{acc} 160s at +0.35 V, guanine peak, model samples	(55)

(Continued on next page)

TABLE 2
Determination of organic compounds using carbon paste electrode-based sensors (Continued)

Analyte	Type of CPE	Technique	LDR (LOD)	Remarks	Ref(s)
*DNA sequence	nPbSe, CTAB, chitosan	DPV	5×10^{-11} – 5×10^{-6} M (1.6×10^{-11} M)	Methylene violet indicator, plant samples	(56)
Dopamine	PPO, TCNQ	AMP, FIA, 0.1 V vs. Ag/AgCl	2×10^{-2} – 2×10^{-4} M (1.5×10^{-4} M)	0.3 M PhB, pH 7.8, pharmaceuticals	(183)
Dopamine	PPO, albumin, nAu	AMP, -0.1 V vs. Ag/AgCl	1×10^{-3} – 2×10^{-7} M (2×10^{-7} M)	0.05 M PhB pH 7.4, in presence of AA	(184)
Dopamine	Apple tissue (PPO)	DPV	0.4 – 25.2 μ M (2×10^{-7} M)	Injections, synthetic samples	(185)
Enalapril	LAAO	SIA/AMP, 0.65 V vs Ag/AgCl	0.08 – 1.5 μ M (4.3 nM)	0.1 M NaCl, raw materials, pharmaceuticals, enantioanalysis	(215)
EPN	CNT, DNA	SWV, CV	10 – 210 ng/L (8×10^{-12} M)	0.1 M $\text{NH}_4\text{H}_2\text{PO}_4$, fruit tissue, fish brain cells	(206)
Ethanol, NADH	Ru complex, Zr phosphate	AMP, CV	10 – 80 mM	0.1 M PhB, pH 8, NADH oxidation in presence of yeast	(216)
α -1-Fetoprotein	nAu and nFe_2O_3 , anti-AFP	POT, EIA	1 – 80 ng AFT (0.5 ng AFT)	0.1 M PhB pH 7, immunosensor	(62)
*Gene sequence	DNA, SA/Al film	CV, DPV	not found	BRB	(63)
*Gene sequence	DNA, SA/Al film	CV, DPV	2×10 nM	BRR, plant extracts	(64)
*Gene sequence	CTAB, ssDNA, MB	CV, DPV	(1×10^{-8}) M	Hybridization detection	(65)
*Gene sequence	CNT, pLys film	CV	1×10^{-12} – 1×10^{-7} M (3.1×10^{-13} M)	5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (1:1) + 0.1 M KCl electrostatic adsorption, PCR amplification	(66)
Glucose	GOX, nAu	AMP, CV	4×10^{-5} – 2.8×10^{-4} M (1×10^{-5} M)	0.1 M PhB, pH 5, no AA and UA interferences	(14)
Glucose	Cu, GOX	AMP, -0.1 V vs. Ag/AgCl	1.5×10^{-4} – 6×10^{-3} M (1.5×10^{-4} M)	0.05 M PhB, pH 7.4, no interferences from common interferents, serum samples	(15)
Glucose	GOX, MnO_2	AMP, FIA, +0.48 V vs. Ag/AgCl	20 – 500 mg/L (10.5 mg/L)	0.2 M PhB, pH 7.5	(16)
Glucose	GOX, RL	AMP, LSV	2 – 20×10^{-3} M, (8×10^{-4} M)	0.1 M KPF_6 , RL oxidation monitoring, blood samples	(17)
Glucose	GOX, Cu, Ir, CNT	AMP, -0.1 vs. Ag/AgCl	1.2×10^{-2} – 2×10^{-5} M, (2×10^{-5} M)	0.05 M PhB pH 7.4, H_2O_2 reduction	(18)
Glucose	Pt, GOX	CV, AMP, 0 V vs. Ag/AgCl	6×10^{-5} – 1.2×10^{-2} M, (2×10^{-5} M)	0.05 M PhB pH 7.4, model samples, 20–30 s RT	(19)
Glucose	GDH, DI, NAD(+), CNT, Os polymer	AMP, +0.2 V vs. Ag/AgCl	1×10^{-5} – 8×10^{-4} M, (1×10^{-5} M)	0.1 M PhB, pH 7, sweet wines samples	(20)
Glucose	$\text{La}(\text{OH})_3$, Cu(II)	VOL, -0.17 V vs. CSE	2×10^{-5} – 8×10^{-7} M, (3.5×10^{-7} M)	AmB pH 9.8, model samples	(21)
Glucose, phenol	CNT, Os complex, microbial cells	AMP, +0.3 V vs. Ag/AgCl	0.05 – 2.0 mM	0.05 M PhB pH 7, RT 35 s, artificial waste waters (for phenol)	(22)
Glucose	PQQ-GDH, CNT, $\text{K}_3\text{Fe}(\text{CN})_6$	AMP, CV, +0.5 V vs. Ag/AgCl	1×10^{-3} – 35×10^{-3} M (0.15 mM)	citrate buffer, pH 6, 2 μ l samples, RT 20 s	(23)

TABLE 2
Determination of organic compounds using carbon paste electrode-based sensors (Continued)

Analyte	Type of CPE	Technique	LDR (LOD)	Remarks	Ref(s)
Glucose	PP, GOX, PTY, Pt	AMP	1×10^{-5} – 1.8×10^{-2} M, (5×10^{-6} M)	2 months stability, almost no interferences, RT 10 s	(24)
Glucose	GOX, IL	AMP, VOL, +0.9 V vs. SCE	1–20 mM	0.05 M PhB, pH 7.5, RT 5 s	(25)
Glucose	nFe ₃ O ₄ -SiO ₂ , GOX, chitosan	AMP, FIA, +0.35 V vs. Ag/AgCl	1×10^{-5} – 4×10^{-3} M, (3.2×10^{-6} M)	0.1 PhB, pH 7.3, RT 10 s	(26)
Glucose	GOX, IL	DPV	1×10^{-7} – 8×10^{-4} M, (3×10^{-8} M)	0.067 M PhB, pH 7, human plasma, no mediator	(27)
Glucose	nNdHCF	SWV	5.0–100.0 μ M (3 μ M)	0.5 M KCl, no interferences	(28)
Glucose	GOX, MCP	AMP, +0.4 V vs. Ag/AgCl	7.2×10^{-5} – 1.5×10^{-2} M, (7.2×10^{-5} M)	0.05 M PhB, pH 7.4	(29)
Glucose, insulin	GOX, RuO ₂	AMP, FIA, +0.6 V vs. Ag/AgCl	0.1–1 μ M and 2–14 mM (23 nM and 500 nM), resp.	0.1 M NaCl/0.05 M PhB, pH 7.4, simultaneous determination	(30)
L-Glutamate	GluOx, TTF-TCNQ, BSA	AMP, +0.05 V vs. Ag/AgCl	sigmoidal shape (5×10^{-5} M)	0.05 M NaCl or KCl, pH 7, tomato foods	(31)
H ₂ O ₂	Mn oxides	AMP, +0.3 V vs. Ag/AgCl	1.0×10^{-4} – 6.9×10^{-4} (2 μ M)	0.01 M PhB pH 7.4, model samples	(32)
H ₂ O ₂	HRP, MB, SiO ₂ , NbO	AMP, –0.05 M vs. SCE	1–700 μ M, (5×10^{-7} M)	0.1 M PhB pH 6.8, RT 1 s, model samples	(33)
H ₂ O ₂	CNT, GOx	AMP, –0.1 V vs. Ag/AgCl	1–50 mM	0.05 M PhB pH 7.4, model samples	(34)
H ₂ O ₂	CNT	CV, AMP, –0.1 V vs. Ag/AgCl	2–20 mM	0.05 M PhB pH 7.4, RT 10 s	(35)
H ₂ O ₂	Coconut tissue	AMP, CV, –0.15 V	2×10^{-4} – 3.4×10^{-3} M (4×10^{-5} M)	pH 5.2, pharmaceuticals, 3 months lifetime	(36)
H ₂ O ₂	GaHCF	AMP, +0.15 V vs. SCE	4.9×10^{-6} – 4×10^{-4} M (1×10^{-6} M)	0.05 M PhB, pH 6.8, model samples	(37)
H ₂ O ₂	HRP, nFe ₃ O ₄ , GA	AMP	1.2×10^{-7} – 8.3×10^{-5} M (4.5×10^{-8} M)	Magnetic microparticles	(38)
H ₂ O ₂	nAu, cytochrome c	CV, 0 or –0.1 V vs. Ag/AgCl	10 μ M–5 mM (1×10^{-5} M)	0.1 M PhB pH 7, pseudo peroxidase activity	(39)
H ₂ O ₂	HRP, nAu, chitosan	CV, AMP –0.3 V vs. SCE	1.2×10^{-5} – 2.4×10^{-3} M (6.3×10^{-6} M)	0.067 M PhB, HQ mediator, real samples	(40)
H ₂ O ₂	HRP, nAu	CV, AMP, 0 to –0.4 V vs. SCE	2×10^{-7} – 5×10^{-5} M (2.1×10^{-7} M)	0.1 M PhB, pH 7, no mediator	(41)
H ₂ O ₂	RuO ₂	CV, AMP +0.6 V vs. SCE	0.029–0.1 mM (7 μ M)	0.1 M PhB, pH 7.4, H ₂ O ₂ consumption monitoring, catalase activity measur.	(42)
H ₂ O ₂ , hydroquinone	nAu, HRP	AMP, –0.25 V vs. Ag/AgCl	5×10^{-7} – 1.3×10^{-4} M (4×10^{-7} M)	0.1 M PhB pH 6.8, thiols inhibition study	(43)
H ₂ O ₂	MB, NaX zeolite	AMP, CV, –0.4 V vs. Ag/AgCl	1×10^{-5} – 1×10^{-3} M (1.4×10^{-4} M)	PhB, pH 6	(44)
H ₂ O ₂	nAu, HRP, PTH	AMP, 0.05 V vs. SCE	9.6×10^{-6} – 1.2×10^{-3} M (7.5×10^{-7} M)	0.1 M AcB pH 6.5, multiporous PTH	(45)
H ₂ O ₂	Heme proteins, IL	AMP, –0.45 V vs. Ag/AgCl	7.6×10^{-5} – 1×10^{-3} M (2.3×10^{-5} M)	0.1 M PhB pH 7, environmental samples, 3 months storage	(46)

(Continued on next page)

TABLE 2
Determination of organic compounds using carbon paste electrode-based sensors (Continued)

Analyte	Type of CPE	Technique	LDR (LOD)	Remarks	Ref(s)
Hydroquinone	Chitosan, plant extracts	DPV	$(2.5 \times 10^{-5} \text{ M})$	0.1 M PhB, pH 7, waste waters	(192)
Hydroquinone	Chitosan, gilo peroxidase, GA	SWV	$(2 \mu\text{M})$	0.1 M PhB, pH 7, 6 months lifetime	(193)
Hypoxanthine	nAu, GA, BSA	AMP, 0 and +0.6 V vs. Ag/AgCl	$0.5\text{--}10.0 \mu\text{M}$ ($2 \times 10^{-7} \text{ M}$)	0.1 M PhB, pH 7.4, sardines, chicken meal	(217)
Hypoxanthine	XOD, luminol	Electrochemi-luminescence	$0.6\text{--}120 \mu\text{M}$ ($0.1 \mu\text{M}$)	0.2 M PhB pH 7, electrically heated CP, 35°C	(218)
*IgG	nFe ₃ O ₄ , cystein, IgG antibody, GA	POT	$0.1\text{--}1.2 \text{ ng/mL}$ (0.023 ng/mL)	0.067 M PhB pH 7.4, immunosensor	(207)
Lactic acid	LCCOXR, mediator, GA	AMP, 0 V vs SCE	$1.5 \times 10^{-5}\text{--}1 \times 10^{-1} \text{ M}$ ($5.6 \times 10^{-5} \text{ M}$)	0.05 M PhB, pH 7, biological samples	(190)
LOX inhibiting drugs	LOX	DPV, +0.9 V vs. Ag/AgCl	$5.5 \times 10^{-5}\text{--}1.5 \times 10^{-4} \text{ M}$	0.1 M Sorensen b., pH 9, linoleic acid as substrate	(219)
Metronidazole	Porfyrine	AMP, -0.4 vs. SCE	$2.9 \times 10^{-3}\text{--}5.8 \times 10^{-8} \text{ M}$ ($5.8 \times 10^{-8} \text{ M}$)	BRB pH 4.3, pharmaceutical preparations	(220)
NADH	Coumestan	CV, ChA, DPV	$1\text{--}400 \mu\text{M}$ ($1 \times 10^{-7} \text{ M}$)	0.1 M PhB, pH 7, in uric acid presence	(47)
NADH	Hematoxylin	CV, ChA, DPV	$0.4\text{--}600 \mu\text{M}$ ($8 \times 10^{-8} \text{ M}$)	0.1 M PhB, pH 7	(48)
NADH	MB, zeolite	AMP, 0 V vs. Ag/AgCl	$3 \times 10^{-5}\text{--}1 \times 10^{-7} \text{ M}$ ($8 \times 10^{-7} \text{ M}$)	Ca ²⁺ fortified zeolite	(49)
NADH, PHEA	NAD(x), PDH, uricase, DHB	CV	$0.5\text{--}10 \text{ mM}$ ($0.5 \times 10^{-3} \text{ M}$)	PhB pH 9, phenylketonuria sensor, human urine	(50)
NADH	CNF	AMP, DPV, +0.45 vs. Ag/AgCl	$2 \times 10^{-8}\text{--}11.5 \times 10^{-6} \text{ M}$ ($2 \times 10^{-8} \text{ M}$)	0.1 M PhB pH 7, mediatorless sensor	(51)
Nicotine	ChOX, Q, BSA, GA	AMP, +0.45 V vs. SCE	$2 \times 10^{-5}\text{--}9.2 \times 10^{-4} \text{ M}$ ($1 \times 10^{-5} \text{ M}$)	0.067 M PhB, pH 7.4, inhibition biosensor	(221)
p-Nitrophenyl-	OPH immob. cells	AMP, +0.6 V vs. Ag/AgCl	$1 \text{ nM--}2 \mu\text{M}$ (1 nM)	50 mM citrate b., pH 7.5, 50 μM CoCl ₂ , organophosphorous nerve agents	(194)
p-Nitrophenol	Microb. cells	AMP, +0.3 V vs. Ag/AgCl	$20 \text{ nM--}20 \mu\text{M}$ (20 nM)	20 mM PhB, pH 7.5, microbial bios.	(195)
p-Nitrophenol (insecticides)	OPH, albumin, nylon net	AMP, +0.85 V vs. Ag/AgCl	$2\text{--}40 \text{ nM}$ (15 nM)	0.1 M PhB pH 7, OP insecticides	(196)
p-Nitrophenol (pesticides)	Bacteria, OPH	AMP, +0.6 V vs. Ag/AgCl	(1.4 ppb)	50 mM citrate b., PhB, pH 7.5, 50 μM CoCl ₂ , lake water	(197)
p-Nitrophenol (pesticides)	Bacteria, OPH	AMP, +0.9 V vs. Ag/AgCl	$0.2\text{--}175 \mu\text{M}$ ($0.2 \text{ to } 1 \mu\text{M}$)	pH 8.5, microbial biosensor, nerve agents	(198)
p-Nitrophenol	Nafion, bacteria	AMP, +0.4 V vs. Ag/AgCl	$5 \mu\text{M--}5 \text{ nM}$ (5 nM)	50 mM citrate b., pH 7.5, water samples	(199)
Pesticides	FePC, AChE, ChOx	AMP, +0.35 V vs. Ag/AgCl	$1 \times 10^{-5}\text{--}1 \times 10^{-9} \text{ M}$ (10 nM)	0.05 M PhB pH 7.5, H ₂ O ₂ detection	(200)
Phenols	HRP, Fc	AMP	$3 \times 10^{-7}\text{--}1.5 \times 10^{-5} \text{ M}$ ($3 \times 10^{-7} \text{ M}$)	wine, tea samples	(201)
Phenol	Tyrosinase, magnetic particles	AMP, -0.15 V vs. SCE	$1 \times 10^{-6}\text{--}2.5 \times 10^{-4} \text{ M}$ ($6 \times 10^{-7} \text{ M}$)	0.1 M PhB + 0.1 M KCl, pH 7, final quinone determination	(202)

TABLE 2
Determination of organic compounds using carbon paste electrode-based sensors (Continued)

Analyte	Type of CPE	Technique	LDR (LOD)	Remarks	Ref(s)
Phenol	nAu, tyrosinase	AMP, -0.15 vs. SCE	4×10^{-6} – 4.8×10^{-5} M (6×10^{-9} M)	0.1 M PhB, pH 7, RT 5 s	(203)
Phenol	Tyrosinase, MPMS	AMP, -0.15 vs. Ag/AgCl	0.025–50 μ M (25 nM)	0.05 M PhB+0.1 M NaCl, pH 7, biological fluids, marker of exposure to OPC	(204)
Psicose	DTE, DFDH	AMP, $+0.4$ V vs. Ag/AgCl	8×10^{-5} – 50×10^{-3} M (8×10^{-5} M)	citrate b.+ PhB, food, environment samples, microflow cell	(205)
Rutin	GP, chitosan, ECH, GA	SWV, $+0.124$ V vs. Ag/AgCl	3.4×10^{-7} – 7.2×10^{-6} M (2×10^{-8} M)	0.1 M PhB, pH 7, 8 months lifetime	(193)
Uracil	La(OH) ₃ , Cu(II)	AMP, $+0.22$ V	3×10^{-8} – 4×10^{-9} M (2×10^{-10} M)	0.1 M PhB pH 6.4, pharmaceuticals	(222)
Uric acid	MWCNT-IL	VOL, $+0.49$ V vs. SCE	1×10^{-8} – 1×10^{-6} M (5×10^{-9} M)	PhB, pH 4, urine samples, t_{acc} 3min	(188)
Uric acid	Uricase, tetracyanoquinodimethane	AMP, FIA, $+0.34$ V vs. Ag/AgCl	1–100 μ M (0.19 μ M)	TRIS-HCL buffer pH 8.6, RT 50 s, biological fluids	(189)
Vitamin B-12	DBCH	SWV	2×10^{-9} – 2×10^{-7} M (8.5×10^{-10} M)	0.2 M PhB pH 2.5, reduction of Co(III), reoxidation to Co(II), pharmaceuticals, biological matrices	(223)

*oligonucleotides confirmation or hybridization proof.

is reportedly not affected by injections of insulin samples while the insulin one is not responding to the large excess of glucose. Direct mediatorless determination of glucose utilizing glucose oxidase and ionic liquid as carbon paste binder was reported (27). Glucose oxidase was immobilized on hydrophobic ionic liquid 1-butylpyridinium hexafluorophosphate, with no other supporting films or mediators needed while retaining stability, repeatability, and reproducibility of performance even in real samples of human plasma.

Biosensors for hydrogen peroxide (32–46) incorporate either horseradish peroxidase and other peroxidases or glucose oxidase. As electron transfer mediators between immobilized enzyme and the electrode surface organic dyes or metal nanoparticles like gold nanoparticles, colloidal gold particles, or metal oxide particles are used. The medium pH for these sensors is almost exclusively around pH 7, with potentials for amperometric detection varying roughly from -0.5 to $+0.5$ V. The sensitivity is around 1 μ L/mol; the highest sensitivity reported (38) (4.5×10^{-8} M) was achieved after covalent immobilization of horseradish peroxidase using 3-(aminopropyl)triethoxysilane and glutaraldehyde on magnetic iron oxide particles used for analyte pre-concentration. Gold nanoparticles together with horseradish peroxidase (40, 41, 43, 45) are successful modifiers of CPE, helping the incorporated enzyme stability and showing electrocatalytic properties.

Reduced nicotinamide adenine dinucleotide is another important analyte (47–51). Its direct oxidation takes place at potentials above $+1$ V; moreover, it is accompanied by electrode

passivation and fouling due to the radical intermediates' formation and their subsequent polymerization. Again, electrode surface modification or electron transfer mediation is the solution. Hematoxylin-modified CE enabled electrocatalytic oxidation of in neutral media at the potential below $+0.2$ V, with LOD 8×10^{-8} M. Even lower LOD (2×10^{-8} M) is claimed for mediatorless CPE modified by carbon nanofibers produced by electrospinning technique. The applied potential is a little bit higher ($+0.45$ V) but still reasonably low and no mediator is needed.

By far the most sensitive methods are connected with DNA (gene)- or protein-based sensors (52–56, 62–66, 206, 207). Methods based on guanine oxidation are not so sensitive (55), although CV with a 3-minute accumulation time enabled determination of DNA concentrations of 1.5 μ g/mL. Immunosensors with antigen attachments allow the detection of proper antigen at the concentration as low as 0.5 ng/mL (59–61). PCR can further decrease LOD of specific oligonucleotides. PCR-amplified short DNA sequences related to hepatitis B virus were determined using methylen blue and chitosan-modified CPE (52). Here, the decrease in electroactive label meldola blue current measured by DPV was measured when evaluating the hybridization of the probe with the target (52). LOD of 3.1×10^{-13} M for genes, for phosphinothricin acetyltransferase (PAT) was recently reported (66). Modified CPE was prepared by the dripping of well-dispersed carboxylic group-functionalized single-walled carbon nanotubes on the CPE surface followed by formation of poly-L-lysine films. The DNA probes were immobilized by

electrostatic adsorption. Hybridization was monitored by electrochemical impedance spectroscopy using $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as an indicator. LDR of this DNA electrochemical sensor is 1×10^{-12} – 1×10^{-7} M.

CONCLUSIONS

As documented above, various types of CPEs, CMCPEs, and CP-biosensors still belong among the most popular laboratory-made configurations. Their wide-spread applicability reflects specific properties of carbon pastes, as well as the versatility of this electrode material in combinations with new technologies. Such adaptability is then apparently the most distinct feature of the present day's electrochemistry with carbon paste-based electrodes compared to previous periods.

Regarding the area of electroanalysis of organic pollutants, pharmaceuticals, and biologically important organic compounds, the following trends can be highlighted, most of them also representing probable future activities in the field (2, 8, 13):

1. More frequent use of new carbon pastes made of alternate materials that simulate the function of some modifiers (e.g., electrocatalytic properties of carbon nanotubes and some ionic liquids) or stabilize the carbon paste mixture for its application in atypical media;
2. Combination of traditional electrochemical principles with other detection techniques such as spectroelectrochemistry, electrochemiluminescence, or modern microscopy (particularly useful for initial characterisations of newly synthesized modifiers);
3. Further miniaturization of selected CPE configurations for detection in flowing streams;
4. Testing and applications of new pre-concentration principles of non-electrochemical character, effective for improvement of the overall electroanalytical performance;
5. Practical preference of methods with favorable ecological parameters (the so-called environmentally friendly procedures connected with "green analytical chemistry"). In this respect, nearly harmless and non-toxic carbon pastes may be a significant advantage;
6. Adaptations of already existing methods and procedures in terms of the above-mentioned features; i.e., the improved electroanalytical performance (sensitivity and selectivity), capability to combine with other techniques, compatibility with analyzers of new generations, plus acceptability given by the actual economical demands. In view of the latter, carbon paste mixtures had always been in the foreground as a cheap and easy-to-prepare material and the same can be expected for the up-coming years.

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ABBREVIATIONS AND SYMBOLS

AA	Ascorbic acid
accum.	Accumulation (pre-concentration)
AcB	Acetate buffer
AChE	Acetylcholin esterase
ACV	Alternating current voltammetry
ADH	Alcohol dehydrogenase
AdSV	Adsorptive stripping voltammetry
AdTSV	Adsorptive transfer stripping voltammetry
AFT	Alpha-1-fetoprotein
AmB	Ammonia buffer
ASV	Anodic stripping voltammetry
BRB	Britton-Robinson buffer
BSA	Bovine serum albumin
C	Carbon (graphite)
CA	Chronoamperometry
CA125	Carcinoma antigen 125
CA19-9	Carbohydrate antigen 19-9
CD	Cyclodextrine
CEA	Carcinoembryonic antigen
ChOx	Choline oxidase
CMCPE(s)	Chemically modified carbon paste electrode(s)
CNF	Carbon nanofibres
CoSal	<i>N,N'</i> -bis(salicylidene)-1,2-phenylenediaminocobalt (II)
CoClSal	Cobalt(II)-4-chlorosalophen
CoNSal	Cobalt(II)-5-nitrosalophen
COU	Coulometry
CP	Carbon paste
CPB	Cetylpyridinium bromide
CPE(s)	Carbon paste electrode(s)
CTAB	Cetyl-trimethyl-ammonium bromide
CuTerpy	(2,2':6',2''-terpyridyl)copper(II) chloride
CV	Cyclic voltammetry
CZE	Capillary zone electrophoresis
DAAOx	D-amino acid oxidase
DBCH	1,2-dibromocyclohexane
DCE	Dropping carbon electrode
DFDH	D-fructose dehydrogenase
DHB	3,4-dihydroxybenzaldehyde
DI	Diaphorase
DME	Dropping mercury electrode
DNA	Deoxyribonucleic acid
DPV	Differential pulse voltammetry
DPA(C)SV	Differential pulse anodic (cathodic) stripping voltammetry
DTE	D-tagatose 3-epimerase
EB	Ethidium bromide
ECH	Epichlorhydrin
ECL	Electrochemiluminescence (signal) detection
EIS	Electrochemical impedance spectroscopy
EPN	O-ethyl-O-4-(nitrophenyl)phenyl phosphonothioate

EtOH	Ethanol
Fc	Ferrocene
FAD	Flavinadenin dinucleotide
FDCA	Ferrocenedicarboxylic acid
FePc	Iron(II) phthalocyanine
FePC	Ferrophthalocyanone
FEPE	1-[4-ferrocenylethynyl]-phenyl]-1-ethanone
FIA	Flow injection analysis
GA	Glutaraldehyde
GaHCF	Gallium hexacyanoferrate
GDH	Glucose dehydrogenase
GluOX	Glutamate oxidase
GOX	Glucose oxidase
GP	Gilo peroxidase
GSH	Glutathione
Hb	Hemoglobin
HPLC	High performance liquid chromatography
HRP	Horse radish peroxidase
IgG	Immunoglobulin G
IL	Ionic liquid
LA AO	L-amino acid oxidase
LDR	Linear dynamic range
LOX	Lipoxygenase
LSV	Linear scan (sweep) voltammetry
LOD	Limit of detection
LOQ	Limit of quantification
M	Molar concentration [mol L ⁻¹]
MB	Methylene blue
MCP	Mesoporous carbon powder
MeOH	Methanol
MMPs	Magnetised silica-based microparticles
modif.	Modifier, modified
MPCA	Monochlorophenoxyacetic acid
MPMS	1-methoxyphenazine methosulfate
MPTMS	3-mercaptopropyl trimethoxysilane
Mtx	Methotrexate
NAD(H)	Nicotinamide dinucleotide (reduced form)
NdHCF	Neodymium(III) hexacyanoferrate
NPN	4-nitrophthalonitrile
OPH	Organophosphorus hydrolase
OPD	O-phenylenediamine
Pc	Phthalocyanine
PCR	Polymerase chain reaction
PDH	Phenylalanine dehydrogenase
PEG	Polyethylen glycol
PhB	Phosphate buffer
PHEA	Phenylalanine
pNP	p-nitrophenol
POT	Potentiometry
PP	Polypyrrol
PPO	Polyphenol oxidase
PQQ-GDH	Pyrrole quinoline quinone glucose dehydroge- nase
PTH	Polythionine

PTY	Polytyramine
PVP	Polyvinylpyrrolidone
PyOX	Pyranose oxidase
Q/HQ	Quinone/hydroquinone
RSD	Relative standard deviation [%]
RT	Response time
RTIL	Room temperature ionic liquid
SA	Stearic acid
SDBS	Sodium dodecylbenzene sulphonate
SDS	Sodium dodecylsulphate
SV	Stripping voltammetry
SWV	Square-wave voltammetry
t_{acc}	Accumulation time (period)
t_{anal}	Analysis time
TCNQ	Tetracyanoquinodimethane
TEA	Triethylamine
TPrA	Tri-n-propylamine
t_R	Response time
TRIS	Buffer (commercial formulation)
TTF-TCNQ	Tetrafulvalene-tetracyanoquinodimethane
U	Enzyme activity unit
UA	Uric acid
VO(Salen)	<i>N,N'</i> -ethylenebis(salicylideneamino)oxo- vanadium (IV)
v/v	Volume ratio
XOD	Xanthin oxidase.

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