Sensing in Electroanalysis

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Utilization of Unmodified Screen-Printed Carbon Electrodes in Electroanalysis of Organic Compounds (An Overview)

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Abstract: This review summarizes basic characteristics of screen-printed carbon-based electrodes and their applications in electroanalysis of organic compounds. Mainly, it is devoted to unmodified, the bare screen-printed carbon electrodes designed for batch voltammetry and amperometric detection in the flowing streams. The varieties in the construction, surface pretreatment, and compatibility with modern electroanalysis are presented and their advantages and drawbacks, possibilities and limitations discussed.

Keywords: Screen-printed (carbon) electrodes; Organic analysis; Voltammetry; Flow injection analysis; HPLC; Review.

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Introduction

Screen-printed electrodes (SPEs) have been developed as single-use, disposable sensors for a variety of applications in environmental, industrial, and clinical analyses [1-5]. Typically, in planar configuration and consisting of different layers of electrically conductive inks machine-printed on plastic, glass, or ceramic substrates, SPEs represent one of the most interesting design among electrochemical sensors.

Their main advantage over conventional electrodes is that the problems with surface fouling can be eliminated, as SPEs are intended to be employed only once and then replaced by new ones from the same batch. Among numerous variants of SPEs, screen-printed carbon-based electrodes (SPCEs) have gained great attention because of their easy-to-make modification of the surface by immobilizing the reagent of choice onto the electrode surface or by adding such a substance into the carbon ink yet before the electrodes (usually in a series) are machined. As a result, modified SPCEs have already been used in a number of analytical studies devoted to metal species [1-3], including their determination in various practical samples, or in the configurations of various sensors / biosensors for detection of biologically active compounds [3-5].

The bare (unmodified) SPCEs are of less importance; nevertheless, a few reports for determination of heavy metals [2] and organic compounds were published [5], the latter being summarized in this short review with emphasis on the pretreatment of the electrode surface and rather specific applicability in both voltammetry and amperometry.

Characterization and Applications of Screen-Printed Carbon Electrodes in Organic Analysis

Design of SPCEs and Other Features

The advancement of screen-printed technology resulted in mass production of various designs of SPEs. Typically, they are produced in the form of small strips, having dimensions in the range from 30 to 61 mm in length, up to 15 mm in width and up to 1 mm in height. Commercial companies supplying SPEs include; *e.g.:* Pine Instrument Company (Grove City, Pennsylvania, USA; http://www.pineinst.com/echem), BI Technologies Corporation (Fullerton, California, USA; http://www.bitechnologies.com), Dropsens, (Llanere (Asturias), Spain; http://www.dropsens.com), Kanichi Research (Manchester, UK; http://www.kanichi-research.com), BVT Technologies (Brno, Czech Republic; http://www.bvt.cz), Gwent Electronic Materials (Pontypool, UK; http://www.gwent.org), Uniscan Instruments (Buxton, UK; http://www.uniscan.com/), Ecobioservices & Research (Firenze, Italy; http://www.ebsr.it), ALS Co. (Tokyo, Japan; http://www.als-japan.com), Zensor R&D (Dali City, Taiwan, R.O.C.; http://www.zensor.com.tw). In addition, many research laboratories in academic sphere possess screen-printing facilities for in-house production of SPEs.

The electrode arrangement and shape can vary at different producers. The working electrode has most frequently the circular or rectangular shape. The examples of such assemblies can be seen in Figure 1. Inks forming the own electrodes are printed predominantly on glass, plastic (PVC, polyester) [6-8] or ceramic base [9].

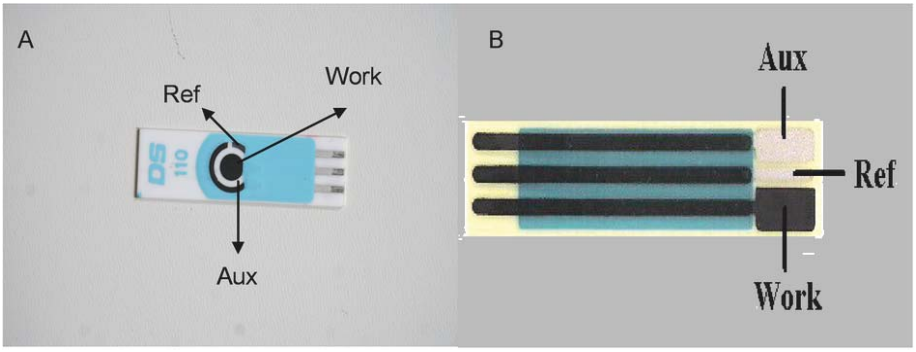

Fig. 1: *Three-electrode assembly on the strip*. Legend: **A**) Circle graphite working electrode, graphite auxiliary electrode and pseudoreference Ag/AgCl electrode, produced by Dropsens (Llanere (Asturias), Spain), **B**) rectangular graphite working electrode, silver ink auxiliary electrode and pseudoreference Ag/AgCl electrode. Produced by FACH (Prešov, Slovakia).

Although SPCEs have been designed to meet the requirements of batch voltammetric analysis, they may be used also as electrochemical sensors in the flowing streams; their small dimensions and the planar construction being particularly advantageous [10-13]. Flow-through detection cells suitable for screen-printed electrodes are produced by several companies including Dropsens, Ecobioservices & Research, Zensor R&D, BVT Technologies, and Uniscan Instruments. An example of a flow-through detection cell for electrochemical detection in HPLC or flow injection analysis (FIA) designed according to the prototype of Dropsens in our laboratory is depicted in Fig. 2 overleaf.

Advantages and Disadvantages of SPCEs

Screen-printed carbon electrodes are advantageous owing to their characteristics in several aspects. Foremost, SPCEs are considered as disposable devices that can be discarded carrying out the only analysis. This handling is acceptable due to their low-cost production.

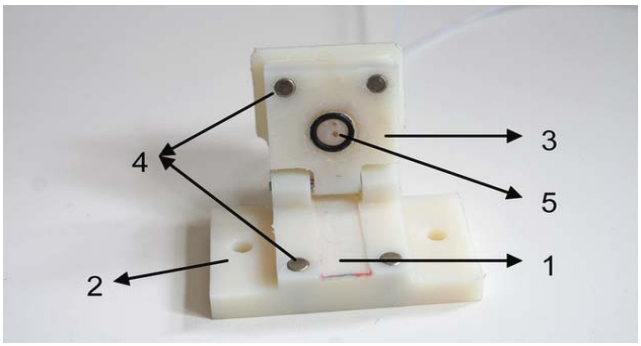

Fig. 2: *Flow-through detection cell for screen-printed carbon electrodes (Polyamide 6 material).* Legend: **1**) electrode position, **2**) base of the cell, **3**) hinged cell cover, **4**) magnetic clamps, **5**) inlet and outlet for mobile phase.

The disposability of the electrodes provides a solution for problems like the electrode surface fouling by products of redox processes and an unintentional adsorption that can arise by using solid electrode materials (e.g. metal, amalgam, composite electrodes) [14].

In the view of their dimensions, SPCEs are applicable as portable devices for in-situ measurements. The working electrode with a small area enables very low sample consumption. In some cases sample volumes smaller than 10 µl are sufficient for the analysis. In this case, the sample is deposited directly on the electrode surface [15]. Furthermore, the easy electrode pretreatment can provide a substantial advantage for the determination of isomeric compounds without a preliminary separation [16].

The certain kind of limitation appears to be content of organic solvents in the buffer solutions used for the analyte accumulation on the electrode surface using batch voltammetric methods or in the mobile phase used in liquid flow methods [8]. Organic solvents can be responsible for the dissolution of insulate inks and consequently the decrease of limit of detection and sensitivity [6,15]. Naturally, the composition of the mobile phase must be compatible with the material of the detection cells housing SPCEs in liquid flow methods so that their dissolution is prevented.

Pretreatment and Reproducibility of SPCEs

SPCEs used in batch voltammetry posses either bare or modified surface. In both cases its pretreatment influences their electrochemical properties, although reliable results were reported also without the electrode pretreatment [7-9,14,17].

The most common pretreatment process includes cyclic voltammetric scan to positive potentials in the first step followed by applying of the positive potential outside the potential window of the electrode. The duration of applied potential varies in different studies in the range from 180 to 900 seconds [11,12]. In a few studies there was reported only the simple preanodization by the applying of a positive potential to the electrode [16,18,19]. The main effect of this step lies in the enhancement of the analytical signal, which results from changes that occur in the electrode surface structure, being treated the above mentioned way. The preanodization leads to the formation of carbonyl or hydroxyl groups. Wang and Su describes in their studies that the surface morphology becomes a rough configuration of large pores, multi-layers and a sponge-like network honeycombed by nanosize cavities as obvious in Fig. 3 [16]. Several authors refer that anodic oxidation of highly oriented pyrolytic graphite results in the destruction of the basal plane and the exposure of a large quantity of edge plane graphite at the electrode surface and thus faster electron transfer characteristics [12,18]. It has been demonstrated comparing the oxidation potentials of selected analytes on the preanodized and the bare electrode surface that the value of analyte peak potential shifts towards less positive potentials after the preanodization, indicating the analyte is more readily oxidizable. Moreover, in the case of simultaneous determination of position isomers, this can result in sufficient separation of the individual analytes due to the preanodization as demonstrated for the simultaneous determination of catechol and hydroquinone [16,19]. The time of analysis isn't affected by the electrode pretreatment in a considerable way because this step is usually incorporated in the program of the computer-controlled instrument.

Although originally the SPCEs were designed as disposable sensors, under certain conditions they may be used repeatedly. In this case, their surface is restored by the electrochemical cleaning or other ways as reported in the studies of Zanoni et al. [9,10]. They achieved relative standard deviation (RSD) of 4.5 % (n = 5) for voltammetric determination of aurothiomalate at the same SPCE treated in 0.1M KCl solution pH 1.0 and potential +1.2 V for 30 s between the measurements. For reproducibility, they received the RSD value of 5.9 % using three different electrodes [9]. For FIA determination of procaine they reported RSD values of 3.2% for fifteen repetitive measurements and announced the possibility of at least 100 measurements performed on the same SPCE [10]. In general, relative standard deviation for repetitive measurements didn't exceed the value 6.0 % in all studies, whether repeatability or reproducibility was mentioned. Needless to say, the possibility of repeated use of SPCEs in amperometric detection cells for liquid flow methods is a basic requirement for their applications as tedious dismantling of detection cells must be prevented.

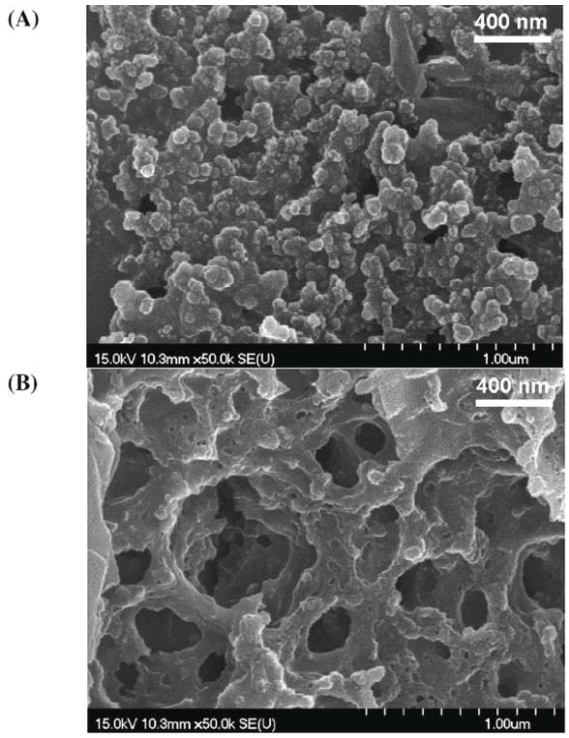

Fig. 3: *Scanning electron micrographs of the electrode surface.*

Legend: (**A**) untreated SPCE and (**B**) electrochemical preanodized SPCE at +2.0 V for 900 s in 0.1 mol.l^{-1} phosphate buffer (pH 7.0).

(Reprinted and reproduced with permission from [16].)

Applications in Organic Analysis

The unmodified screen-printed carbon-based electrodes have been applied widely in the fields of pharmacology [9,10,14,18], ecology [6,8,16,17,19,20] and food-processing industry [7,14]. The variety of tested organic compounds is documented by the table I, which involves the studies, where at least some of the analytical characteristics (i.e., linear dynamic range (*LDR*), slope and intercept for linear calibration dependences, limit of detection or quantitation (*LOD* or *LOQ*), repeatability / reproducibility of the electrode signal) appeared.

SPCEs were tested for the determination of procaine in drugs [10] and aurothiomalate in human urine samples [9]. Chen and Kumar employed them for the enzymeless creatinine determination without not to be interfered by any common biochemical compounds co-existing in blood [18]. The foodstuff analysis includes successful determination of the antibiotic lincomycin in feeds, honey, and milk [11] and the determination of vitamin B_2 in a corn flake cereal, dietetic milk powder and vitamin B complex premix [7]. Bare SPCEs fulfill the function of very sensitive sensors for the determination of selected oxidizable environmental pollutants including amino derivatives of polycyclic aromatic hydrocarbons

Table I: *Applications of screen-printed carbon electrodes in analysis of organic compounds*

Analyte (compound)	Pretreatment / regeneration of SPCE	Electroanalytical method, arrangement, conditions	Linear dynamic range [μmol.l^{-1}]	Limit of detection [μmol.l^{-1}]	Ref.
Clinical and drug analysis					
Aurothiomalate	-	LSAdSV (anodic), t_{acc} = 60 s, E_{acc} = –1.5 V, 0.1M KCl (pH 1.0)	1.43 – 155	0.65	[9]
Procaine		FIA/AD, 0.1M sodium acetate pH 6.0	9.0 – 100.0	6	[10]
Cysteine Tyrosine	-	Amperometry in stirred solution, 0.1M phosphate buffer pH 7.0	10 – 200 10 – 300	Not given	[14]
Lincomycin	CV in 0.1M phosphate buffer pH 7.0, +2.0 V for 180 s	HPLC/AD, acetonitrile/methanol/ 0.1M phosphate buffer pH 6.0 (5:20:75)	0.05 – 1000	0.08	[11]
Foodstuff analysis					
Vitamin B2	-	DPV, acetate-phosphate/KCl buffer pH 6.0	2.66 – 61.1	2.39	[7]
Environmental analysis					
Chlorophyll "a"	-	LSAdSV, ex-situ accumulation in 0.1M phosphate buffer pH 7.0, 1% acetone, t_{acc} = 60 s at open circuit voltage, LSV in 0.1M phosphate buffer pH 7.0	0.4 – 2.24	0.014	[8]

(**Table I**, continued)

2-Aminophenol 3-Aminophenol 4-Aminophenol	CV in 0.1M phosphate buffer pH 7.0	NPV, 0.1M phosphate buffer pH 7.0	0.2 – 100 3.0 – 200 0.2 – 200	0.07 0.16 0.05	[19]
Hydroquinone Catechol	+2.0 V for 900 s in 0.1M phosphate buffer pH 7.0	SWAdSV (anodic), t_{acc} = 180 s, E_{acc} = –0.3 V, 0.1M phosphate buffer pH 6.0	0.1 – 50 0.1 – 70	0.05 0.05	[16]
2,6-Dinitrotoluene	-	LSAdSV (anodic), t_{acc} = 30 s, E_{acc} = –1.1 V, 50 mM phosphate buffer pH 1.8	0.88 – 752	0.88	[17]
Other compounds					
Thioglycolic acid	CV in 0.1M phosphate buffer pH 7.0, +2.0 V for 240 s	**HPLC/AD**, acetonitrile/ 0.075M phosphate buffer pH 3.0 (5:95) with 10 mM SHS	2.2 – 220	0.46	[12]

Abbreviations and symbols used: AD – amperometric detection, AdSV – adsorptive stripping voltammetry, CV – cyclic voltammetry, DPV – differential pulse voltammetry, E_{acc} – accumulation potential, FIA – flow injection analysis, HPLC – high-performance liquid chromatography, LDR – linear dynamic range, LSAdSV – linear sweep adsorptive stripping voltammetry, NPV – normal pulse voltammetry, SHS – sodium 1-heptane sulfonate, SWAdSV – square wave adsorptive stripping voltammetry, t_{acc} – accumulation time

[20], aminophenols [19], hydroquinone and catechol [12] as well as reducible 2,6-dinitrotoluene [17]. Yet some other applications of SPEs and SPCEs can be found in special reviews (see *e.g.* [2-5,21,22]), concerning environmental and food samples, as well as methods of clinical analysis with biosensoric configurations [21].

It follows from the Table I that *LDR* of reported calibration dependencies reach usually two to three orders of magnitude; the widest *LDR* more than four orders of magnitude was reported for the lincomycin determination by HPLC with amperometric detection [11]. In the most of the studies, analytes were successfully determined below the micromolar level. The lowest *LOD*s reported without any preconcentration step are in the 10^{-8} mol.l^{-1} concentration range [8,11,16,19]. In the case of creatinine determination *LOD* of 8.6 μmol.l^{-1} is more than adequate [18], because human urine contains creatinine usually at the concentration from 2.5 to 18.0 mmol.l^{-1}.

Conclusions

The screen-printing process is capable of producing a wide range of geometries and the resultant screen printed carbon-based electrodes hold the advantages of low cost and easy-to-handle usage. Despite the fact that the feasibility of modification of the surface of SPCEs widens substantially the field of applications in the development of selective and sensitive biosensors [2-5,21,22], also the utilization of bare SPCEs still offers attractive possibilities in batch voltammetry or amperometry coupled with the detection in flowing streams with respect to the determination of various organic compounds in real samples.

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