Metallic Pins as Electrodes in Low-Cost (Bio)Electroanalytical Devices †

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Abstract: The increasing demand for fast and on-site information has generated great interest in developing simple and portable analytical devices that provide reliable responses. Electroanalytical devices fit perfectly with these purposes because of their ease of use, low cost and facility of miniaturization. Moreover, the growing interest in the construction of do-it-yourself electronic devices has spread the use of common and mass-produced materials for the development of analytical devices. In this context, it is presented here the use of gold-plated pins, from standard connections, and stainless-steel pins, from needlework, as electrodes in (bio)electroanalytical platforms. Three different analytical platforms combining those pins with paper, transparency sheets or micropipette tips were constructed and applied in food and environmental analyses: glucose determination in beverages and surfactant analysis in water.

Keywords: electrochemical sensor; electroanalytical device; paper-based analytical device; pin-based electrodes; micropipette-tip electrochemical cell; enzymatic sensor; glucose; water analysis; sodium dodecyl sulfate

1. Introduction

Important current trends in Analytical Chemistry, such as simplicity, miniaturization, reduction of costs and portability, have led to the exploration of the use of common mass-produced materials for the construction of analytical devices. The use of these materials (e.g., paper [1–5], sewing pins [6–9], office transparency sheets [7,10], thread [11], etc.) provides cheap, highly versatile, and, above all, easily available devices. Many of them, especially those based on paper, employ a colorimetric detection, being cheap and easy-to-use and avoiding the use of instrumentation; however, they can only give semiquantitative information. Electrochemical detection is a good alternative due to its sensitivity and accuracy, as well as its ability for miniaturization. Moreover, it neither requires high volume of reagents/sample nor complex instrumentation.

Taking this into account, here, the construction of three different platforms based on paper and/or pin electrodes is briefly described. In the first example, gold-plated pins from a standard commercial connection acted as reference (REs) and counter (CEs) electrodes that were combined with a paper-based working electrode (WE) [12,13]. This platform showed good analytical features, and it was used for developing an enzymatic glucose sensor. The good performance of the electrodes based on stainless-steel pins was also demonstrated constructing an enzymatic glucose sensor in which a transparency sheet was used as a substrate and the pin acting as WE was modified with
carbon ink [7]. In a different and last design, the high versatility of the pins allowed to insert them in a micropipette tip to obtain a system able to take the sample and perform electrochemical measurements inside the same tip [14]. This device was used for determining anionic surfactants in water using methylene blue as indicator.

2. Materials and Methods

2.1. Chemicals, Materials, and Apparatus

For the construction of the electrochemical devices, the following reagents and materials were employed: N,N-dimethylformamide (DMF), carbon paste, Whatman™ paper grade 1, gold-plated connector headers, stainless-steel pins, 100–1000 μL polypropylene micropipette tips, transparency sheets (cut in 3 × 2 cm, approximately). A wax printer was used to delimit hydrophobic areas in the paper.

As analytes, glucose and sodium dodecyl sulfate (SDS) were considered. Other important reagents were glucose oxidase (GOx), horseradish peroxidase (HRP), potassium ferrocyanide, methylene blue (MB), and chloroform. Working solutions of glucose, GOx, HRP, and potassium ferrocyanide were prepared in 0.1 M Tris-HNO₃ pH 7.2. These of SDS were prepared in water and those of MB in 0.5 M HCl.

For the electrochemical measurements, an Autolab potentiostat controlled by Nova 2.1.2 software was used. A 3-pin Dupont cable or an edge connector was used as the interface to connect the devices with the potentiostat.

2.2. Construction of the Paper-Based Electrochemical Cell

The paper-based working electrodes were fabricated as follows [12,13]: a circle pattern was wax-printed on the Whatman™ paper; then, the wax was diffused at 100°C on a heating plate for 1 min, and 2 μL of a carbon ink (23% of carbon paste in DMF) was deposited on the hydrophilic area delimited by the wax. After 12 h during which the carbon ink dried completely, the piece of paper containing this working electrode (WE) was placed between the pins of the connector header as indicated in Figure 1B. In this way, these pins act as reference (RE) and counter (CE) electrodes and also as a connection for the WE.

To perform electrochemical measurements with this device, 10 μL of working solution was deposited covering the three electrodes.

2.3. Construction of the Pin-Based Electrochemical Cell

For the construction of the pin-based device [7], the pins were previously cleaned by sonication in isopropyl alcohol and then, those used as WEs were modified with carbon ink (50% carbon paste in DMF). The procedure for pin modification was as follows: the head of the pin was immersed in the ink and left to dry for 15 min at 70 °C; this procedure was repeated three times, and in the last immersion, the pin was allowed to dry for 12 h. The design of the pin-based electrochemical cell is shown in Figure 1A. The three pins, acting as WE (the carbon-ink modified one) and RE and CE (both unmodified) were inserted in the transparency sheet taking advantage of the sharp tip of the pins to drill the sheet. For the connection of this device with the potentiostat, a 3-pin Dupont female cable was used.

To perform electrochemical measurements with this device, 70 μL of the working solution was deposited covering the heads of the three pins.

2.4. Construction of the Micropipette-Tip Electrochemical Cell

For the construction of the micropipette-tip electrochemical cell [14], the pins used as the WE were modified with carbon ink (50% of carbon paste in DMF) painting their shaft using a brush. After drying for 15 min at 70°C, the painting step was repeated twice more, and after the last one, the pins were left to dry for 1 h instead 15 min. Then, two unmodified pins (i.e., RE and CE) were inserted in the micropipette tip as indicated in Figure 1C. After this, the desired volume of solution was
aspirated, and the tip was sealed introducing the carbon-ink modified pin (i.e., WE) at the bottom. The connection of this WE to the potentiostat was made through a conductive copper adhesive tape; the RE and the CE were connected by conventional crocodile clamps.

To perform electrochemical measurements with this device, 360 μL of the working solution were aspirated into the tip contacting the three electrodes.

3. Results

3.1. Paper-Based Electrochemical Cell

This electrochemical cell was used to construct an enzymatic sensor for glucose determination [12]. With this aim, the paper-based WE was modified depositing 5 μL of a mixture of GOx (1.6 U·μL⁻¹), HRP (2.5 U·μL⁻¹), and potassium ferrocyanide (0.1 M). The analytical signal for glucose concentration was obtained by chronoamperometry (at −0.1 V for 100 s). In this way, this paper-based sensor was able to quantify glucose in the concentration range between 0.3 and 15 mM with a sensitivity of −1.19 μA·mM⁻¹ and a reproducibility, in terms of relative standard deviation (RSD), of 5.4%. Moreover, this sensor was applied to the determination of glucose in beverages, such as orange juice and cola, and the results obtained were compared to those obtained with a spectrophotometric enzymatic kit obtaining very similar results (relative errors lower than ±4%).

The high versatility of this platform allowed the construction of a multiplexed device (with eight complete electrochemical cells) and the integration of a sampler that takes the sample without the need of micropipettes [13].

3.2. Pin-Based Electrochemical Cell

This pin-based platform was also used as transducer of an enzymatic glucose sensor [7]. The recognition phase of this sensor was prepared in a very similar way as the above mentioned: 3 μL of a mixture of GOx (3 U·μL⁻¹), HRP (5 U·μL⁻¹), and ferrocyanide (20 mM) were deposited onto the head of the pin acting as WE. In this case, the analytical signal for glucose concentration was obtained by
chronoamperometry, applying $-0.2$ V for 50 s. The calibration curve obtained covered the range comprised between 0.05 and 1 mM with a sensitivity of 1.44 $\mu$A·mM$^{-1}$. An RSD value lower than 8% was obtained for this sensor. It was also applied for glucose analysis in honey and orange juice. When the results obtained with the sensor were compared to those obtained with the spectrophotometric enzymatic kit, the high accuracy of this sensor was demonstrated (relative errors lower than ±5%).

The versatility of the pins to design electrochemical cells allowed for the construction of, not only a multiplexed cell with four WEs sharing the RE and the CE [7], but also flow [9] and batch [8] injection analysis systems.

3.3. Micropipette-Tip Electrochemical Cell

This micropipette-tip was used for the determination of SDS in water based on the increase that the presence of SDS causes in the cathodic peak of MB, which is related to SDS concentration. In this way, the analytical signal was the current intensity of the cathodic peak obtained when 360 µL of a solution containing a fixed concentration of MB (25 µg·mL$^{-1}$) and SDS (in different concentrations) were aspirated and a linear sweep voltammetry was recorded (from 0.1 to $-0.3$ V at 100 mV·s$^{-1}$). A calibration curve for SDS between 2.5 and 20 µg·mL$^{-1}$ was obtained with a sensitivity of $-0.26$ $\mu$A·mL·µg$^{-1}$. The reproducibility obtained for this tip-based cell, in terms of RSD, was 7%. The concentration of SDS in spiked tap water was determined obtaining recoveries values of 93–111%.

4. Conclusions

The innovative electrochemical cells here described demonstrate the high potential of common and low-cost materials for the development of miniaturized, simple, and cheap, but also robust and accurate electroanalytical devices. Moreover, the small size of the presented platforms makes possible their integration with portable instrumentation (potentiostats), obtaining highly useful devices for point-of-need analysis. This is very interesting for a great number of applications, such as clinical diagnosis or environmental analysis, that require decentralized analysis, allowing decisions to be made in real time.

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