



Spectroelectrochemical study of acetylsalicylic acid in neutral medium and its quantification in clinical and environmental samples



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ABSTRACT

This paper describes the application of simultaneous electrochemical reduction and UV absorbance methods (spectroelectrochemical techniques, highlighting the derivative linear scan voltabsorptometry) in the determination of acetylsalicylic acid in neutral medium, using a platinum gauze electrode modified with nanocomposite of reduced graphene oxide with gold nanoparticles (rGO/AuNPs). In solution, the process involving one electron to produce the radical acetylsalicylate was observed. Such mechanism was confirmed by electronic paramagnetic resonance (EPR). This study demonstrated that the voltabsorptometric sensor is highly sensitive for the determination of acetylsalicylic acid, with a limit of detection of $0.26 \mu\text{mol L}^{-1}$. No significant interference was detected for ascorbic and uric acid in the determination of acetylsalicylic acid. The platinum gauze with rGO/AuNPs modified electrode device was successfully applied in the acetylsalicylic acid determination in an environmental samples (wastewater) and clinical (tablets of drugs and human urine) samples, and is a promising platform for a simple, rapid, direct and very sensitive analysis of acetylsalicylic acid.

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1. Introduction

Painkillers are the most popular class of pharmaceuticals, being consumed in huge amounts throughout the world. Among them, acetylsalicylic acid (ASA) is, by far, consumed in the larger scale. This is also related with its medicinal properties for the treatment of headache (even migraine), muscle aches, arthritis, toothaches, backaches, fever, flu, thromboembolic disorders, colorectal cancer, etc. [1,2], and ASA can be sold without a prescription in some countries. The amount consumed each year is estimated to be around one hundred billion tablets.

However, ASA has an important drawback regarding human health. It is readily hydrolyzed to salicylic acid in acidic environments such as the human stomach. Salicylic acid promotes a series of hazardous effects in the human body including gastrointestinal ulcers, tinnitus and Reye's syndrome [3]. To avoid its hydrolysis in the stomach, advanced formulations of ASA are available in aspirin delayed-release tablets, which stabilize ASA until the pH neutralizes allowing for drug release and adsorption in the intestine.

Supposing that only 40% of the ingested pills are eliminated from the body in their original chemical form or as metabolites, the pollution potential from this drug is enormous. Several research studies indicate that pharmaceuticals are one of the main contaminants in environmental waters due to their partial metabolism by the human body, subsequent urinary or fecal excretion and their inefficient removal from water in sewage treatment plants [4–9]. Furthermore, an increased demand for ASA leads to increased production, resulting in a greater volume of wastewater containing pharmaceutical waste.

Analytical techniques have been developed to measure trace levels of ASA directly in water or its metabolites in urine samples. These methodologies include techniques such as capillary liquid chromatography [10], high performance liquid chromatography [11,12], fluorimetry [13] and voltammetry [14,15] among others. Reliable detection of ASA in natural water is becoming increasingly important due to its chronic toxicity and the side effects that can occur when it is continuously ingested [16,17]. It is also critical to control incidental ingestion of ASA in tropical countries where diseases that cause generalized bleeding, such as infection by zika, dengue or chikungunya viruses, can be aggravated by the ability of ASA to inhibit platelet aggregation [18–26].

Considering the urgent need for methods to detect non-metabolized ASA in neutral environmental samples, in this work

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we developed a protocol to identify this pollutant using spectroelectrochemical techniques. We highlight the capabilities of derivative linear sweep voltabsorptometry (DLSVA), which is considered a more sensitive analytical technique in applications involving complex matrices relative to other electrochemical techniques such as voltammetry. In principle, this technique combines electrochemical and optical signals at the molecular level, measuring absorbance in the ultraviolet region during oxidation-reduction processes [27].

One interesting material that has been widely used in the development of electroanalytical sensors is reduced graphene oxide (rGO). rGO has characteristics similar to graphene nanosheets, i.e. a singular two-dimensional structure formed by a few layers of sp^2 carbon atoms generating a π -conjugated system leading to high electron mobility and fast charge transfer, which gives the appearance of an electrocatalytic effect. rGO can serve as a solid support for the immobilization of several species and can be used as platform for the development of biosensors and sensors including enzymes [28], DNA [29], biomarker [30], quantum dots [31,32], metallic oxides [32] and metallic nanoparticles [33].

This work describes the synthesis, characterization and application of a spectroelectrochemical sensor based on gold nanoparticles (AuNPs) supported on rGO immobilized on a platinum gauze electrode. This nanostructured material had excellent sensitivity for ASA due to its high electrocatalytic activity, yielding a very low detection limit. We demonstrate that a platinum gauze electrode modified with rGO/AuNPs is a fast, simple and sensitive tool to measure the levels of ASA in clinical and environmental samples.

2. Experimental

2.1. Chemicals and solutions

All solutions were prepared using purified water from a Barnstead Nanopure System (Thermo Scientific, USA) with a resistivity $\geq 18.2 \Omega \cdot \text{cm}^{-1}$. The following analytical grade reagents were used without further purification: ASA, KNO_3 and 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) (Sigma-Aldrich), H_2SO_4 (Tedia), H_2O_2 and NaOH (Synth). Graphite powder ($< 20 \mu\text{m}$, Sigma), potassium permanganate (KMnO_4 , Sigma-Aldrich), hydrogen peroxide (H_2O_2 – Synth), sodium nitrate (NaNO_3 – Sigma-Aldrich), HAuCl_4 and sodium citrate purchase from Sigma-Aldrich.

2.2. Apparatus and procedures

Cyclic voltammetry (CV) and chronoamperometry experiments were performed using an AUTOLAB potentiostat, model PGSTAT 128N (Eco Chemie, Utrecht, Netherlands). Spectrophotometric measurements were performed on an Avaspec 2048 spectrophotometer (Avantes, Apeldoorn, Netherlands) integrated with an AVALIGHT DHS radiation UV–vis source (Avantes, Apeldoorn, Netherlands), with deuterium and halogen lamps and a support for cuvettes. Connections to the spectrophotometer were made via optical fibers. The spectroelectrochemical cell used (Basi, West Lafayette, USA) was a bucket with an optical path of 0.1 cm and contained an arrangement of three electrodes: platinum gauze was the working electrode; the system $\text{Ag}/\text{AgCl}/\text{KCl}$ (3.0 mol L^{-1}) was the reference electrode; and a platinum wire was the auxiliary electrode. The volume used for all experiments in the spectroelectrochemical cell was $800 \mu\text{L}$.

Electronic paramagnetic resonance (EPR) spectra were obtained in an EMXplus™ X-band spectrometer (Bruker, Billerica, USA) at the temperature of liquid nitrogen.

Pre-treatment of the platinum gauze was performed in two steps. First, the gauze was immersed in a piranha solution of

$\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ (3:1 v/v) for 3 min. Then it was washed with ultrapure water and subjected to cyclic voltammetry in a 0.1 M H_2SO_4 solution with a potential range between 1.30 V and -0.23 V in the following stages: 100 cycles at 1 V s^{-1} , 50 cycles at 0.50 V s^{-1} , 25 cycles at 0.25 V s^{-1} and 10 cycles at 0.10 V s^{-1} .

2.3. Synthesis of graphene oxide

Single layer graphene oxide (GO), prepared according to the modified Hummers method [34]. Typically, 10 g of graphite and 10 g of NaNO_3 was mixed with 450 mL of H_2SO_4 (98%) in a 2500 mL flask. The mixture was then stirred for 30 min in an ice bath, and subsequently 60 g of KMnO_4 was added with vigorous stirring. The reaction mixture was then kept at 4°C for 24 h. Next, the mixture was stirred vigorously at 35°C and 450 mL of H_2O was added. The reaction temperature was rapidly increased to 98°C and 450 mL more H_2O was added, followed by 300 mL of a 30% H_2O_2 aqueous solution. The reaction mixture was refrigerated again at 4°C for 24 h. The GO solution obtained was centrifuged for 30 min at 8000 rpm and washed several times with 5% HCl and then distilled water until the pH of the filtrate was neutral. Finally, the GO was lyophilized for 24 h.

2.4. Synthesis of rGO/AuNPs

The nanocomposite material was prepared by dispersing 150 mg GO in 150 mL double-distilled water by ultrasound treatment for 30 min. Subsequently, 1.0 mL of HAuCl_4 ($2.5 \times 10^{-3} \text{ mol L}^{-1}$) was added to the reaction flask. The mixture was heated to boiling under continuous magnetic stirring and then 750 μL of a 1% (w/v) sodium citrate solution was added. After 5 min of boiling, 100 mg NaBH_4 in 5 mL of water was added. The mixture was stirred with heating for another 30 min, then cooled to room temperature and filtered. The resulting solid was repeatedly washed with water and ethanol, dried under vacuum at room temperature and kept dry until use.

To evaluate the synergistic effect of rGO and AuNPs, the chemical synthesis of rGO alone was also performed as described above except HAuCl_4 was not added.

3. Results and discussion

3.1. Scanning electron microscopy images and transmission electron micrographs

Scanning electron microscopy (SEM) images for the rGO/AuNPs hybrid material were obtained using backscattered electrons at a magnification of 250,000X and are presented in Fig. 1. Nanoparticles of gold are represented by bright white spots and were homogeneously distributed throughout the rGO nanosheets.

To gather further information about the structure of rGO and the rGO/AuNPs hybrid material, transmission electron microscopy (TEM) images were evaluated. The rGO and rGO/AuNPs nanosheet images are shown in Fig. 2a and Fig. 2b, respectively. Particle diameters were measured directly from the TEM images using ImageJ software (Fig. 1S, supplementary material). From those images we obtained a mean value of $5.65 \pm 1.64 \text{ nm}$ for immobilized AuNPs in the reduced graphene sheet.

To confirm the formation of Au nanoparticles on the rGO nanosheets, energy dispersive X-ray analysis (EDX) was performed and counts were obtained to verify the presence of the metal in the synthesized hybrid nanomaterial (data not shown). The TEM micrographs and EDX analysis confirmed the incorporation of AuNPs deposited on the rGO in the hybrid rGO/AuNPs material, which was consistent with the SEM images.

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