



# Nanostructured cupric oxide electrode: An alternative to amperometric detection of carbohydrates in anion-exchange chromatography



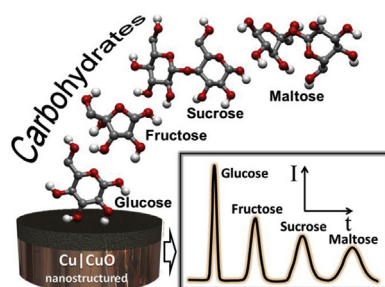
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## HIGHLIGHTS

- Low cost electrodes for carbohydrates detection.
- High stability at constant potential detection and use in wall jet flow cell.
- Limits of detection around picomole.
- Fast synthesis of CuO nanostructures on the electrode surface.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this paper, a new and low cost copper/cupric oxide nanostructured electrode is presented as an alternative to the amperometric detection of carbohydrates in high-performance anion exchange chromatography. The modified copper electrodes were prepared by a simple and fast method which resulted in the obtainment of homogeneously distributed nanostructures adhered to the surface with controlled chemical nature. The results, when compared to conventional copper electrodes, exhibited considerable improvements in analytical results, including: 1) Better repeatability in consecutive glucose detections, in which the percent relative standard deviation improved from 15.1% to 0.279%. 2) Significant improvements in the stability of the baseline and a decrease of the stabilization time, going from several hours to approximately 15 min. 3) Considerable increase in the sensitivity towards glucose, from 5.02 nA min mg L<sup>-1</sup> to 25.5 nA min mg L<sup>-1</sup>. 4) Improvements in the detectability with limits as low as 1.09 pmol. 5) Wide working range of concentrations (1 × 10<sup>-2</sup> to 1 × 10<sup>4</sup> mg L<sup>-1</sup>). 6) Good linearity with correlation coefficients greater than 0.998. 7) Possibility of detecting different molecules of carbohydrates (lactose, maltose, sucrose, cellobiose, sorbitol, fructose, glucose, galactose, manose, arabinol, xylose, ribose and arabinose). In comparison to the electrode that is more employed for this type of application (gold electrode), the low cost, the possibility of detection at constant potential and the equivalent detection limits presented by the new electrode material introduced in this work emerge as characteristics that make this material a powerful alternative considering the detection of carbohydrates in anion exchange chromatography.

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## 1. Introduction

The determination of carbohydrates is a classical analytical problem and is currently broadly employed in industrial routine analysis, clinical diagnosis and research & development. The need or analysis methodologies of complex mixtures with low detection limits and high accuracy have increased in recent years [1,2], mainly due to advances related to the discovery of new drugs [3], biomass conversion [4,5] and the control of industrial losses.

Among both the separation and detection options available, the high performance anion exchange chromatography (HPAEC) with pulsed amperometric detection (PAD) using gold electrodes is one of the main options chosen for the analysis of carbohydrates and also one of the most employed in commercial instruments [6–9].

Despite the good performance of this detection system, it still has some drawbacks. 1) The necessity of polishing the electrode periodically. This frequency of maintenance is high when compared to other detectors commonly used in ion chromatographs, such as spectrophotometric and conductometric detectors, and it is also one of the main difficulties when you do not have the skills and tools needed. 2) Gold is a very expensive rare metal, which is the reason that makes its use difficult in innovations such as disposable electrodes [10]. 3) It shows a limited number of electrons extracted by the anodic process when compared to the enzymatic one [11]. 4) To minimize the fouling of the electrode and the consequent decrease of sensibility, it is necessary to apply pulsed modes of detection, which not only increase the unwanted capacitive current, but also limit the sample rate of points in the chromatograms. 5) The oxygen dissolved in the eluent has great influence, especially during the application of more cathodic potentials ( $<0$  V vs Pd|PdO), commonly employed in pulsed modes of detection. 6) The presence of some ions in the samples, such as chloride, bromide, iodide, cyanide, thiocyanate and thiourea, promote the dissolution of the gold electrode surface [12].

Other electrode materials such as copper, rhodium, nickel, cobalt, silver, iridium, palladium and iron also allow the detection of carbohydrates [13,14]. Among these, the copper electrodes are highlighted due to their low toxicity, low cost and the possibility of employing amperometric detection at constant potential (AD) [13–15]. One of the main reasons that restrict the use of other electrode materials is usually related to low chemical or physical stability and its effects on the repeatability and reproducibility of measurements.

The copper oxides are currently seen as a promising technological equipment because these materials are present in significant advances as memristors [16], supercapacitors [17], hydrogen photogeneration [18], and photoreduction of  $\text{CO}_2$  [19]. Copper oxides are also currently in numerous articles that discuss obtaining sensitive point of care devices and non-enzymatic [20–30]. In such cases, the selective determination of glucose is highlighted, however, as far as we know there are no other papers that explore the universal determination of carbohydrates using copper oxide nanostructures and we consider this characteristic relevant to the development of new carbohydrate detectors for ion chromatographs.

In this paper, we show that one of the ways found to solve the problems of stability of the copper electrodes in chromatographic systems is achieved through the growth of a nanostructured copper oxide film on the surface of the electrode. For this, the modification of the electrode was based on a simple method described in the literature [31] To simplify the process, some changes were made to the time of reaction and the temperature of the heat treatment. These changes also resulted in different nanostructures from the ones previously reported. In addition, this article shows that the analytical results were appreciably improved when compared to

the copper electrode. Thus, this electrode emerges as a new option, which is reproducible and inexpensive for the detection of carbohydrates using AD, and its detectability can be higher than for the gold electrode using PAD.

## 2. Experimental procedure

### 2.1. Reagents

The reagents D-Glucose (Sigma CAS 50-99-7), D-Fructose (Sigma CAS 57-48-7), D-Sucrose (Sigma CAS 57-50-1), D-Maltose (Sigma CAS 6363-53-7), D-Lactose (Sigma CAS 5989-81-1), D-Cellulose (Sigma CAS 528-50-7), D-Sorbitol (Sigma CAS 50-70-4), D-Galactose (Sigma CAS 59-23-4), D-Manose (Sigma CAS 3458-28-4), L-Arabitol (Sigma CAS 7643-75-6), D-Xylose (Sigma CAS 58-86-6), D-Ribose (Sigma CAS 50-69-1), D-Arabinose (Sigma CAS 10323-20-3), Ammonium persulfate (Sigma CAS 7727-54-0) and Sodium Hydroxide (CAS 1310-73-2 Sigma) were used as received without further purification. All solutions were prepared with deionized water obtained from a Direct-Q®3UV Millipore system with resistivity higher than 18.2 M $\Omega$  cm and subjected to ultraviolet radiation to prevent the growth of microorganisms.

### 2.2. Apparatus

For the chromatographic measurements, an 881 Compact IC pro ion chromatograph (Metrohm AG, Herisau, Switzerland) was used connected to a Dell Latitude computer and controlled by the MagIC Net 2.3 software. This system was composed by an ion exchange column Metrosep Carb1 150  $\times$  4.0 mm with particle size of 5  $\mu$ m of polystyrene/divinylbenzene copolymer. The amperometric detector and wall jet cell (Fig. S1) were composed of a Pd|PdO|OH<sup>-</sup> (0.100 mol L<sup>-1</sup>) reference electrode ( $E = -0.038$  V vs Ag|AgCl|KCl (3 mol L<sup>-1</sup>)), a stainless steel auxiliary electrode and a gold electrode (Au), a copper electrode (Cu) or a nanostructured copper oxide electrode (Cu|CuO) with a diameter of 2 mm as a working electrode. The run system was isocratic with a controlled temperature of the column kept at 26 °C and of the detector at 35 °C. The solutions were injected by means of a 20  $\mu$ L sample loop and the elution was kept at a flow rate of 1.0 mL min<sup>-1</sup>.

### 2.3. Preparation of solutions

A solution of 0.100 mol L<sup>-1</sup> sodium hydroxide was used as the eluent and the electrolyte was prepared by weighing NaOH pellets in a beaker and then transferred quantitatively to a 2.00 L volumetric flask. To ensure the removal of particles in the eluent, this solution was subjected to a vacuum filtration system with a Quimis pump and a Millipore system with a Büchner funnel and 0.22  $\mu$ m membranes. After this step, so as to minimize the presence of dissolved gas in the eluent, the solution was transferred to a Schott flask and subjected to vacuum and ultrasound (Unique Ultracleaner 1400) for 60 min.

The solution used for modifying the electrodes was prepared prior to use, and consisted of 10 g of NaOH (2.5 mol L<sup>-1</sup>) and 2.85 g of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (0.125 mol L<sup>-1</sup>) dissolved in individual beakers and mixed into 100.00 mL volumetric flask.

### 2.4. Preparation of copper based working electrodes

The working electrodes were made of copper with purity higher than 99% in the form of disks and embedded in polyether ether ketone (PEEK). The electrodes were made in a way to permit their use in a chromatograph wall jet cell as well as in a conventional cell. The geometric area of the electrodes was 0.0314 cm<sup>2</sup>.

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