

Synthesis and characterization of polymeric films and nanotubule nets used to assemble selective sensors for nitrite detection in drinking water

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Abstract

Platinum electrodes were modified by electropolymerized films and polymer nanotubule nets and were applied to nitrite detection in drinking water. Several analytical parameters were investigated such as: different monomers (1,2-, 1,3-, 1,4-DAB, pyrrole, *o*-anisidine, 1,8-DAN), permeability toward nitrites and other interferences, permselectivity toward nitrites, operational and long-term stability. The best performances were obtained with a poly(1,3-DAB) film and the assembled sensor was characterized morphologically by scanning electron microscope and electrochemically by cyclic voltammetry and amperometry coupled to flow injection analysis (FIA), in terms of linear range of concentration (10–1000 μM), limit of detection (2 μM), reproducibility (R.S.D.%: 0.4) and linear regression (y (μA) = 1.14 x (μM) + 2.6). Finally real samples (tap and mineral drinking water) were analyzed by adding standard nitrite solutions and the recovery was evaluated showing no matrix effect on sensor performances. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

The quantitative determination of nitrite concentration is of rapidly increasing interest, especially for the monitoring of drinking water quality and in the food industry when water is often used as a raw material. Nitrite ions are a precursor in the formation of nitrosamines, which have been shown to be carcinogenic [1]. Moreover, nitrites are routinely added to meat products as a preservative against food poisoning microorganisms such as *Clostridium botulinum* [2]. Furthermore, when nitrites are present at high concentration in blood, they can react with the iron (III) of the haemoglobin, forming methemoglobin, which has no oxygen carrying ability; this disease is called methemoglobinemia or “Blue Baby Syndrome” [3]. For these reasons, nitrite’s presence in drinking water must be limited and in Italy legal limits are fixed at value of 2 μM [4].

Many methods have been reported [5,6] for quantitative determination of nitrite including chromatography, potentiometry and fluorimetry, but nitrites are traditionally determined spectrophotometrically by their reaction with sulphanilamide and *N*-naphthylethylenediamine (Griess reaction). Nitrites are also electroactive species that are readily oxidized at platinum electrodes polarized at +900 mV versus Ag|AgCl. Since the potential for nitrite oxidation is high, many other electroactive compounds present in complex media can interfere in the nitrite analysis. Permselective coatings offer the promise of bringing higher selectivity and stability to electrochemical devices. This is accomplished by exclusion from the surface of unwanted matrix constituents, while allowing transport of the target analyte. Different avenues to control the access to the surface, based on different transport mechanisms, have been proposed. These include the use of charged-exclusion coating [7], hydrophobic lipid [8] or alkylthiol layers [9] or size-exclusion polymeric films [10]. Such anti-interference membrane barriers offer an effective separation step in situ on the surfaces and hence protect the surface against adsorption of large macromolecules or minimize overlapping signal from undesired electroactive interference. Size-exclusion

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properties are attributed to the morphology of electropolymerized films [11].

In this work, platinum electrodes were covered by different electropolymerized barriers which have size exclusion properties and which have been synthesized by two different techniques: polymeric films traditionally [12] obtained by cyclic voltammetry and polymeric nanotubule nets obtained by “template synthesis” approach [13]. Permeability toward nitrites and interferences and the correspondent permselectivity were evaluated. For the first time, the influence of the polymer structure on permeability was explained by morphological studies. The best performances were obtained using poly(1,3-DAB) film and poly(1,2-DAB) nanotubule nets in terms of permselectivity and the resulting sensors were characterized to detect nitrites by amperometry in flow injection analysis (FIA). Best analytical performances were obtained modifying the platinum electrode by traditional electropolymerized film and operational and long-term stability, were studied. Real samples (drinking mineral and tap water) were analyzed and recovery studies were performed, showing the absence of matrix effects.

2. Experimental

2.1. Reagents and solutions

1,2-Diaminobenzene (1,2-DAB), 1,3-diaminobenzene (1,3-DAB), 1,4-diaminobenzene (1,4-DAB), NaNO_2 , Na_2SO_3 , phenol and NaClO_4 were purchased from Sigma Chemical Co. (St. Louis, MO); 1,8-diaminonaphthalene (1,8-DAN), *o*-anisidine, pyrrole were from Fluka (Buchs, Switzerland); CH_3COOH , NaH_2PO_4 , CH_3COONa , HCl , HClO_4 , H_2SO_4 , ascorbic acid (AA) and CH_2Cl_2 were from Carlo Erba (Milan, Italy). Pt foils (thickness 0.025 mm) were purchased from Sigma–Aldrich and polycarbonate nanoporous particle track-etched membranes (PC nanoPTMs) having a thickness of 10 μm , a pore density of 1×10^8 pores/ cm^2 and pore diameters ranging from 15 to 100 nm, were obtained from Nucleopore (Italy).

2.2. Apparatus

An AUTOLAB PGstat/12 potentiostat/galvanostat was used for voltammetric studies and electropolymerizations. The amperometric measurements were carried out with a 641 VA-Detector (Metrohm, Switzerland) and currents were recorded using a Linseis L6512 recorder (Linseis, Selb, Germany). A Pt–Ag|AgCl|3 M (model 805/CPG/6, from AMEL, Milan, Italy) was used as combined auxiliary/reference electrode, and a platinum electrode (model 492/Pt/3, AMEL, Milan, Italy) represented the working electrode.

For FIA measurements combined with electrochemical detection, we used a wall-jet cell (model 656, Metrohm, Herisau, Switzerland), a peristaltic pump Minipuls 3 (Gilson, France) with a six-way injection valve (model 5020) and a closed loop of 250 μl (Rheodyne, USA) and PTFE connection tubes (i.d. 0.5 mm from Supelco, Bellefonte, CA).

Morphologic studies were carried out at room temperature using a Field Emission Scanning Electron Microscope

(model S-4000, Hitachi, Japan) having an accelerating voltage of 20 keV.

2.3. Procedure

2.3.1. Electrode polishing

The platinum electrode surfaces were polished with alumina powder (Al_2O_3 , Buehler, Evanston, IL) having different particle size: 1, 0.3 and 0.05 μm before use. After rinsing with distilled water, the electrodes were pre-treated by potential cycling in 0.5 M H_2SO_4 from -0.2 to $+1.2$ versus Ag|AgCl at a scan rate of 20 mV/s, until no changes were observed in the cyclic voltammograms [12].

2.3.2. Synthesis of polymeric films

Traditional polymeric films were synthesized directly on the electrode surface by cyclic voltammetry [14]. All the monomers, except the substituted naphthalene derivative, were used at a concentration of 5 mM and dissolved in 0.1 M phosphate buffer solution at pH 6.5 [15]. Solutions were deoxygenated with N_2 for 15 min just before the electropolymerization experiment. The potential was continuously cycled from 0 to $+0.8$ V (versus Ag|AgCl) for 20 scans at a scan rate of 2 mV/s for 1,2-DAB, 1,3-DAB, 1,4-DAB, pyrrole and *o*-anisidine. 1,8-DAN (5 mM) was electropolymerised in HCl 1 M. This greater acidity was required for its solubilization presumably because of its higher hydrophobicity. The potential was continuously cycled from -0.15 to $+1.3$ V (versus Ag|AgCl) for 20 scans at a scan rate of 2 mV/s.

2.3.3. Synthesis of polymeric nanotubule nets

Polymeric nanotubule were produced by the “template synthesis” [13] approach. A metallic Pt foil (1 cm^2) has been used as working electrode. The polycarbonate nanoporous particle track-etched membranes were used as a template membrane for the synthesis of polymer nanostructured nets and they were assembled as working electrode in a conventional one-compartment cell on a platinum foil. The electropolymerization was performed, at room temperature using platinum as counter electrode, and an Ag|AgCl as reference electrode. All the monomers were used at a concentration of 5 mM and dissolved in 0.01 M HClO_4 + 0.1 M NaClO_4 , as supporting electrolyte. Solutions were deoxygenated with N_2 for 15 min just before the electropolymerization experiment. Different potentials were applied for 250 s during the chronocoulometric experiment, depending on the monomer: 0.6 V for the three diaminobenzene isomers, 0.75 V for 1,8-DAN, 0.8 V for pyrrole and *o*-anisidine. Then, the template was dissolved by dichloromethane and the polymer nanotubules were placed directly on the platinum electrode surface, by drop coating. For the preliminary investigations 50 nm pore of PC template membrane, were used for all the monomers. Then the pore diameter was varied in order to evaluate the size exclusion effect of the nanostructured polymeric film on nitrite ion permeability.

2.3.4. Study of permeability and permselectivity

The permeability toward nitrites and several common interferences such as ascorbic acid, sulfites and phenols, was eval-

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