



Optimization of the electrochemical reduction of nitromethane for the development of an integrated portable sensor



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ABSTRACT

During the past ten years, the use of artisanal explosive compositions in terrorism attacks has increased and efficient detectors are greatly needed. Nitromethane is an interesting target for detection due to its uses in artisanal explosive compositions and also for its carcinogenic characteristics. Several techniques including electrochemistry have been developed but require laboratory equipment, preparative steps or complex working electrodes. We here describe the development of a robust, simple and commercially available electrochemical detection system. Square wave voltammetry was used for this purpose with a gold working electrode and a phosphate buffer at pH 7.5. The limits of detection (LOD) were 2.3 μM without dissolved oxygen in the solution and 12.5 μM in air. Furthermore, a mechanistic investigation enabled us to confirm, under these conditions, a 4-electron reduction mechanism from nitromethane to *N*-methylhydroxylamine. However, under real conditions of use, *N*-methylhydroxylamine is not the sole product of the reduction reaction. Other products have been identified by nuclear magnetic resonance characterization and a reaction scheme was established. The system could be minimized for on-site measurements by using screen-printed electrodes with a portable potentiostat. A vapor concentration of 20 ppm of nitromethane could be detected within 1 min thanks to this electrochemical sensing system.

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1. Introduction

During the past decade the threat of terrorism has increased, leading to considerable human and material damages [1]. To ensure security, the development of fast and efficient bulk and vapor explosive detectors has become an urgent worldwide necessity [2,3]. The need for sensitive and portable systems for trace detection requires the development of new approaches. One of the most important threats lies in the possibility for terrorists to use common products to make home-made explosive compositions. Nitromethane (hereafter denoted as NM) is the simplest molecule among the nitrated organic compounds. It has an activated structure that is envisioned to produce a highly energetic formulation. Commonly used as an organic solvent, NM is also known to behave as a very powerful explosive under certain circumstances [4]. The development of specific devices for the detection of NM is thus

foremost a question of global security. The substance is also interesting when it comes to occupational health monitoring since NM is potentially carcinogenic for humans (group 2B) [5,6] and numerous workers are exposed due to its range of uses [7].

Several techniques have already been investigated for the detection of NM such as colorimetry [8], fluorimetry [9–11], solid-phase micro-extraction–gas chromatography–mass spectroscopy [12] and gas chromatography with a flame ionization detector [13]. Most of these techniques are sensitive and selective but require laboratory preparation and equipment (gas chromatography, spectrophotometer) or toxic compounds as the polycyclic aromatic hydrocarbons used as fluorophores, for instance. Due to the high electroactivity of the nitro group, electrolytic reduction is also an excellent alternative for the detection of NM.

The electrochemical reduction of NM has been widely studied as a model for electrochemical mechanisms involving a chemical step between two electrochemical ones (ECE) [14]. The reduction mechanism, which was proposed for a long time proceeds with the uptake of four electrons thus giving *N*-methylhydroxylamine (NMHA). It requires several intermediate steps including an irreversible chemical reaction leading to cleavage of an N–O bond [15–18]. It has also been demonstrated that the reduction of NM is heterogeneous and that its electrocatalytic properties are nonsurface-dependent [15].

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The electrochemical detection of nitroaromatic traces such as 2,4,6-trinitrotoluene (TNT) has received significant interest from the scientific community [19–25]. Conversely, only a few studies dealing with NM have been reported [26–29]. The focus of these investigations has been to show the sensitivity enhancement provided by the electrocatalytic properties of heme proteins and porphyrins. Interesting limits of detection (LOD) as low as 0.6 nM [26] were effectively established. However, it should be noted that all the measurements were carried out after the removal of oxygen by bubbling of argon in the supporting electrolyte solution. This procedure avoids oxygen reduction which occurs at a less negative potential than NM and decreases the baseline stability of voltammetric scans. Moreover, the electrocatalytic properties of heme proteins for the reduction of nitroalkanes are known to be significantly affected by the presence of dioxygen [27]. In a real situation, preliminary bubbling is not an option as it would slow down the detection process and inevitably reduce the NM concentration due to its high volatility.

In this work, the experimental conditions for the electrochemical detection of NM have been optimized to fit the objective of developing a system for on-site monitoring with constraints of portability, non-toxicity, real atmosphere with oxygen, as well as a commercial availability of equipment and products. The miniaturization of this system and the association with a vapor bubbling unit was also explored. Finally, the electrochemical reduction mechanism of NM under our experimental conditions was revisited. Bulk electrolysis measurements were performed to determine the electron uptake of the process and the reaction products were characterized mainly by nuclear magnetic resonance (NMR) experiments based on both natural-abundance and ^{13}C -enriched NM.

2. Experimental

2.1. Apparatus

Most of the voltammetric measurements were obtained using a PalmSens potentiostat (Palm Instrument BV) with gold, platinum or glassy carbon working electrodes (3 mm in diameter, Metrohm), platinum wire as the counter electrode and Ag/AgCl KCl 3 M as the reference electrode (Metrohm). In case of the mercury working electrode, measurements were recorded using an MDE150 polarographic stand (Radiometer) with a platinum wire as the counter electrode and Ag/AgCl KCl sat. as the reference electrode (Radiometer). Bulk electrolysis measurements were realized with the same equipment, both with and without liquid junction to protect the counter electrode, and for rapid electrolysis with a 2 cm² gold foil as the working electrode (99.9%, 25 μm thickness, Sigma–Aldrich). A PHM201 (Meterlab) pH-meter was used with an XC161 (Radiometer) combined electrode.

Screen-printed electrodes (SPEs) were also employed instead of the classical three-electrode system for on-site measurements (Dropsens). A GilAir5 (Sensidyne) portable pump was utilized to sample the vapors. All experiments were carried out at 20 ± 1 °C. The NMR measurements were performed on a Bruker Avance 400 MHz spectrometer. We used a standard Bruker 5 mm BBO+ probe for the ^1H and ^{13}C runs and a 10 mm H-X Broadband probe for the ^{14}N experiments.

2.2. Reagents and solutions

All employed chemicals were of analytical grade and were used without further purification. All solutions were prepared with deionized water with a resistivity above 18.2 M Ω at 25 °C (Milli-Q direct UV3, Millipore).

Buffer solutions were prepared by dissolving in water the right amount of KCl salt (Sigma–Aldrich) to obtain a final concentration of 1 M of KCl, and the correct amount of K_2HPO_4 (Fluka), H_3BO_3 (Alfa Aesar) or citric acid (Sigma–Aldrich) salt providing a final concentration of 0.1 M of buffer. The pH was adjusted to the desired value by adding 1 M solutions of KOH or HCl (Fluka).

NM stock solutions were prepared on a monthly basis by dissolving the correct quantity of NM (99%, Aldrich) in water. These solutions were stored in the dark at room temperature. The same procedure was used for the *N*-methylhydroxylamine (Aldrich), methylamine (Aldrich) and formic acid (VWR) stock solutions.

Labeled NM was used for the ^{13}C NMR experiments (^{13}C 99% enrichment, Cambridge Isotope Lab. Inc.) and deuterated dichloromethane and acetonitrile were employed for the liquid/liquid extraction of bulk electrolysis products (deuterium 99.8% enrichment, Eurisotop).

2.3. Experimental procedure

2.3.1. Pretreatments of electrodes

Classical working electrodes were mechanically polished to a mirror finish by means of an aqueous emulsion of alumina powder (0.3 μm , Metrohm) and a polishing cloth. Subsequently, the electrodes were cleaned ultrasonically in water to remove residual alumina and finally rinsed and dried in ambient air.

SPEs cannot be mechanically polished, wherefore a chemical and electrochemical pretreatment was used (for the gold working electrode) following the procedure given in Ref. [30]. In a few words, the SPE was rinsed with water, and dipped in a solution of 50 mM KOH + 250 g/L H_2O_2 for 10 min. Then, the SPE was rinsed again with water, dipped in a 50 mM KOH solution and the potential was swept from -0.2 to -1.2 V at 50 mV/s. Finally, the SPE was rinsed once more with water and dried in ambient air.

The silver reference electrode spot of the SPEs was transformed into Ag/AgCl by electrolysis in KCl solution. The SPE was dipped in a 1 M KCl solution and 1.4 V (vs. Pt) was applied between the Ag spot of SPE and a Pt foil. The SPE was then rinsed with water and dried in air. This procedure aimed at improving the stability of measurements and the repeatability of the potential between several SPEs.

2.3.2. Electrochemical measurements

Each buffer solution was transferred into an electrochemical cell and aliquots of NM were added. Unless otherwise specified, dissolved oxygen was removed from the solution by argon bubbling during 20 min.

Voltammetric measurements involving mercury were performed on a static mercury drop electrode (0.5 s growth time). The parameters for the differential pulse voltammetry (DPV) included a 5 mV/s scan rate, a 50 mV pulse potential and a 40 ms pulse duration. The parameters for the square wave voltammetry (SWV) were: a 4 mV step, a 20 Hz frequency and a 30 mV amplitude. Finally, a 50 mV/s scan rate was used for the cyclic voltammetry (CV). The chronoamperometric technique was used for both bulk electrolysis and amperometric detection, the applied potential was -0.8 V vs. Ag/AgCl or pseudo AgCl.

2.3.3. NMR characterizations

We initially tried to use D_2O as the solvent, but we observed a rapid change and finally a loss of NM proton signal due to the fast exchange of methyl protons with water. The supporting electrolytes were thus prepared with normal water without further addition of any deuterated solvent for NMR analysis. ^1H NMR spectra were recorded following a water pre-saturation procedure allowing signal enhancement for weakly concentrated compounds.

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