



## Flow injection analysis of picric acid explosive using a copper electrode as electrochemical detector

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### ABSTRACT

A simple and fast electrochemical method for quantitative analysis of picric acid explosive (nitro-explosive) based on its electrochemical reduction at copper surfaces is reported. To achieve a higher sample throughput, the electrochemical sensor was adapted in a flow injection system. Under optimal experimental conditions, the peak current response increases linearly with picric acid concentration over the range of 20–300  $\mu\text{mol L}^{-1}$ . The repeatability of the electrode response in the flow injection analysis (FIA) configuration was evaluated as 3% ( $n=10$ ), and the detection limit of the method was estimated to be 6.0  $\mu\text{mol L}^{-1}$  ( $S/N=3$ ). The sample throughput under optimised conditions was estimated to be 550 samples  $\text{h}^{-1}$ . Peroxide explosives like triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) were tested as potential interfering substances for the proposed method, and no significant interference by these explosives was noticed. The proposed method has interesting analytical parameters, environmental applications, and low cost compared with other electroanalytical methods that have been reported for the quantification of picric acid. Additionally, the possibility to develop an in situ device for the detection of picric acid using a disposable sensor was evaluated.

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### 1. Introduction

High explosives consist of an intimate mixture of a chemical oxidant and reductant that on initiation undergo a highly exothermic decomposition to yield gaseous products [1]. Picric acid or 2,4,6-trinitrophenol is one of the explosive compounds that can be used for the manufacture of weapons and explosives. The detection of explosives is important because of the potential applications in fields such as tactical and humanitarian demining, remediation of explosives manufacturing sites, and forensic and criminal investigations. There are also environmental health and safety concerns on nitroaromatics [1]. Given the importance of monitoring these species in military security and forensic analyses, it is necessary to develop a simple, fast, and cheap analytical method for their detection and quantification [2].

In the literature [2], the methods for the quantification of 2,4,6-trinitrophenol have used the following techniques: spectrophotometry [3,4], fluorimetry [5–7], electrochemistry [8–11] and chromatography or chromatography/mass spectrometry [12,13]. In most cases, a preliminary derivatisation step is necessary, which will result in longer analysis times. Additionally, some methods need high-cost equipment, are labour-intensive or

require professionals with good training, because they involve several analytical steps. An example of such a method is ion mobility spectrometry (IMS), which is commonly used as an explosive detection system at airports and has sensitivity in the range of picograms or nanograms. However, it is expensive, operator-dependent, prone to false positives, and spectrometers must be frequently calibrated [14]. Detecting picric acid is also important in the indirect analysis of other compounds or when it is used as a reagent for colorimetric tests, for example, in the quantification of creatinine based on Jaffe's reaction [15,16].

The development of electrochemical sensors for the detection of explosives is focused on the possibility of in situ measurements, and it often includes high sensitivity and selectivity, a wide linear range, minimal space and power requirements, and low cost instrumentation [2,17]. The catalytic activity of copper electrodes has been evaluated by using sulphite, nitrate, sugars, polyols, carboxylic acids, amino acids and amines as substrates [18–31]. Notwithstanding, no specific study on the use of copper electrodes as electrochemical sensors for quantification of picric acid was found in the literature. In this paper, we propose a copper-based electrochemical sensor coupled to a flow injection analysis system for the detection of picric acid, without the need of modification of the electrode surface or previous stages of treatment or accumulation. This results in a rapid, accurate, and inexpensive analysis. Besides these analytical features, copper-based disposable devices, which are cheap, practical and

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miniaturisable, could be used in developing a portable method for the fast in situ detection of picric acid, and some preliminary studies will be reported in this article.

## 2. Methods and materials

### 2.1. Safety note

Different kinds of explosives were used in this work. It is important to highlight that an extra care must be taken when handling these type of materials. Their explosion may occur spontaneously, and not more than 1 g should be handled each time.

### 2.2. Chemical and materials

All solid reagents were of analytical grade and were used without further purification. Acetic acid, acetone, acetonitrile, boric acid, citric acid, hydrogen chloride, hydrogen peroxide, methanol, sodium acetate, sodium hydroxide, sodium phosphate dibasic, sodium phosphate monobasic, sodium sulphate, sodium tetraborate decahydrate, and sulphuric acid were purchased from Merck (Darmstadt, Germany). Picric acid was purchased from Reagen (Rio de Janeiro, Brazil); nitrobenzene, from Carlo Erba (Milano, Italy); and hexamethylenetetramine, from Acros Organics (Geel, Belgium). Solutions were prepared by dissolving the reagents in deionised water, which was processed through a water purification system (Direct-Q<sup>®</sup> 5 Ultrapure Water Systems, Millipore, MA, USA).

### 2.3. Electrodes and instrumentation

A  $\mu$ AUTOLABIII (Eco Chemie, The Netherlands) with data acquisition software available from the manufacturer (GPES 103 4.9.007 version) was used for the electrochemical measurements. Gold, bismuth, glassy carbon, copper, and platinum were used as working electrodes. A homemade Ag/AgCl<sub>(KCl sat.)</sub> electrode and a platinum wire were used as reference and auxiliary electrodes, respectively. All the working electrodes were polished with an alumina suspension (0.3  $\mu$ m, Alfa Aesar, MA, USA) on a micro-cloth polishing pad between each electrochemical measurement and washed thoroughly with deionised water.

#### 2.3.1. Disposable devices

The procedure is based on the use of toner masks to protect the copper surface during a chemical etching process, as previously reported in the literature for gold electrodes [25,32,33]. Briefly, the layout of the electrodes was drawn using the graphic software (OpenOffice.org 2.4, Sun Microsystems Inc.) and it had three electrodes (working, reference, and auxiliary electrodes). The layout was then printed on the same type of waxed paper that is used as a support for adhesive label paper using an HP Laser Jet P2015 printer. No pre-treatment was performed on the copper-clad paper-phenolic laminate (Pertech<sup>®</sup> of Brazil, São Bernardo do Campo, Brazil) used as a substrate to fabricate the devices. The heat transfer of the toner mask on the substrate was carried out with a model HLM 230 thermal press (Metalnox, Santa Catarina, Brazil) adjusted to 120 °C (1–2 min). Exposed copper layers, which were not covered with toner, were removed by approximately 6–10 min exposure to ferric chloride (42% w/v) solutions. The toner mask was then removed with acetonitrile by cotton swabs to expose the electrode surface. A small amount (5–10  $\mu$ L) of silver epoxy (Joint Metal Comércio LTDA, São Paulo, Brazil) was also manually deposited onto the copper surface in the integrated sensor to construct a

pseudo-reference electrode. All fabricated sensors were disposable, i.e., they were used only for a single experiment.

### 2.4. Electrochemical analysis

Picric acid determinations were performed by flow injection analysis (FIA) using 0.1 mol L<sup>-1</sup> phosphate buffer (pH=7.4) as a carrier solution. All the parameters involved in the FIA were optimised and are as follows: potential: -0.9 V, flow rate: 4.0 mL min<sup>-1</sup>, sample volume: 75  $\mu$ L.

### 2.5. Syntheses of peroxide explosives

Triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD) were synthesised as reported previously [34,35]. Solutions of these explosives were prepared by dissolving the reagents in an acetonitrile/methanol solution (1:1).

## 3. Results and discussion

### 3.1. Voltammetric experiments and reduction mechanism

The electrochemical response of picric acid was first evaluated using five different electrodes (gold, bismuth, glassy carbon, copper, and platinum) to estimate which electrode surface provides the highest analytical signal. Cyclic voltammograms were registered using these electrodes in a 0.1 mol L<sup>-1</sup> phosphate buffer solution containing 5 mmol L<sup>-1</sup> of picric acid. Except for the platinum electrode (voltammogram E), all electrode materials showed a well-shaped faradaic current signal for the picric acid reduction. Fig. 1 shows all the voltammograms obtained. With gold and glassy carbon electrodes (voltammograms A and C), the picric acid reduction occurs at around -1.0 V with currents of approximately -80 and -130 mA mm<sup>-2</sup>, respectively. The best responses were obtained with bismuth and copper electrodes (voltammograms B and D) and the faradaic signal appears at less negative potentials than with gold and glassy carbon electrodes. With the bismuth electrode, a peak of -136 mA mm<sup>-2</sup> can be observed at -0.63 V, whereas the copper electrode gives a peak of -145 mA mm<sup>-2</sup> at a very similar potential (-0.67 V). Based on these results, copper was chosen as the working electrode material due to the best analytical signal in comparison with other bare electrode materials.

The reduction of picric acid on the copper surface was then evaluated at several pH values. The tested electrolytes were as follows: 0.1 mol L<sup>-1</sup> sodium sulphate (pH=2.2), 0.1 mol L<sup>-1</sup> acetate buffer (pH=4.7), 0.1 mol L<sup>-1</sup> phosphate buffer (pH=7.4), 0.1 mol L<sup>-1</sup> borate buffer (pH=9.1), and 0.1 mol L<sup>-1</sup> NaOH (pH=13). The voltammograms obtained at each pH value are shown in Fig. 2. The peak related to the picric acid reduction process could be observed at all conditions. The first conclusion we can draw from Fig. 2 is that the maximum peak potential shifts towards more negative potentials as the pH increases, as already observed by Ni et al. [36]. This is related to the fact that picric acid is deprotonated at a more basic medium and as a result, the negative charge of oxygen is strongly stabilised by the nitro groups, making the reduction more difficult.

At highly acidic conditions (pH 2.2, Fig. 2A), it is possible to see two overlapped electrochemical reduction processes in the current peak (-0.4 V and -0.5 V). At a higher reduction potential, -0.85 V, a small electrochemical reduction process can also be observed. This process could be clearly visualised at low concentrations of picric acid and when differential pulse technique was used to record the voltammetric behaviour (not shown). Earlier papers on the electrochemical reduction of three nitro explosives,

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