Talanta 104 (2013) 162–168

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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

João R.C. Junqueira, William R. de Araujo, Maiara O. Salles, Thiago R.L.C. Paixão*

Instituto de Química, Universidade de São Paulo, São Paulo, SP 05508-900, Brazil

A R T I C L E I N F O

Article history:
Received 15 October 2012
Received in revised form
14 November 2012
Accepted 16 November 2012
Available online 23 November 2012

Keywords:
Explosive sensor
In situ device
Disposable
Voltammetric
Flow injection analysis
Homeland security
Electrochemistry
Copper electrode

A B S T R A C T

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 μmol 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 μmol L^{-1} (S/N=3). The sample throughput under optimised conditions was estimated to be 550 samples 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.

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 Jaffé'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

---

* Corresponding author. Tel.: +55 11 30919150
E-mail address: trlcp@iq.usp.br (T.R.L.C. Paixão).

0039-9140/$ - see front matter Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.11.036

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® 5 Ultrapure Water Systems, Millipore, MA, USA).

2.3. Electrodes and instrumentation

A μAUTOLABIII (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 $Ag/AgCl_{(KCl sat.)}$ 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 mm, Alfa Aesar, MA, USA) on a microcloth 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® of Brazil, São Bernando 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 μL) 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^{-1} 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^{-1}, sample volume: 75 μL.

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^{-1} phosphate buffer solution containing 5 mmol L^{-1} 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^{-2}, 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^{-2} can be observed at -0.63 V, whereas the copper electrode gives a peak of -145 mA mm^{-2} 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^{-1} sodium sulphate (pH=2.2), 0.1 mol L^{-1} acetate buffer (pH=4.7), 0.1 mol L^{-1} phosphate buffer (pH=7.4), 0.1 mol L^{-1} borate buffer (pH=9.1), and 0.1 mol L^{-1} 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,

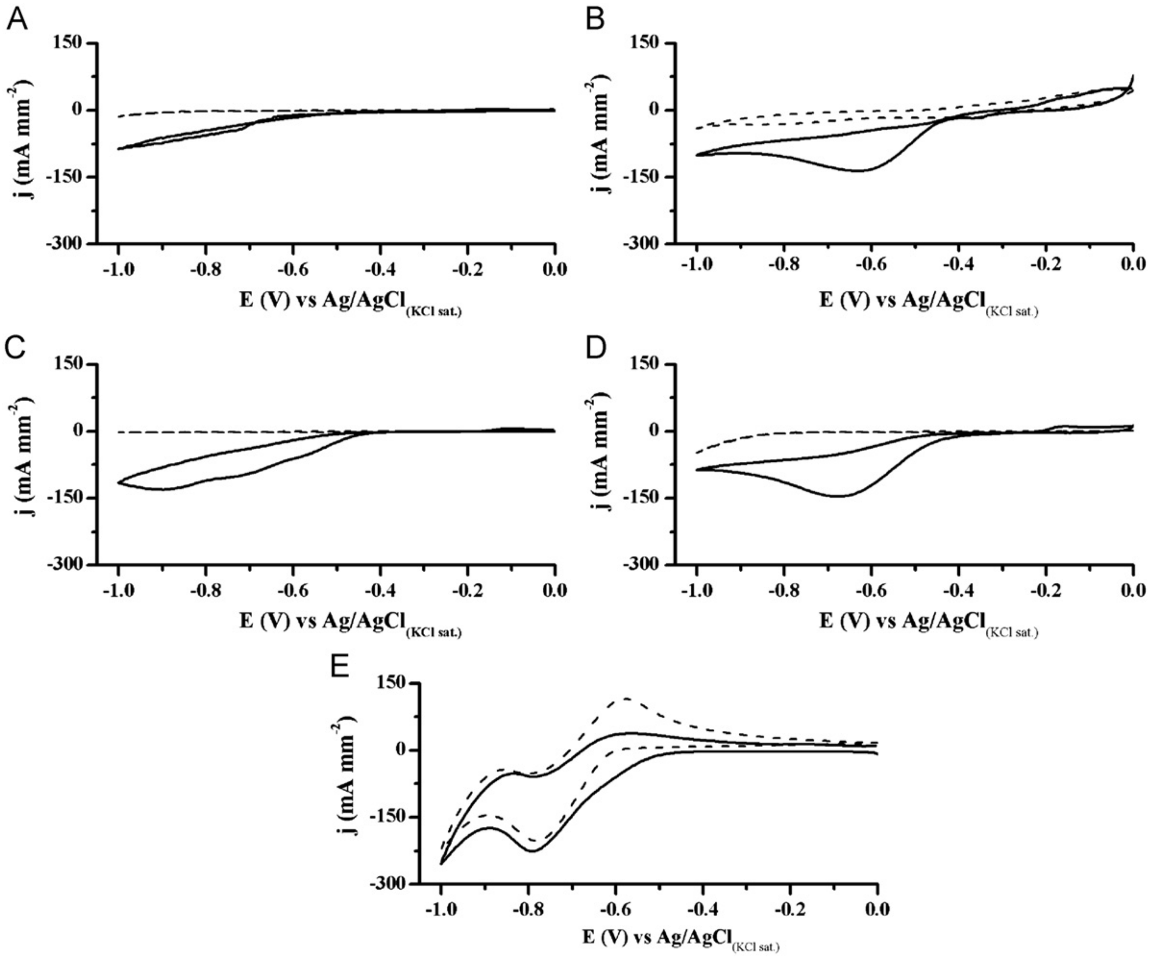

Fig. 1. Cyclic voltammograms recorded in a 0.1 mol L^{-1} phosphate buffer solution (pH=7.4) in the absence (dashed line) and presence (solid line) of 5 mmol L^{-1} picric acid. Working electrodes used: (A) gold (r=0.78 mm), (B) bismuth (r=0.33 mm), (C) glassy carbon (r=0.71 mm), (D) copper (r=1.02 mm), and (E) platinum (r=0.76 mm). Scan rate 50 mV s^{-1}.

such as 2,4,6-trinitrotoluene (TNT) [37–39], have shown that the reduction of the nitro group usually occurs in two steps; through the reduction of the amino group to hydroxylamine (Eq. (1)), followed by the reduction of the hydroxylamine to amine (Eq. (2)).

$$RNO_2+4H^++4e^-\leftrightarrows RNHOH+H_2O \tag{1}$$

$$RNHOH+2H^++2e^-\leftrightarrows RNH_2+H_2O \tag{2}$$

$$RNO_2+6H^++6e^-\leftrightarrows RNH_2+2H_2O \tag{3}$$

Each nitro group goes through a sequential six-electron reduction to the amine form (Eq. (3)). Hence, the three electrochemical signals could be attributed to the stepwise reduction of three amino groups of picric acid to the corresponding amines [37–39]. In addition, the voltammograms recorded in Fig. 2A and B were similar, and both currents were approximately −250 μA. Upon increasing the pH value to 7.4, a much higher reduction peak is observed (almost two times higher than that at lower pH values). With a continuous increase in pH, the values of current decrease. Thus, the phosphate buffer solution (pH=7.4) was the preferred electrolyte to achieve better analytical performance.

The reduction of picric acid (Fig. 1) has already been reported in the literature. However, depending on the experimental conditions, one–four reduction signals were observed [8,11,40,41]. This means that the reduction of nitroaromatic compounds, such as picric acid, is a rather complex process and can occur via several paths, depending on the number of nitro groups, their relative position in the aromatic ring, and the nature and position of other groups [37–39,41].

Previous works [10,36] have shown that at moderately acidic conditions, the nitroaromatic compounds are reduced to hydroxylamines in two steps involving four electrons (Eq. (1)). In the slow first step (Eq. (4)), the nitro compound is reduced to a radical anion ($RNO_2^{\bullet -}$). In the second step (Eq. (5)), three electrons and four protons are consumed and the radical is reduced to a hydroxylamine (RNHOH) [10,36]. However, it has been reported in the literature [11] that in a strong alkaline medium, the first step (Eq. (4)) involves a fast reversible uptake of one electron, and the second one corresponding to Eq. (5) is a slow and irreversible three-electron process. Hence, a decrease in the current of overlapped peaks and a shift in the potential of the second step towards more negative values could be observed at acidic conditions, which could explain the new process observed in Fig. 2 D and E at the more negative potentials and the decrease in current upon increasing the pH values above 7.

$$RNO_2+e^-\leftrightarrows RNO_2^{\bullet -} \tag{4}$$

$$RNO_2^{\bullet -}+3e^-+4H^+\rightarrow RNHOH+H_2O \tag{5}$$

3.2. *Flow injection analysis*

After the voltammetric studies, the analysis of picric acid was conducted by a flow injection system. The parameters were optimised to achieve best possible analytical figures of merit.

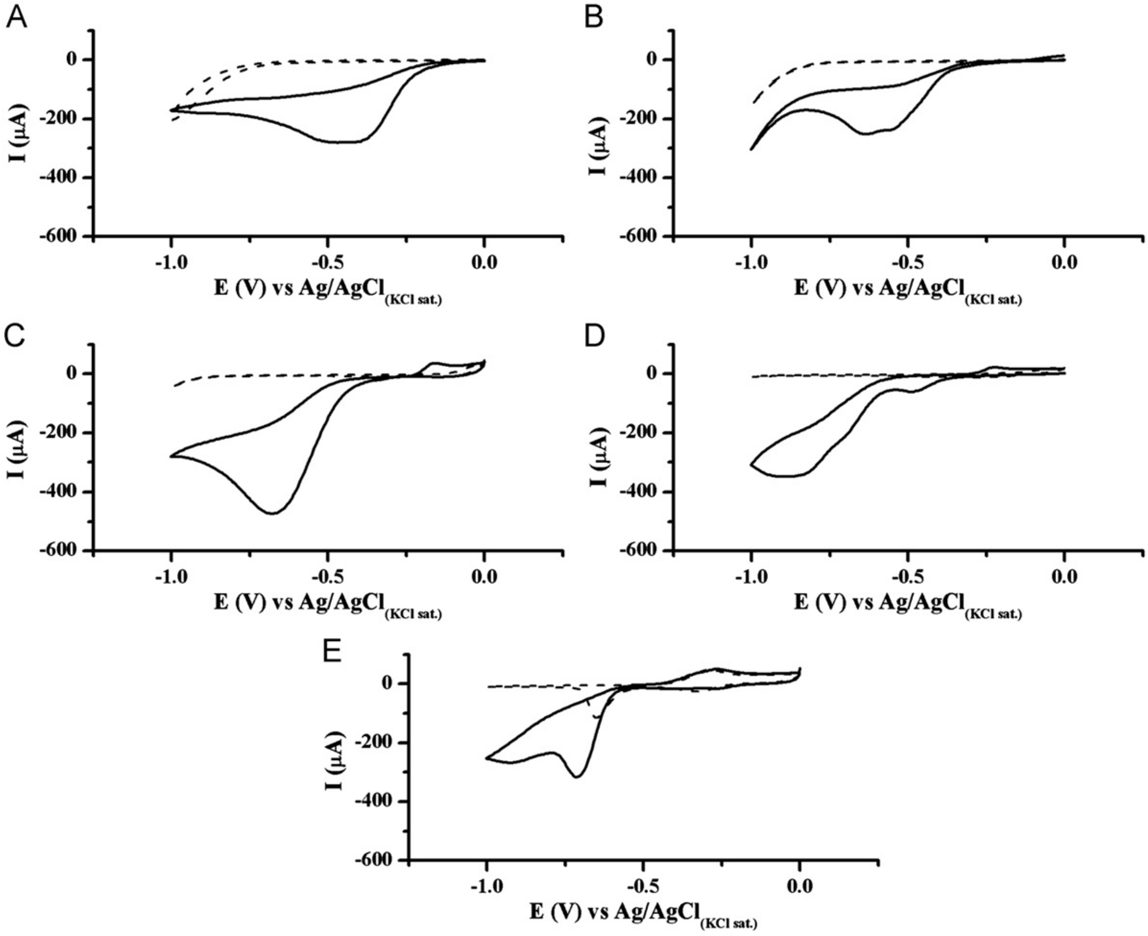

Fig. 2. Cyclic voltammograms recorded with a copper electrode in the absence (dashed line) and presence (solid line) of 5 mmol L^{-1} picric acid. Electrolytes used: (A) sodium sulphate (pH=2.2), (B) acetate buffer (pH=4.7), (C) phosphate buffer (pH=7.4), (D) borate buffer (pH=9.1) and (E) NaOH (pH=13), all solutions at 0.1 mol L^{-1}. Scan rate 50 mV s^{-1}.

The first optimised parameter was the potential applied to the electrode. Fig. 3 shows that the highest cathodic current was obtained at -0.9 V. The cathodic current decreased with higher potential values, which could be associated with the electrochemical consumption of hydrogen ions at the bare electrode. This affects the electrochemical process described in Eq. (2), i.e., it decreases the current responsible for the electrochemical reduction of picric acid. Based on this hydrodynamic voltammogram behaviour, taking into consideration that the FIA determinations were performed at the best sensitivity conditions, the value of $E=-0.9$ V (against Ag/AgCl$_{(KClsat.)}$) was chosen as the working potential.

Fig. 4 shows the optimisation of the flow rate and sample volume. From Fig. 4A, it can be seen that the peak current increases with the flow rate up to 4.0 mL min^{-1}. This confirms that up to this flow rate, the electrochemical reduction is governed by a mass transport rather than by the electron transfer process. For the higher flow rate values, mass transport does not dominate over the electron transfer process. To obtain the best sensitivity for the developed analytical method without consuming more carrier solution, a flow rate of 4.0 mL min^{-1} was chosen. On the other hand, no significant changes in the peak current values were observed with the sample volume. For this reason, a low sample volume of 75 μL with enhanced peak current value was chosen. Under these experimental conditions, the sample throughput was calculated as 550 samples h^{-1}.

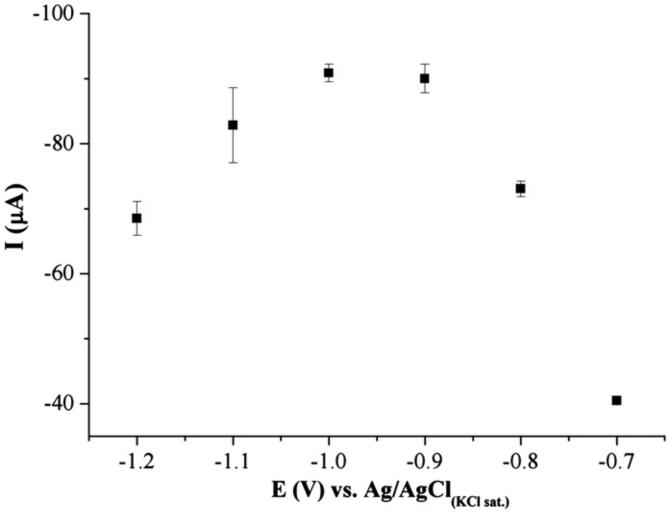

Fig. 3. FIA hydrodynamic voltammogram recorded using a copper electrode in a 0.1 mol L^{-1} phosphate buffer solution (pH=7.4) with 1 mmol L^{-1} picric acid. Flow rate: 2 mL min^{-1}, sample volume: 75 μL, carrier solution: 0.1 mol L^{-1} phosphate buffer (pH=7.4).

An analytical curve was then constructed, and a linear relation between the peak current and concentration was obtained in the range from 20 to 300 μmol L^{-1} (Fig. 5). The straight line obeys the equation $((I(\mu A))=-2.6+0.18(C_{picricacid}/(\mu mol\ L^{-1}))$ $(R=0.996)$. The detection limit of the method and the repeatability were

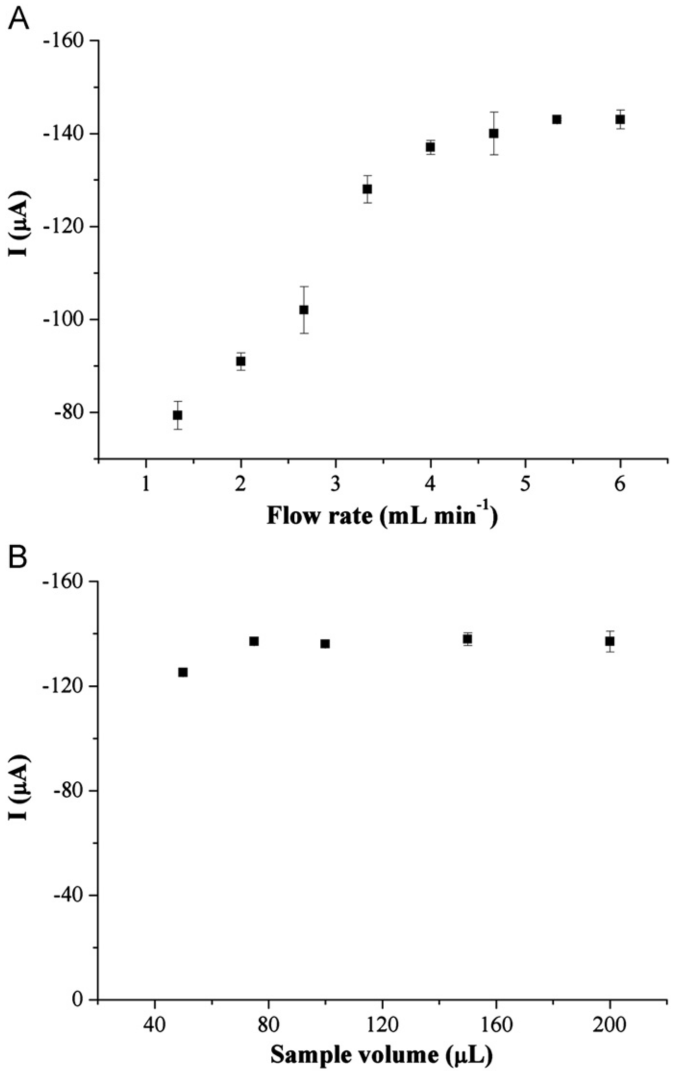

Fig. 4. (A) Peak current recorded at increasing flow rates for a 0.1 mol L^{-1} phosphate buffer solution (pH=7.4) with 1 mmol L^{-1} picric acid. Potential: −0.9 V, sample volume: 75 μL, carrier solution: 0.1 mol L^{-1} phosphate buffer (pH=7.4). (B) Peak current recorded at increasing sample volumes for 0.1 mol L^{-1} phosphate buffer solution (pH=7.4) with 1 mmol L^{-1} picric acid. Potential: −0.9 V, flow rate: 4 mL min^{-1}, carrier solution: 0.1 mol L^{-1} phosphate buffer (pH=7.4).

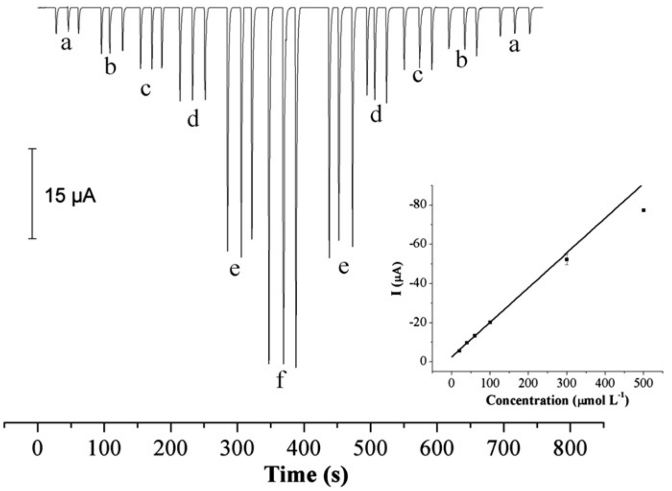

Fig. 5. Flow injection peaks recorded for injections for a 0.1 mol L^{-1} phosphate buffer solution (pH=7.4) containing picric acid at the following concentrations: 20 (a), 40 (b), 60 (c), 100 (d), 300 (e), and 500 μmol L^{-1} (f). Inset: analytical calibration curve. Potential: −0.9 V, flow rate: 4 mL min^{-1}, sample volume: 75 μL, carrier solution: 0.1 mol L^{-1} phosphate buffer (pH=7.4).

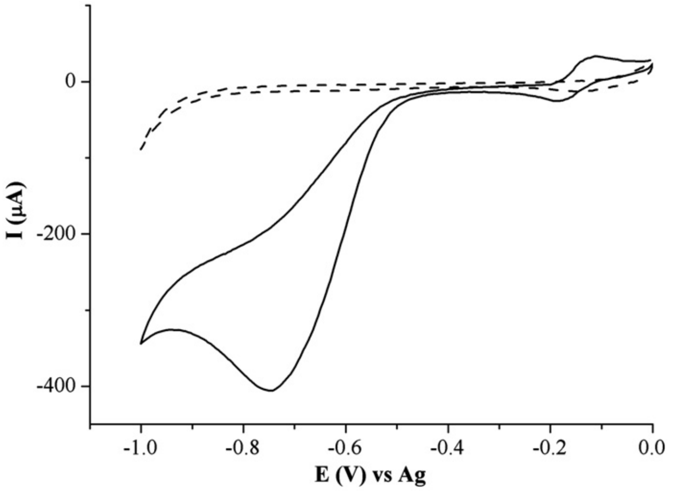

Fig. 6. Cyclic voltammograms recorded in a 0.1 mol L^{-1} phosphate buffer solution (pH=7.4) in the absence (dashed line) and presence (solid line) of 5 mmol L^{-1} picric acid. Scan rate 50 mV s^{-1}. Sample volume: 300 μL.

estimated to be 6 μmol L^{-1} and 3% ($n=10$), respectively. Additionally, the lack of system memory reported in Fig. 5 could be attributed to the configuration of the flow injection system and/or to the small sample volume used.

Some of the advantages of the proposed method, as mentioned earlier in Section 1, are the use of non-chemically modified electrode and simple materials to fabricate an electrochemical device for a rapid detection of explosives. The disposable devices reported in the literature [25] could be fabricated for in situ measurements. Fig. 6 shows a cyclic voltammogram recorded for a small sample volume (300 μL) in the presence and absence of picric acid explosive using a disposable device made of copper sheets.

The analytical figures of merit for the proposed method have been compared with the literature in Table 1. The proposed method has a similar detection limit with the bismuth sensor and a better detection limit than the potentiometric sensor. Moreover, it is important to note that these analytical figures of merit were obtained without any pre-concentration steps or prior modification of the electrode surface.

3.3. Interference experiments

Interference experiments were conducted to find out if other explosives had an effect on the picric acid reduction signal. Three explosives were tested: two peroxi-explosives (TATP=triacetone triperoxide, and HMTD=hexamethylene triperoxide diamine) and one nitro-explosive (nitrobenzene).

The interference from nitrobenzene was evaluated by a flow injection analysis. Both picric acid and nitrobenzene were solubilised in a phosphate buffer. Picric acid concentration was maintained at 0.1 mmol L^{-1} with a 0–5-fold increase in the nitrobenzene concentration. According to the results shown in Fig. 7, interference of the picric acid signal can be seen at all ratios. This effect increases with the increasing concentration of nitrobenzene. As commented previously, the reduction process of nitrocompounds is strong dependents of the position of the nitrogroup at the ring and the structure of the species. Voltammetric experiments not shown and the literature [17] demonstrates that the reduction of nitrobenzene occurs at different potential than the picric acid (i.e. it is more difficult than the

Table 1
Detection limit, potential, and electrodes used in the literature and in the proposed method for the electrochemical picric acid analysis.

Reference	LD (μmol L^{-1})	Linear range (μmol L^{-1})	E (V)	Electrode
[11]	1[a]	–	−1.1 vs. Ag/AgCl(1 mol L^{-1} KCl)	Solid amalgam composite electrode
[43]	8.73×10^{-4} [b]	–	−0.339 vs. $Ag/AgCl_{(KClsat.)}$	Drop mercury electrode
[44]	1.3	4.5–30	−0.735 vs. SCE	Bismuth electrode
[9]	13	25–100,000	Potentiometric sensor	$Cu|Hg|Hg_2(Pic)_2|$graphite
Proposed method	6	20–300	−0.9 vs. $Ag/AgCl_{(KClsat.)}$	Copper electrode

[a] Using differential pulse voltammetry with an accumulation step.
[b] Using square wave voltammetry with an accumulation step.

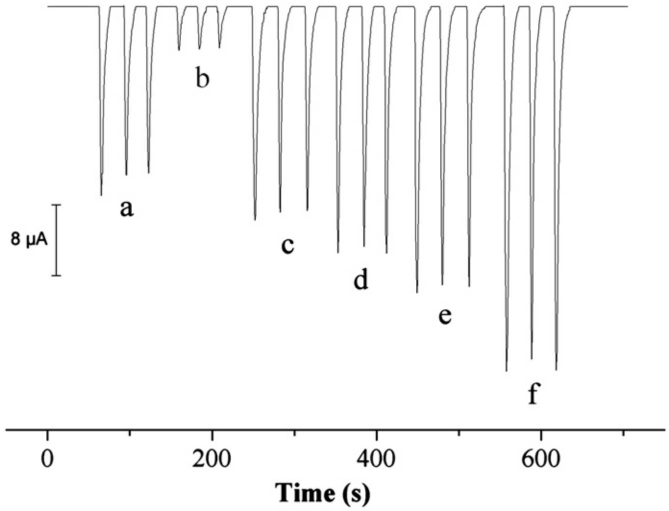

Fig. 7. Flow injections peaks recorded for a 0.1 mol L^{-1} phosphate buffer solution (pH=7.4) containing 100 μmol L^{-1} picric acid (a) or 100 μmol L^{-1} nitrobenzene (b). Nitrobenzene concentrations: 100 (c) 200 (d), 300 (e), and 500 μmol L^{-1} (f). Potential: −0.9 V, flow rate: 4 mL min^{-1}, sample volume: 75 μL, carrier solution: 0.1 mol L^{-1} phosphate buffer (pH=7.4).

Table 2
Explosives that can potentially interfere with the electrochemical reduction signal of picric acid. Experiments were performed in a 0.1 mol L^{-1} phosphate buffer solution with 0.1 mmol L^{-1} picric acid and 0.1–0.5 mmol L^{-1} of the interfering substance. Potential: −0.9 V, flow rate: 4 mL min^{-1}, sample volume: 75 μL, carrier solution: 0.1 mol L^{-1} phosphate buffer (pH=7.4). *Note*: the interfering compounds (TATP and HMTD) were solubilised in an acetonitrile/methanol (1:1) solution.

Compound	Signal ratio ($I_{compound}/I_{picric\ acid}$)
Picric acid	1.00 ± 0.07
Nitrobenzene	0.24 ± 0.01
Picric acid+nitrobenzene (1:1)	1.20 ± 0.06
Picric acid+nitrobenzene (1:2)	1.41 ± 0.07
Picric acid+nitrobenzene (1:3)	1.63 ± 0.08
Picric acid+nitrobenzene (1:5)	2.1 ± 0.1
Picric acid+TATP (1:1)	1.01 ± 0.07
Picric acid+HMTD (1:1)	1.02 ± 0.06

All the experiments were performed in triplicate.

picric acid reduction). Hence, the interference problem could be clearly solved by a chemometric treatment or with a system of equation with two variables [42].

Table 2 summarises the results by showing the signal ratio of the current obtained with the interfering substance and with picric acid. Since both TATP and HMTD are insoluble in phosphate buffer, they had to be solubilised in an acetonitrile/methanol (1:1) solution. The interfering substances were evaluated at the same concentration as picric acid (0.1 mmol L^{-1}) by FIA. On the basis of the signal ratios shown in Table 2, no significant electrochemical reduction of the picric acid signal was observed at the aforementioned experimental conditions.

4. Conclusions

Copper is an interesting material to promote the electroreduction of picric acid. Its use as an amperometric detector in a flow injection system provides a new, rapid, low-cost, and simple analytical method for the identification of picric acid explosives. The proposed method could be employed by a person without a chemical background, it could give fast results (in less than 10 min) by using a flow injection system or a disposable device, and it can have potential field applications.

Acknowledgements

The authors are grateful to Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP); Grant numbers 2012/12106-5, 2011/11115-8, and 2011/19903-5), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq); Grant numbers 470919/2011-6 and 302700/2011-0) for financial support.

References

[1] S.J. Toal, W.C. Trogler, J. Mater. Chem. 16 (2006) 2871–2883.
[2] J.S. Caygill, F. Davis, S.P.J. Higson, Talanta 88 (2012) 14–29.
[3] H. Parham, B. Zargar, M. Rezazadeh, Mater. Sci. Eng. C 32 (2012) 2109–2114.
[4] R. Shkumbatiuk, Y.R. Bazel, V. Andruch, M. Torok, Anal. Bioanal. Chem. 382 (2005) 1431–1437.
[5] N. Venkatramaiah, S. Kumar, S. Patil, Chem. Commun. 48 (2012) 5007–5009.
[6] B. Xu, X. Wu, H. Li, H. Tong, L. Wang, Macromolecules 44 (2011) 5089–5092.
[7] Y. Peng, A.-J. Zhang, M. Dong, Y.-W. Wang, Chem. Commun. 47 (2011) 4505–4507.
[8] M. Jacobsen, H. Duwensee, F. Wachholz, M. Adamovski, G.U. Flechsig, Electroanalysis 22 (2010) 1483–1488.
[9] M. Moghimi, M. Arvand, R. Javandel, M.A. Zanjanchi, Sensors Actuators B 107 (2005) 296–302.
[10] J. Carbajo, S. Bollo, L.J. Nunez-Vergara, P. Navarrete, J.A. Squella, J. Electroanal. Chem. 494 (2000) 69–76.
[11] V. Vyskocil, T. Navratil, A. Danhel, J. Dedik, Z. Krejcova, L. Skvorova, J. Tvrdikova, J. Barek, Electroanalysis 23 (2011) 129–139.
[12] C. Steuckart, E. Bergerpreiss, K. Levsen, Anal. Chem. 66 (1994) 2570–2577.
[13] M. Astratov, A. Preiss, K. Levsen, G. Wunsch, Int. J. Mass Spectrom. 167 (1997) 481–502.
[14] E. Wallis, T.M. Griffin, N. Popkie, M.A. Eagan, R.F. McAtee, D. Vrazel, J. McKinly, Proc. SPIE Chem. Biol. Sensing IV (2005), http://dx.doi.org/10.1117/12.609920.
[15] W.R. de Araujo, M.O. Salles, T.R.L.C. Paixão, Sensors Actuators B 173 (2012) 847–851.
[16] T. Songjaroen, T. Maturos, A. Sappat, A. Tuantranont, W. Laiwattanapaisal, Anal. Chim. Acta 647 (2009) 78–83.
[17] J. Wang, Electroanalysis 19 (2007) 415–423.
[18] Y.Q. Xie, C.O. Huber, Anal. Chem. 63 (1991) 1714–1719.
[19] P.F. Luo, F.Z. Zhang, R.P. Baldwin, Anal. Chim. Acta 244 (1991) 169–178.
[20] J.M. Marioli, T. Kuwana, Electrochim. Acta 37 (1992) 1187–1197.
[21] M.Z. Luo, R.P. Baldwin, J. Electroanal. Chem. 387 (1995) 87–94.
[22] T.R.L.C. Paixão, D. Corbo, M. Bertotti, Anal. Chim. Acta 472 (2002) 123–131.
[23] A.H. Maruta, T.R.L.C. Paixão, Fuel 91 (2012) 187–191.
[24] L.M.F. Dantas, A.P.R. De Souza, P.S. Castro, T.R.L.C. Paixao, M. Bertotti, Electroanalysis 24 (2012) 1778–1782.
[25] W. Novakowski, M. Bertotti, T.R.L.C. Paixao, Microchem. J. 99 (2011) 145–151.
[26] T.R.L.C. Paixao, J.L. Cardoso, M. Bertotti, Talanta 71 (2007) 186–191.

[27] T.R.L.C. Paixao, J.L. Cardoso, M. Bertotti, Fuel 86 (2007) 1185–1191.
[28] J.C.M. Gamboa, R.C. Pena, T.R.L.C. Paixao, M. Bertotti, Talanta 80 (2009) 581–585.
[29] H. Wei, J.-J. Sun, L. Guo, X. Li, G.-N. Chen, Chem. Commun. (2009) 2842–2844.
[30] Z.L. Chen, D.B. Hibbert, J. Chromatogr., A 766 (1997) 27–33.
[31] N. Torto, T. Ruzgas, L. Gorton, J. Electroanal. Chem. 464 (1999) 252–258.
[32] L. Bueno, T.R.L.C. Paixão, Talanta 87 (2011) 210–215.
[33] D. Daniel, I.G.R. Gutz, Electrochem. Commun. 5 (2003) 782–786.
[34] J. Pachman, R. Matyas, Forensic Sci. Int. 207 (2011) 212–214.
[35] C. Guo, J. Persons, G.S. Harbison, Magn. Reson. Chem. 44 (2006) 832–837.
[36] Y. Ni, L. Wang, S. Kokot, Anal. Chim. Acta 431 (2001) 101–113.
[37] J. Zang, C.X. Guo, F. Hu, L. Yu, C.M. Li, Anal. Chim. Acta 683 (2011) 187–191.
[38] H.X. Zhang, A.M. Cao, J.S. Hu, L.J. Wan, S.T. Lee, Anal. Chem. 78 (2006) 1967–1971.
[39] K. Bratin, P.T. Kissinger, R.C. Briner, C.S. Bruntlett, Anal. Chim. Acta 130 (1981) 295–311.
[40] F. Wachholz, K. Biala, M. Piekarz, G.U. Flechsig, Electrochem. Commun. 9 (2007) 2346–2352.
[41] M. Adamovski, A. Zajac, P. Grundler, G.U. Flechsig, Electrochem. Commun. 8 (2006) 932–936.
[42] T.R.L.C. Paixão, R.C. Matos, M. Bertotti, Electroanalysis 15 (2003) 1884–1889.
[43] Y. Zimmermann, J.A.C. Broekaert, Anal. Bioanal. Chem. 383 (2005) 998–1002.
[44] O. El Tall, D. Beh, N. Jaffrezic-Renault, O. Vittori, Int. J. Environ. Anal. Chem. 90 (2010) 40–48.