Electrochemical Sensing of Picric Acid Using µPADs Integrated with 3D Pen-Extruded Electrodes

Lauro A. Pradela Filho, Julia O. Cardoso, Thiago R. L. C. Paixão

Institute of Chemistry, University of São Paulo, São Paulo, SP, Brazil

e-mail: lauropradela@usp.br

2,4,6-Trinitrophenol (picric acid, PA) is a nitroaromatic compound historically used in explosives, posing significant forensic, environmental, and health concerns due to its high toxicity and potential use in illicit activities.[1,2] This work presents a low-cost, portable electrochemical platform for PA detection, integrating 3-electrode thermoplastic chips with paper-based microfluidic devices (µPADs). The electrochemical chip was fabricated using poly (methyl methacrylate) molds, a 3D printing pen, and a commercial carbon black filament. The electrochemical behavior of PA was initially evaluated by differential pulse voltammetry (DPV) using the reference electrode (RE) $Ag/AgCl/KCl_{3M}$. DPV measurement (Figure 1A) showed this analyte is reduced on the electrode surface, resulting in well-defined voltammetric peaks. The reduction peaks shifted towards a more positive potential under acid conditions. Next, the supporting electrolyte solution was evaluated, and no substantial signal difference was observed for HCl, HNO_3, and buffer BR. Considering the simplicity of the preparation, HCl 0.1 mol L^{-1} was selected as the supporting electrolyte. Compared to the RE $Ag/AgCl/KCl_{sat}$, the PA reduction peak shifted to approximately -100 mV with the Ag/AgCl pseudo-RE. After optimizing the experimental conditions, the thermoplastic chips were combined with a circular paper substrate, generating µPADs operated with amperometry. For µPAD optimization, the paper substrate type was evaluated with Whatman 41 (25 µm pore size), 40 (8 µm pore size), and 42 (2.5 µm pore size) filter papers. Whatman 41 offered sharper and more intense amperometric peaks because of the ability to provide faster mass transport for the analyte. Injection volumes of 1, 2, 4, and 6 µL were also evaluated, with 2 µL generating sharper amperometric peaks and minimizing paper saturation during multiple injections. The detection potential was next evaluated from -0.3 to -0.7V. Even though applying more negative potential produced higher I_p values, oxygen reduction is also favored in acid conditions under these conditions. Considering this, -0.5V was selected for subsequent studies, offering selectivity in the presence of urea, NO_3^-, NO_2^-, and nitrobenzene. Under optimized conditions, µPADs showed injection repeatability (RSD = 5.3%, n = 13 injections) and fabrication reproducibility (RSD = 9%, n = 3 devices). Additionally, the µPADs exhibited a linear correlation of I_p with PA concentration from 10 to 100 µmol L^{-1} (Figure 1B). Next, a lake water sample was spiked with four different PA concentrations, providing signals consistent with those obtained with standard solutions (Figure 1C). The developed µPAD platform demonstrates potentiality for on-site forensic and environmental monitoring of picric acid, offering the advantages of low cost, simplicity, portability, and minimal sample consumption.
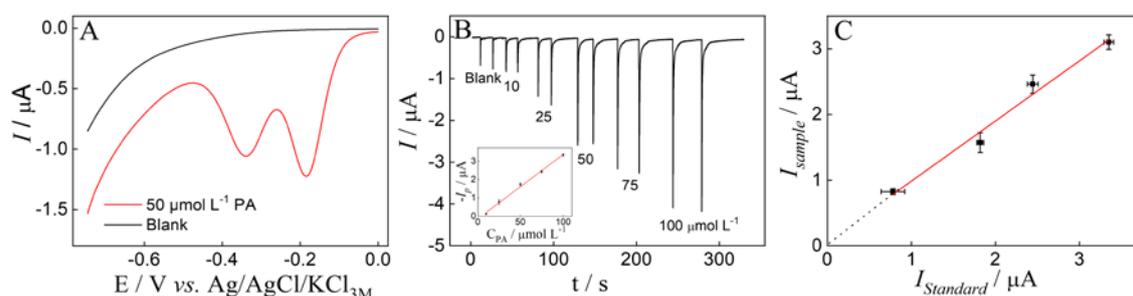

Figure 1 - A) DPV measurements recorded in 0.04 mmol L^{-1} BR buffer pH 2. B) Amperometric response for a µPAD recorded with injections of different PA concentrations in HCl 0.1 mol L^{-1}. Insert: Analytical curve for PA. E detection = -0.5 V vs. Ag/AgCl pseudo-RE. C) Graphic of I_p obtained for spiked lake water sample vs. I_p acquired for standard PA solutions.

1 - Rai A et al. Talanta 275 (2024) 126113

2 - Corsato P.C.R et al. Chemosphere 363 (2024) 14277