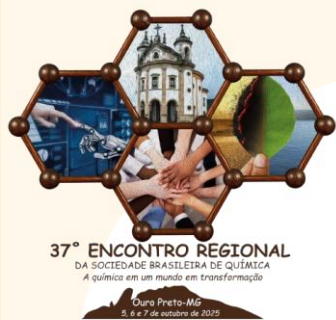




Optimization of Square Wave Voltammetry and Differential Pulse Voltammetry Parameters for Thiocyanate Determination in Human Saliva

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RESUMO

O íon SCN^- é encontrado em fluidos biológicos e pode indicar exposição ao cianeto presente no tabaco, podendo ser usado para identificar fumantes e não fumantes. Neste estudo, foram otimizados diferentes parâmetros operacionais da DPV e SWV para a detecção do SCN^- utilizando um eletrodo de G-ABS. A voltametria cíclica (CV) indicou um pico de eletrooxidação do SCN^- em +1,33 V, porém com baixa intensidade e linha de base ruim. Os parâmetros de DPV e SWV foram otimizados, obtendo picos mais intensos e melhor resolução, os resultados indicam que as condições otimizadas melhoraram significativamente o perfil voltamétrico.

Palavras-chave: Eletroanálise, Tiocianato, Voltametria de Pulso Diferencial, Voltametria de Onda Quadrada.

Introduction

Thiocyanate (SCN^-) is found in the tissues and body fluids of various mammals¹, as well as in organism metabolites², and can be quantified through human urine and saliva. Elevated concentrations of SCN^- can be used to distinguish between smokers and non-smokers, since this ion is a detoxification product of hydrogen cyanide present in tobacco; therefore, smokers tend to exhibit higher concentrations of this ion in their saliva compared to non-smokers. Given the need for new analytical methods for its quantification, voltammetric techniques stand out due to several advantages, such as the use of low reagent volumes, instrumental simplicity, high sensitivity, and low limits of detection (LOD) and quantification (LOQ). Thus, the aim of this study was to evaluate the influence of instrumental parameters of differential pulse voltammetry (DPV) and square wave voltammetry (SWV) on the voltammetric response of the SCN^- ion using a modified G-ABS electrode.

Experimental

Fabrication of the G-ABS Electrode

The composite was prepared by dissolving ABS filament in acetone under stirring. Then, graphite powder with a particle diameter $< 20 \mu\text{m}$ (Sigma-Aldrich) was added. A 3D-printed ABS substrate was immersed in the composite, thus being coated with a G-ABS layer. The electrodes were left to dry at 24°C for 72 hours. After drying, the electrodes were polished using sandpapers with different grits (2000 and 3000).

Electrochemical Measurements

All electrochemical measurements were performed in an ABS-printed electrochemical cell filled with 500 μL of solution. The SCN^- stock solution and the phosphate buffer (PB) 0.5 mol L^{-1} used as the supporting electrolyte were prepared using high-purity reagents.

Instrumental Parameters

The voltammetric response for SCN^- was initially evaluated using cyclic voltammetry (CV). Subsequently, differential pulse voltammetry (DPV) and square wave voltammetry (SWV) techniques were employed, and their instrumental parameters were optimized. For DPV, different values of pulse amplitude (10–100 mV), pulse time (5–75 ms), and step potential (1–5 mV) were evaluated. For SWV, different values of amplitude (10–200 mV), frequency (10–200 Hz), and step potential (2–8 mV) were investigated.

Results and Discussion

Cyclic voltammograms were recorded in the absence and presence of 1 mM SCN^- , as shown in Figure 1. The CV results indicated that the electrooxidation of SCN^- produced an anodic peak at +1.33 V vs. $\text{Ag/AgCl/KCl}_{\text{sat}}$. However, the voltammetric peak exhibited low intensity and a poorly defined baseline.

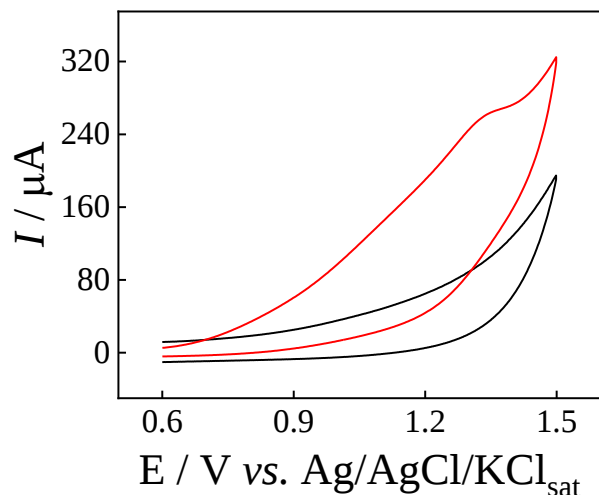


Figure 1. Cyclic voltammograms recorded in PB 0.5 mol L⁻¹ (pH = 7) in the absence (—) and in the presence (—) of 1 mmol L⁻¹ SCN⁻ using a G-ABS electrode. Voltammetric conditions: $v = 100 \text{ mV s}^{-1}$. Potential range: 0.6 to 1.5 V.

Therefore, due to the limitations of CV, DPV and SWV techniques were further evaluated. Table 1 presents the evaluated parameter values and the selected values, considering a higher peak current and a lower full width at half maximum. The parameters were optimized using a univariate approach.

Table 1. Optimized Experimental Parameters for DPV and SWV.

Technique	Evaluated Conditions	Selected Conditions
DPV	$\Delta E = 10\text{--}100 \text{ mV}$	$\Delta E = 75 \text{ mV}$
	$t_{\text{pulse}} = 5\text{--}75 \text{ ms}$	$t_{\text{pulse}} = 25 \text{ ms}$
	$\Delta E_s = 1\text{--}5 \text{ mV}$	$\Delta E_s = 2 \text{ mV}$
SWV	$\Delta E = 10\text{--}200 \text{ mV}$	$\Delta E = 50 \text{ mV}$
	$f = 10\text{--}200 \text{ Hz}$	$f = 25 \text{ Hz}$
	$\Delta E_s = 2\text{--}8 \text{ mV}$	$\Delta E_s = 2 \text{ mV}$

An initial combination of the operational parameters for the DPV technique was selected, using the following combination: $\Delta E = 50 \text{ mV}$, $t_{\text{pulse}} = 50 \text{ ms}$, and $\Delta E_s = 2 \text{ mV}$. The concentrations of SCN⁻ and PB were kept at 500 $\mu\text{mol L}^{-1}$ and 0.5 mol L⁻¹, respectively. The optimized conditions were: $\Delta E = 75 \text{ mV}$, $t_{\text{pulse}} = 25 \text{ ms}$, and $\Delta E_s = 2 \text{ mV}$, as shown in Table 1. For SWV, the initial combination of operational parameters was: $\Delta E = 50 \text{ mV}$, $f = 50 \text{ Hz}$, and $\Delta E_s = 5 \text{ mV}$. As with DPV, the concentrations of SCN⁻ and PB were maintained the same during the SWV studies. The optimized operational parameters were: $\Delta E = 50 \text{ mV}$, $f = 25 \text{ Hz}$, and $\Delta E_s = 2 \text{ mV}$. Additional studies are necessary for the evaluation of figures of merit such as linear range, LOD, LOQ, sensitivity, and linearity.

Conclusions

According to the results obtained, the peak observed at +1.33 V is attributed to the electrooxidation of the SCN⁻ ion, since this peak is not observed in the presence of only the supporting electrolyte. The instrumental parameters for each of the evaluated techniques were satisfactorily optimized, resulting in more intense peaks, with a better baseline and narrower peak width at half height.

Acknowledgments

FAPEMIG

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