

Flow injection amperometric determination of persulfate in cosmetic products using a Prussian Blue film-modified electrode

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Abstract: A flow-injection system with a glassy carbon disk electrode modified with Prussian Blue film is proposed for the determination of persulfate in commercial samples of hair bleaching boosters by amperometry. The detection was obtained by chronoamperometric technique and the sample is injected into the electrochemical cell in a wall jet configuration.

Potassium chloride at concentration of 0.1 mol L^{-1} acted as sample carrier at a flow rate of 4.0 mL min^{-1} and supporting-electrolyte.

For 0.025 V (vs. Ag/AgCl) applied voltage, the proposed system handles *ca.* 160 samples per hour ($1.0 \cdot 10^{-4}$ - $1.0 \cdot 10^{-3} \text{ mol L}^{-1}$ of persulfate), consuming about $200 \text{ }\mu\text{L}$ sample and 11 mg KCl per determination. Typical linear correlations between electrocatalytic current and persulfate concentration was *ca.* 0.9998. The detection limit is $9.0 \cdot 10^{-5} \text{ mol L}^{-1}$ and the calculated amperometric sensibility $3.6 \cdot 10^3 \text{ }\mu\text{A L mol}^{-1}$. Relative standard deviation ($n = 12$) of a $1.0 \cdot 10^{-4} \text{ mol L}^{-1}$ sample is about 2.2%. The method was applied to persulfate determination in commercial hair-bleaching samples and results are in agreement with those obtained by titrimetry at 95% confidence level and good recoveries (95 - 112%) of spiked samples were found.

Keywords: Prussian Blue film-modified electrode; Persulfate; Flow injection analysis; Amperometry

Introduction

Chemical deposition of electroactive species in inert solid electrodes has been used to produce electrochemical sensors for different types of samples and analytes [1,2]. Modified electrodes are widely used sensors due to simplicity, high selectivity and sensitivity and relative low cost [3]. When electrochemical catalysis is present, a significant reduction in activation overpotential occurs and a less prone of surface contamination and oxide formation in comparison to inert electrodes [4]. Several methods have been described for electrode modification such as addition of redox polymers [5], ion-exchange polymers [6], clays [7], metal cyanometallates [8] and metal oxides [9].

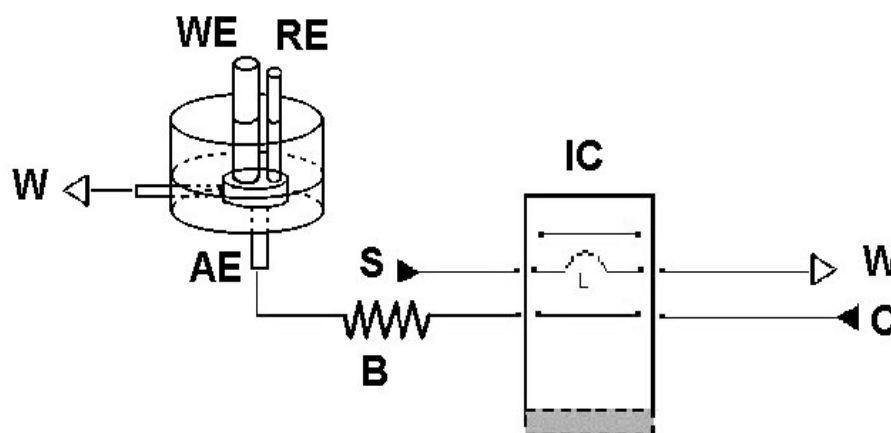
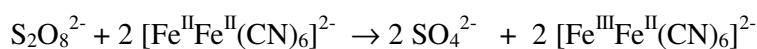


Figure 1. Flow diagram of the system for persulfate determination. IC: injector-commutator; S: sample or analytical solution (2.5 ml min^{-1}); C: sample carrier stream (4 ml min^{-1}); L: sampling loop ($200 \mu\text{l}$); W: waste; B: coiled reactor (100 cm); WE: working electrode (PB-modified glassy carbon); RE: reference electrode (Ag/AgCl); AE: auxiliary electrode (platinum tube).

Prussian Blue (PB) [iron(III) hexacyanoferrate(II)] modified electrodes have been used for the determination of several organic and inorganic compounds [10-19] due to its high stability, operation under highly reproducible conditions, user friendly, simple preparation and applicability to different workable samples.

Electrocatalytic effect in the reduction of persulfate (peroxodissulfate) anions on PB modified carbon paste electrodes has been presented by Weissenbacher and co-workers [20]. By using direct current voltammetric measurements, the reduction reaction of persulfate is supposed to yield the corresponding PB complex of Fe(III) and the sulfate anions:



This catalytic property has allowed the application of PB as a modifier substrate for different electrodes for persulfate determination. An example of PB carbon paste-modified electrode can be obtained by mechanical mix of graphite powder and substrate for persulfate analysis [20]. Afterwards,

a PB film-modified electrode was obtained by electrochemical deposition of this film in platinum disk electrode [21], exhibiting a better mechanical stability in relation to carbon paste and easiness of preparation. These sensors were used for voltammetric determinations of persulfate anions in commercial samples, using conventional electrochemical cells and exhibiting good agreement with titrimetry.

Flow-injection analysis (FIA) is attractive for procedures involving electrochemical detection due to their operation under highly reproducible conditions [22,23].

A manual procedure has been proposed for persulfate determination using PB modified electrode [21], but its applicability to routine analysis in large scale is seriously limited by the time and reagent consumption. Little attention has been given for the use of electrode modified by PB film and wall jet configuration electrochemical cell for automated determination of persulfate.

This study reports on a flow injection amperometric procedure for the determination of persulfate in real samples by using glassy carbon disk electrode modified by PB film and an wall jet configuration electrochemical cell. The performance of the proposed procedure was checked after analyzing commercial hair bleach booster samples.

Experimental

Reagents, analytical solutions and samples

All solutions were prepared with high-purity chemicals and distilled-deionized water.

Potassium chloride stock standard solution (0.1 mol L^{-1}) was prepared by dissolving appropriate amount of KCl in water. This solution was used as supporting-electrolyte for voltammetric measurements and also used as sample carrier stream (C, Fig. 1).

Iron(III) stock standard solution (FeCl_3 0.01 mol L^{-1}) and hexacyanoferrate(III) stock standard solution ($\text{K}_3[\text{Fe}(\text{CN})_6]$ 0.01 mol L^{-1}) were prepared by dissolving respective salts in appropriate amounts of the previously prepared KCl standard solution (0.1 mol L^{-1}) in order to prevent dilution effect of the supporting-electrolyte.

Persulfate working standards ($1.00 \cdot 10^{-4}$ - $10.0 \cdot 10^{-4} \text{ mol L}^{-1} \text{ K}_2\text{S}_2\text{O}_8$) were prepared by appropriate dilution of the stock solution in previously deaerated 0.1 mol L^{-1} KCl.

Hair bleach booster samples were purchased at a local super market. A mass of 250 mg of each sample was dissolved in about 200 mL 0.1 mol L^{-1} KCl solution and acidified with 1.0 mol L^{-1} HCl until pH 7 in order to eliminate alkaline substances as carbonates. Thereafter the volume was completed to 1000 mL with KCl solution. The final solution should be deaired for 15 minutes before injection in the FIA system. Further dilutions can be necessary for some sample lots to match the analyte concentration to those of calibration curve.

The flow injection system

The system comprised a IPC-8 Ismatec peristaltic pump furnished with Tygon® pumping tubes, an injector-commutators (IC), a 173 Princeton Applied Research potentiostat interfaced through a 273 Princeton Applied Research electrochemical software, polyethylene tubing (i.d. 0.7 mm), coiled

reactors and accessories. A conventional three-electrode cell was employed with a glassy carbon disk electrode (0.25 cm^2) as working electrode, an Ag/AgCl reference electrode and a platinum plate as auxiliary electrode.

The flow diagram of the system is shown in Fig. 1. In the position specified of the figure, a sample (S) volume of $200 \mu\text{L}$ is selected by the sampling loop L. After loop-based injection, the established sample zone passes through the electrochemical cell in where persulfate is reduced to sulfate. A transient current is recorded as a peak with height proportional to the persulfate content in the sample. After peak maximum measurement, the injector-commutator is switched back and another cycle can be started.

Concentration of persulfate, sample volume, flow-rate and applied potential were investigated in order to optimize the system stability, sensitivity and sampling rate.

Procedure

Glassy carbon disk electrode (0.25 cm^2) was polished to a mirror finish with alumina ($0.03 \mu\text{m}$), then rinsed thoroughly with water, cleaned in an ultrasonic bath with water and finally rinsed with water before using. The formation of Prussian Blue film on the glassy carbon disk surface (0.25 cm^2) was obtained by immersing the electrode in an oxygen-free solution containing 0.1 mol L^{-1} KCl plus 1 mmol L^{-1} FeCl_3 plus 1 mmol L^{-1} $\text{K}_3\text{Fe}(\text{CN})_6^{3-}$ and by repetitive potential cycling within -0.2 and $+0.6$ V vs. Ag/AgCl, at a scan rate of 0.010 V s^{-1} . After film formation, the electrode was rinsed with deionised water. The resulting modified electrode was cycled in 0.1 mol L^{-1} KCl within the -0.1 and $+0.5$ V range (vs. Ag/AgCl) at a scan rate of 100 mV s^{-1} in order to verify the film stability for use in further experiments. A steady current-voltage profile was attained after at least 10 cycles.

Cyclic voltammograms at 0.100 V s^{-1} in different medium were carried out in order to verify the electrochemical catalysis of persulfate reduction: PB film; 0.1 mol L^{-1} KCl solution; 0.1 mol L^{-1} KCl plus $1.0 \cdot 10^{-3} \text{ mol L}^{-1}$ persulfate solution; 0.1 mol L^{-1} KCl plus $1.0 \cdot 10^{-3} \text{ mol L}^{-1}$ persulfate solution at PB modified electrode.

The optimum potential for amperometric measurements at the PB film was obtained by means of hydrodynamic voltammograms. The voltage was varied from 0 to 0.150 V vs. Ag/AgCl and the sample carrier was a 0.1 mol L^{-1} KCl solution (C, Fig. 1) flowing at 4.0 mL min^{-1} . The concentration and volume of persulfate solution were $2.0 \cdot 10^{-4} \text{ mol L}^{-1}$ and $200 \mu\text{L}$, respectively.

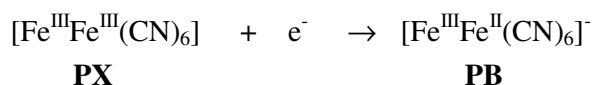
The influence of the sample carrier stream on signal and sampling rate was investigated by varying the rotation speed of the peristaltic pump in order to obtain different flow rates ($0.5 - 5.0 \text{ mL min}^{-1}$) for the channel C. The influence of sample volume was studied in the range of $40 - 400 \mu\text{L}$ by varying the length of loop L from 10 to 100 cm, respectively.

The electrocatalytic determination of persulfate at the Prussian Blue modified electrode was obtained by chronoamperometry, being measured the current variation according to addition of standard solutions by the commutator trough the flow cell. Calibration curves were drawn in order to verify the linear response interval for persulfate determination. All measurements were done in triplicate, and precision was evaluated after twelve successive injections of an analytical solution ($1.0 \cdot 10^{-4} \text{ mol L}^{-1}$) in the flow system. The concentration of analyte was determined by interpolation of current values in the calibration curve.

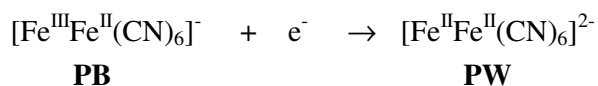
Results and discussion

Prussian blue film formation

The electrodeposition of Prussian Blue at the glassy carbon surface is reported at Figure 2, where the 5 first cycles are shown. After complete film formation (10 cycles) the surface coverage was calculated in $1.3 \times 10^{-8} \text{ mol.cm}^{-2}$ by integrating the curve current vs. time. The initial reduction process of brown-yellow soluble complex (PX) [(iron(III) hexacyanoferrate(III))] in the insoluble Prussian Blue (PB) forms consist in one electron transfer process:



Subsequently, the reduction of PB yields to the Prussian White (PW) form [3] in an also one electron process, whose this latter redox process was applied in this work:



Stability study for PB-modified in supporting-electrolyte was carried out for 20 cycles of potential to the PB/PW redox couple, with no loss of charge observed.

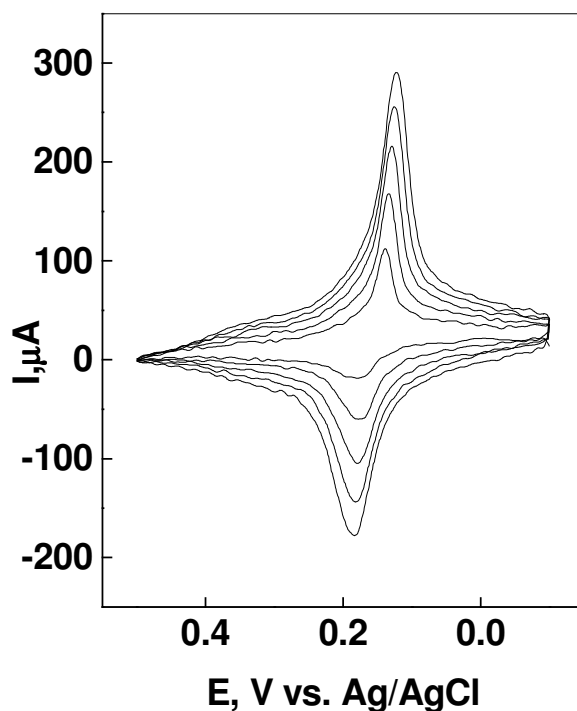


Figure 2. Prussian Blue film formation. Supporting-electrolyte: 0.1 mol L^{-1} KCl solution; area of the glassy carbon disk electrode: 0.25 cm^2 ; number of cycles: first 5; scan rate: 100 mV s^{-1} .

Electrocatalysis of persulfate reduction

Shown in Fig. 3 are voltammograms for supporting-electrolyte (curve a), persulfate reduction at glassy carbon (curve b), Prussian Blue modified electrode (curve c) and persulfate reduction at the modified electrode (curve d). A shift of 700 mV to more positive potential in the persulfate reduction is observed, being decreased the overpotential in relation of solid electrodes. Additionally, an increasing of 10 times at the reduction peak current is obtained for persulfate at modified Prussian Blue electrode, showing up catalysis effect. The increase in cathodic peak current is linear and proportional to the concentration of added persulfate, corresponding to the reduction of $\text{Fe}(\text{CN})_6^{3-}$ to $\text{Fe}(\text{CN})_6^{4-}$ of the Prussian Blue film (curve d).

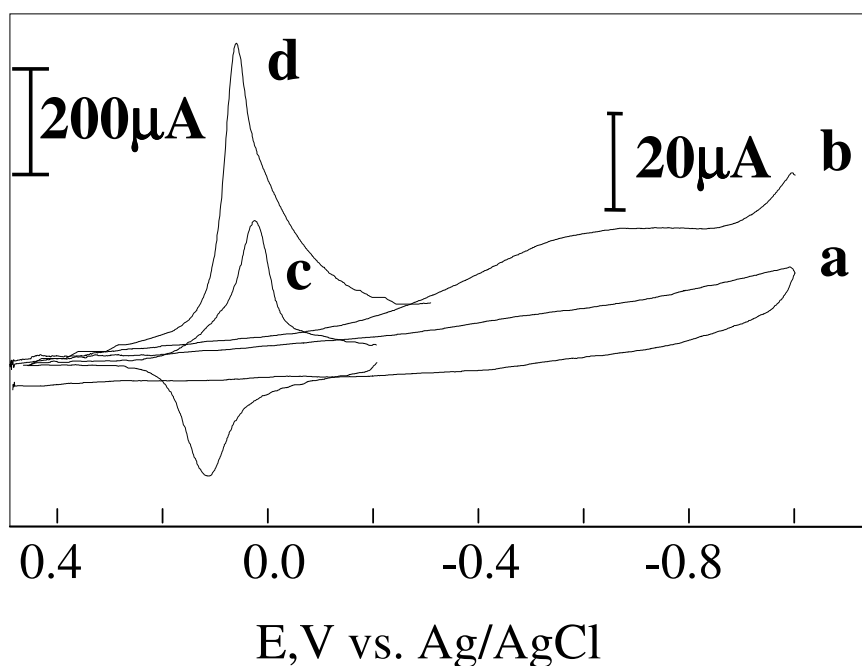


Figure 3. Cyclic voltammograms of the PB film-modified electrode. Curves correspond to measurements in $0.1 \text{ mol L}^{-1} \text{ KCl}$ (a), $1.0 \cdot 10^{-3} \text{ mol L}^{-1}$ persulfate in $0.1 \text{ mol L}^{-1} \text{ KCl}$ at glassy carbon electrode (b), Prussian Blue film at supporting-electrolyte (c) and $5.0 \cdot 10^{-4} \text{ mol L}^{-1}$ persulfate plus $0.1 \text{ mol L}^{-1} \text{ KCl}$ at Prussian Blue-modified electrode (d). The scan rate was 100 mV s^{-1} .

Flow-injection amperometric detection of persulfate

Electrocatalytic reduction current for persulfate at modified electrode was applied in FIA system. To determine the optimum potential for amperometric measurements with the Prussian Blue film, hydrodynamic voltammograms were obtained. Figure 4 shows a plot of current vs. applied potential for the reduction of $2.0 \cdot 10^{-4} \text{ mol L}^{-1}$ persulfate solution at the modified electrode, where a maximum amperometric response was obtained for a potential value of 0.025 V vs. Ag/AgCl . The current decrease at potentials higher than 0.025 V can be attributed to the irreversible passivation of the electrocatalyst at potentials high enough to reduce persulfate anions. Consequently, in subsequent experiments with this electrochemical detector, a value of 0.025 V was selected for the detection potential of persulfate at Prussian Blue film.

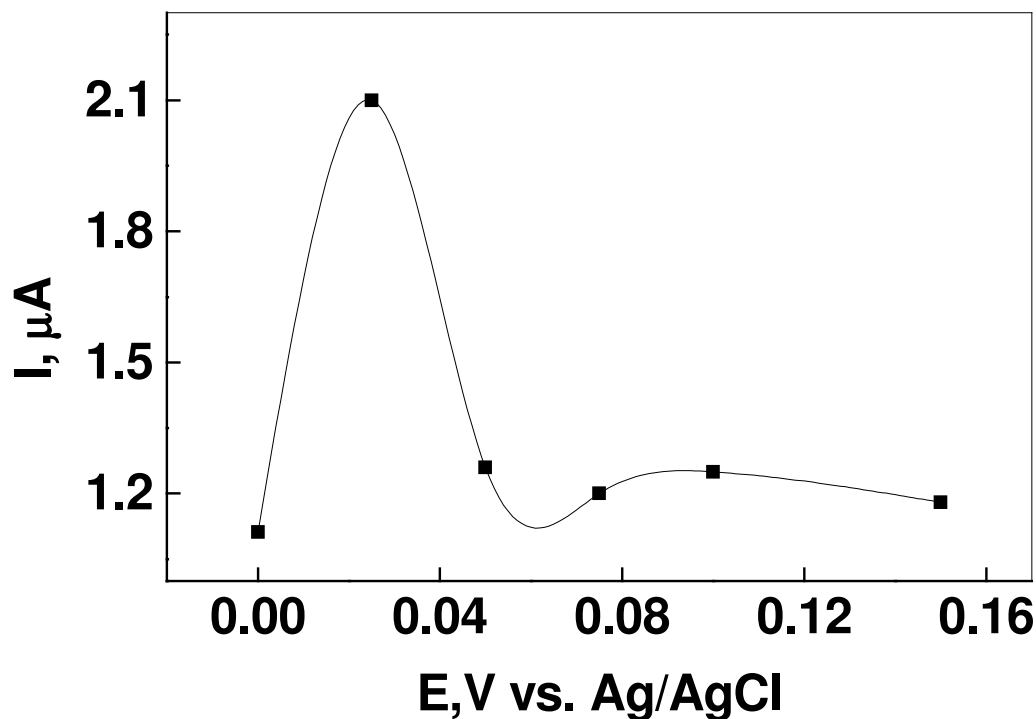


Figure 4. Hydrodynamic voltammogram for the reduction of persulfate. Curve correspond to $2.0 \cdot 10^{-4}$ mol L⁻¹ persulfate solution at Prussian Blue modified electrode; carrier C: 0.1 mol L⁻¹ KCl (4.0 mL min⁻¹); sampling loop L: 200 μL.

The influence of flow rate of carrier C on peak profile and sampling rate was investigated within the 0.5 - 5.0 mL min⁻¹ interval. For flow rates < 1.6 mL min⁻¹, peaks for $2.0 \cdot 10^{-4}$ mol L⁻¹ persulfate were broadened, the sampling rate was low and the sensitivity unsatisfactory. When the flow rates increased from 1.6 to 4 mL min⁻¹, the signal profile improved and peak heights increased linearly. Flow rates > 4.0 mL min⁻¹ resulted in solution leakage at the inlet of the electrochemical cell. As a compromise between system stability, sensitivity and sampling rate, 4.0 mL min⁻¹ was selected.

In the study of the injected volume on transient signals in the 40 - 400 μL volume range, peak heights increased linearly with the volume of the sample injected into the FIA system from 40 to 200 μL. For higher injected volume samples the transient signal reached a constant value. The best sensitivity was attained with 200 μL $\{I = 4.1 \cdot 10^{-9} + 2.5 \cdot 10^{-5}[\text{persulfate}]\}$, the volume selected for subsequent experiments.

After all parameters had been chosen, analytical solutions within the $0.1 - 1.0 \cdot 10^{-3}$ mol L⁻¹ persulfate concentration range were injected in triplicate and calibration curves with good linearity were consistently obtained ($R = 0.9998$), with an amperometric sensibility of $3.6 \cdot 10^3 \mu\text{A} \cdot \text{L} \cdot \text{mol}^{-1}$. The detection limit of this method was $9.0 \cdot 10^{-5}$ mol L⁻¹. The transient peaks of a typical calibration curve are depicted in Fig. 5. Accuracy was assessed by analyzing two commercial samples of hair bleaching boosters (Table 1). The results obtained with the proposed procedure were not statistically

Table 1. Comparative results. Results ($n = 3$) for persulfate [as mg/g] in cosmetic samples as determined by the proposed FIA system and by titrimetry [25]. For experimental conditions, see Fig. 5

Sample*	FIA	Titrimetry
280	274 ± 9	267 ± 12
280	275 ± 8	269 ± 13

* labeled by manufacturer and expressed as mg/g

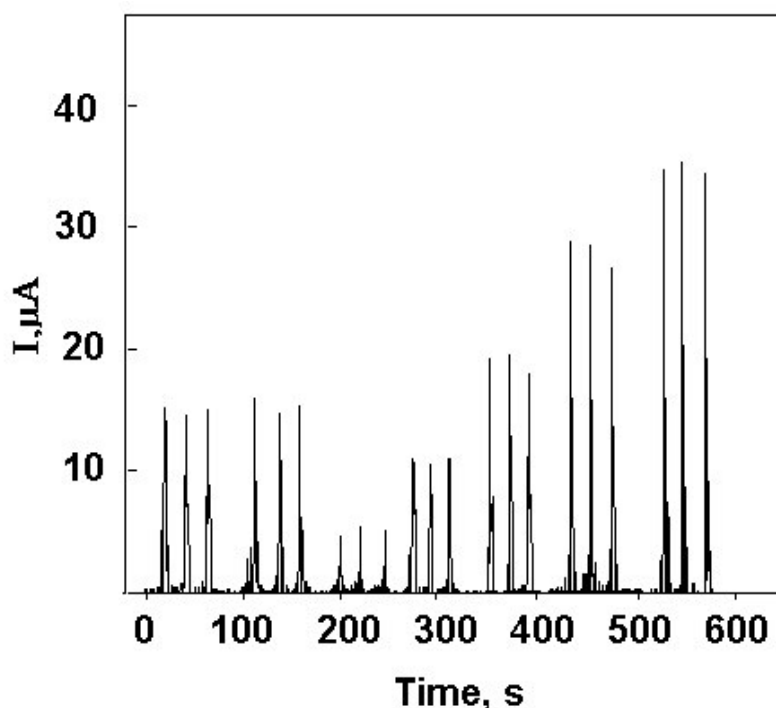


Figure 5: Recorded peaks for persulfate determination. From left to right, each set of triplicate corresponds sample #1, sample #2, and five working standard solutions (0.1 mmol L^{-1} , 0.2 mmol L^{-1} , 0.5 mmol L^{-1} , 0.8 mmol L^{-1} and 1.0 mmol L^{-1} , respectively). L: $200 \mu\text{L}$; C: 0.1 mol L^{-1} KCl at 4.0 mL min^{-1} ; applied potential: 0.025 V (vs. Ag/AgCl).

different from those obtained by titrimetry and from those labeled values by the manufacturer at 95% confidence level (t-test). The system handles up to 160 samples to be examined per hour, requires about 11 mg KCl and $200 \mu\text{L}$ sample consumed per determination. The relative standard deviation was estimated as $\leq 3.4\%$ for 0.5 mmol L^{-1} persulfate solution after twelve successive injections.

Conclusions

Modified electrodes by Prussian Blue films function as amperometric sensors for persulfate ions as much as they present electrocatalytical activity, with an increase on the anodic current of the film, which occurs in a potential value lower than the overpotential of reduction of this ion without the film, in the same experimental conditions. The modified electrode can be applied in FIA systems as an

amperometric sensor for persulfate ions in a concentration range from $1.0 \cdot 10^{-4}$ to $1.0 \cdot 10^{-3}$ mol.L⁻¹, exhibiting a linear peak current variation, with a linear correlation coefficient of 0.9998 and a detection limit of $9.0 \cdot 10^{-5}$ mol.L⁻¹. Due to its electrocatalytic property, high analytical frequency and good accuracy, this methodology allows the employment of Prussian Blue-glassy carbon modified electrodes in flow injection systems for analysis of persulfate concentration in hair bleaching commercial products in large scale.

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Sample Availability: Available from the authors.