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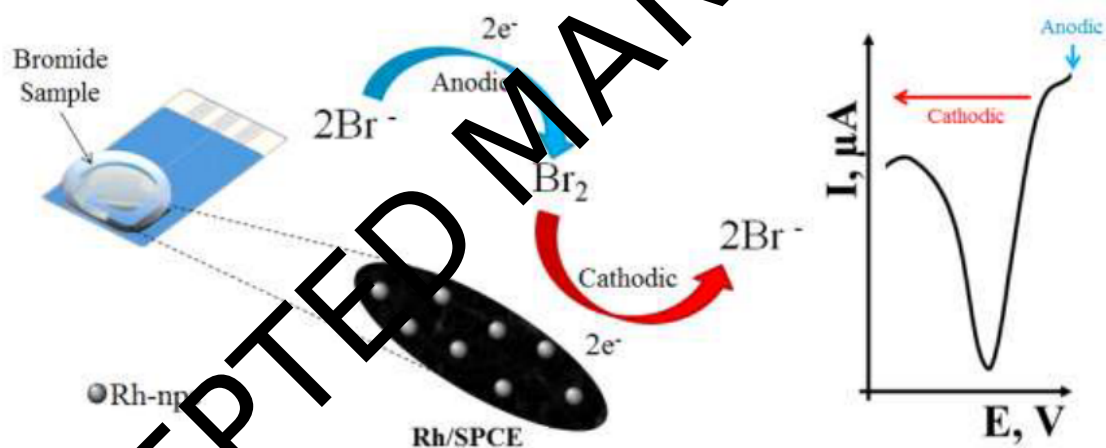
***A Disposable Rhodium Nanoparticle-Modified Screen-Printed Sensor for
Direct Determination of Bromide Anions***

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Graphical abstract



Highlights:

- New rhodium Nps-based sensitive sensor for bromide determination.
- Rhodium nanoparticles and chloride improve the detection limit of the method.
- Bromide cathodic voltammetric peaks generated after an anodic stripping step.
- Rh/SPCE sensor shows ~ 100% bromide recovery in real samples analysis.

Abstract

The demand for bromide determination has increased over recent years. Sources of bromide contamination can be found in brines from hydraulic fracturing, pesticides and brominated polymers. Widely used in different applications, the bromide anion is present in the composition of several compounds. In this paper, we present a new selective voltammetric method for bromide determination, based on a screen-printed carbon electrode (SPCE) modified with rhodium nanoparticles (Rh-Nps), that is used as a sensing platform. The modification of the electrode surface with Rh-Nps and the presence of chloride in the sample, improved device performance, increasing the sensitivity of the Rh/SPCE-based sensor for bromide determination. The proposed sensor is simple to manufacture, easy to operate, and it offers a fast and accurate analysis. A single drop of the sample on the sensor is sufficient for the determination of bromide through measurement of voltammetric cathodic peaks, generated after a previous anodic stripping step. This disposable sensor offers a detection limit of 39 μM , with a calibration range up to 40 mM, and a sensitivity of 23.28 $\mu\text{A}/\text{mM}$. Its application to real-life samples evidenced recovery values close to 100%, demonstrating the powerful analytical performance of the proposed method.

Keywords: Bromide; Rhodium nanoparticles; Cathodic stripping voltammetry; Screen-printed electrode

1. Introduction

Bromide has been extensively applied in several fields and is present in pesticides, medicines, industrial solvents, gasoline additives, and water purification compounds [1]. This halide anion was first used in medicine as potassium bromide in the 19th century, when applied in the treatment of epilepsy, and as both a sedative and an anxiolytic [2]. It remains in use in clinical veterinary, due to its antiepileptic properties [3,4]. Several other pharmaceuticals contain bromide concentrations, which make this anion an important parameter to control in formulations [5].

Bromide properties have also been applied to polymeric materials, particularly for fireproofing. Brominated flame retardants consist of polymer additives, employed in the production of electronic devices, clothing, furniture, and electrical appliances. Issues relating to brominated polymers emerged from the weakly bond characteristic of this additive, making it highly susceptible to be released into the environment. Actually, current regulations restrict the use of organobrominated compounds, categorizing them as persistent pollutants, due to their potential bioaccumulation in ecosystems and their toxic effects on wildlife [6].

Widely applied in hydrogeology, bromide can occur naturally or can be artificially introduced as a tracer to track subsurface water flows. Wastes and unused residues from the use of this halide have resulted in widespread ground water contamination [1]. Additional sources of bromide contamination are the brines generated from oil and natural gas production. Flowback and produced waters from hydraulic fracturing of shale gas are recognized to contain high concentrations of bromides (~12 mM). A major concern with these brines is the formation of brominated disinfection byproducts, especially problematic for the treatment of potable water [7,8].

Bromide as an analyte was not of great interest until the last decade and there are very few papers on its determination. Approaches based on volumetric techniques [9], spectrophotometry [10,11], colorimetry [12], ion-exchange chromatography [13,14], molecular absorption spectrometry [6], and neutron activated analysis [11], have been used to determine bromide content in several types

of samples. Despite the fragility of the electrodes and the need for sample preparation, bromide-ion selective electrodes have proven their simplicity and selectivity in the potentiometric determination of bromide [15–17].

The need to control brominated species led to the development of alternative electrochemical approaches. Bennett [18] performed an electrochemical study of the voltammetric behavior of the redox pair Br^-/Br_2 in non-aqueous solvents. Other approaches, such as wastewater treatment, were designed to allow the selective oxidation of bromide in brines from hydraulic fracturing [7]. Also, the use of silver electrodes has permitted the study of halide reactions onto the electrode surface [19].

More recently, the great advantages of screen-printed electrodes (SPE) have been recognized, mainly due to the great adaptability of these transducers, their portability for analysis, as well as their low cost, disposability and reproducibility. The easy handling and the wide range of possibilities for SPE modifications, contribute as significant improvements to this sensing platforms [20]. Silver SPE [21] and the modification of SPEs with silver nanoparticles [22] have proved to be suitable for bromide quantification in real samples.

Electrodeposition of metallic nanostructures has been successfully accomplished in numerous SPE systems, offering unique advantages in terms of sensitivity, selectivity, working stability and electroactive surface area increase [22–27]. Rhodium nanoparticles (Rh-Nps) are the least represented among the nanoparticle-based electrochemical sensors. Nevertheless, the utility of this nanosized Rh has improved the performances of various electrochemical devices [28–31].

Only few works regarding the electrochemical determination of bromide were found, revealing a research gap in the determination of this anion. The increased interest in determining bromide led us to develop a new, sensitive, selective, rapid, disposable, low cost, and easy-to-use method for analysis of this halide.

Thus, the direct reduction of bromine to bromide, oxidized in a previous anodic step, is investigated in this manuscript. The working carbon SPE modification with Rh-Nps, together with the presence

of a chloride supporting electrolyte, allowed to achieve an efficient method for the determination of a wide concentration range of the interest halide. Hence, the successful application of the sensor to seawater, used to simulate the brines from hydraulic fracturing, showed suitable recovery values (~100%). Additionally, the satisfactory application of the method to a hexadecyltrimethylammonium bromide (CTAB) surfactant synthetic solution, provide a method for this tensioactive determination. Also, the bromide content of pharmaceutical formulations such as dextromethorphan hydrobromide and ipratropium bromide, was correctly determined matching the sensor results with the labeled concentrations.

2. Materials and methods

Rhodium (III) chloride hydrate, potassium bromide, sodium chloride, potassium sulfate, sodium phosphate dibasic dihydrate, sodium phosphate monobasic dihydrate, potassium nitrate, sodium carbonate, methanol, and sulfuric acid, were obtained from Merck (Darmstadt, Germany). Sodium nitrite, potassium iodide and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich (Steinheim, Germany).

All reagents were of analytical grade and all solutions were prepared with Milli-Q water (Millipore, Bedford, USA).

Seawater samples were collected from Pontevedra coast, in the northwest of Spain. The samples were subsequently stored in high density polyethylene bottles in a freezer until the analysis.

Dextromethorphan hydrobromide and ipratropium bromide commercial formulations were obtained from a local pharmacy.

The inks used for the fabrication of the screen-printed carbon electrodes (SPCE), Electrodag PF-407 A (carbon ink), Electrodag 6037 SS (silver/silver chloride ink), Electrodag 418 (silver ink) and

Electrodag 452 SS (dielectric ink), were supplied by Achenson Colloiden (Scheemda, Netherlands). Polyester films (PET) of 0.5 mm thickness (HIFI Industrial Film, Dardilly, France), were used as the printing substrates. The SPEs were fabricated as recently described elsewhere [26].

Voltammetric measurements were performed using a PalmSens® portable electrochemical potentiostat with the PS Trace 4.2 program (PalmSens® Instruments BV, Houten, The Netherlands). Microscopy imaging was performed using a scanning electron microscope (SEM) JEOL JSM-6460LV (Abingdon-on-Thames, UK).

Electrodeposition of rhodium nanoparticles (Rh-NPs) was performed using chronoamperometric technique, by drop-casting 150 μL of a solution of rhodium (III) chloride (0.1 mM) in sulfuric acid (0.5 M) onto the SPCE, and applying a potential of -0.25 V for 480 s. The electrode was then rinsed with water to prepare it for use in the experiment.

Cyclic voltammetry (CV) experiments for the electrochemical screening of bromide were performed by drop-casting 150 μL of phosphate buffer saline (PBS) (0.05 M, pH 7 and 0.05 M of NaCl), containing 0.5, 1, 2.5, 5, 10, 20, 40 and 60 mM of KBr. Voltammograms were recorded between 0.00 and 1.80 V (vs Ag/AgCl) at 0.10 V s⁻¹.

For bromide determination, 150 μL of problem solution was drop-cast onto the sensor working area, and an anodic step of 1.25 V was applied over 20 seconds. Immediately after, a cathodic linear sweep voltammetry scan, from 1.11 to -0.25 V at a scan rate of 0.10 V s⁻¹ was performed, returning

a reduction peak at 0.50 V. The sensor was rinsed with milli-Q water prior to subsequent measurements.

The pharmaceutical formulation of dextromethorphan hydrobromide, due to the high viscosity of the matrix, required an additional step before the electrochemical measurement. A mixture of dextromethorphan hydrobromide and methanol (1:1) was stirred for 30 minutes at room temperature. The methanolic mixture was then diluted in supporting electrolyte (1:1) and measured following the indications in the previous section.

3. Results and discussion

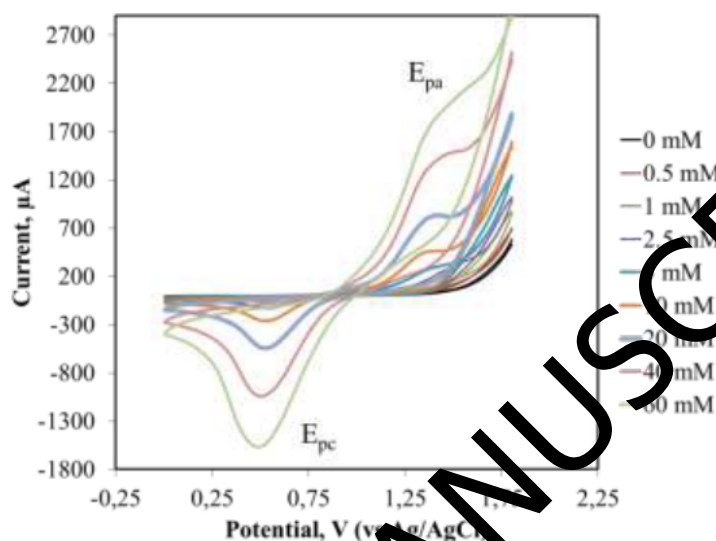
The cyclic voltammograms of different potassium bromide concentrations are shown in fig. 1. The voltammograms revealed a quasi-reversible redox process, developing the corresponding oxidation and reduction peaks, at 1.35 V and 0.50 V (vs Ag/AgCl), respectively. The observed behavior is described in equations 1 and 2.

(1)

(2)

Considering both processes, the oxidation of bromide requires very positive potentials for the reaction to take place, growing a peak in the buffer discharge zone. Thus, this oxidation process is more susceptible to peak deformation, as it is developed from a non-stable base line, which difficult the correct quantification of the electrochemical signals. In contrast, the reduction peak was

developed at lower potentials (0.50 V), demonstrating a stable behavior and a good correlation with bromide concentrations. Accordingly, the cathodic process was selected for bromide determination.

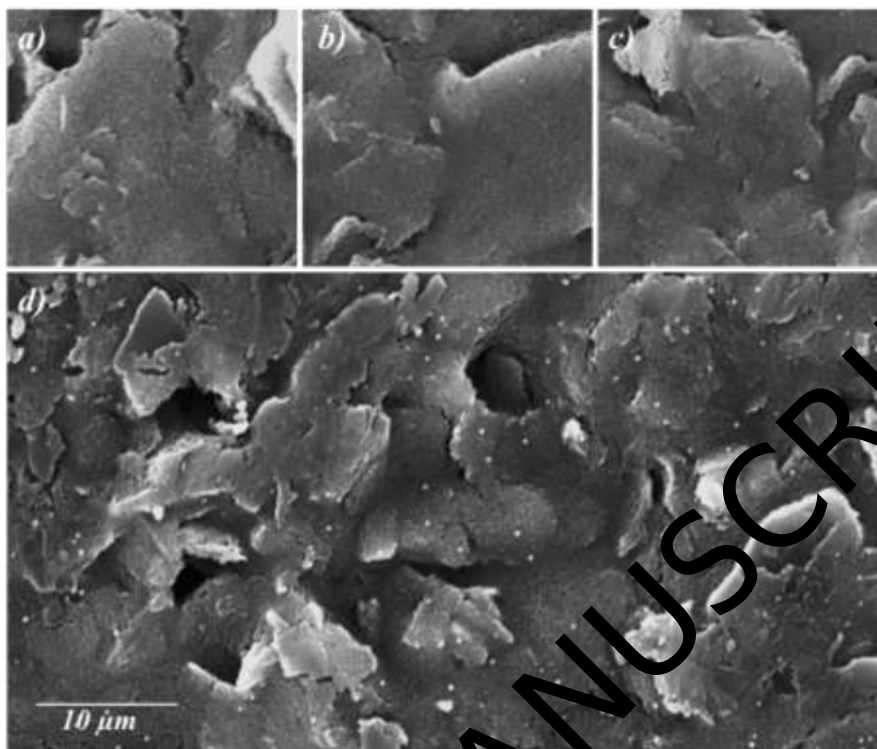


Once checked the electrochemical behavior of bromide, cathodic stripping voltammetry (CSV) was selected as the technique for the study of the anion, since a quick analysis can be performed achieving well defined and stable peaks. In fact, the anodic step of CSV increased the bromide oxidation process (equation 1), thereby favoring bromine reduction (equation 2) in the cathodic step. However, the high potential required in the anodic step can be problematic in a real sample analysis, because several species can be oxidized that might interfere later with the bromide cathodic peaks. The potential and time of anodic stripping were therefore optimized, setting the CSV measurement at 1.25 V during 20 s (fig. S1 in Supplementary data).

The reduction of high bromide concentrations on the carbon working electrode originated well-defined peaks. However, the sensitivity required for several samples, where bromide can be found in the μM concentration range, was not achieved. Regarding that, it was found that smaller concentrations of bromide could be detected, by modifying the carbon surface with rhodium nanoparticles (Rh-Nps).

The Rh-Nps were generated by chronoamperometric measurements of a Rh solution drop cast onto the SPCE. For that, deposition potentials of -0.80, -0.50, -0.25, -0.1, 0.18 and 0.25 V were applied during 480 s, and the cathodic peak of bromide concentrations (lower than 1 mM), were compared with the one obtained in an unmodified SPCE (fig. S2 in Supplementary data).

Deposition of Rh-NPS at -0.25 V yielded a linear slope for the tested bromide concentrations and was selected as the deposition potential for Rh-Nps. The time required for Rh-Nps deposition was also optimized and the SPCE surface was characterized by SEM analysis. The chronoamperometry at -0.25 V, was performed during 0, 30, 120 and 480 s, and the effect on bromide detection was evaluated. In Fig. 2, the SEM image shows rhodium nanostructures on the carbon surface, following an electrodeposition time of 480 s. These data agree with the electrochemical determination of low bromide concentrations, which was only possible when 480 s for Rh electrodeposition are performed, showing the extent to which this nano-deposit favored the bromide redox process.



Chloride is a ubiquitous anion, frequently found in samples that also contain bromide. Hence, it was considered of interest to evaluate the effect of chloride in the Rh/SPCE-based sensor performance, as bromide detection can be altered in its presence. The chloride effect in the bromide CSV peaks was checked when using SPCE and Rh/SPCE. Moreover, the anodic stripping effect was verified under those same conditions.

Electrode modification with Rh-Nps proves to be essential in the determination of lower concentrations of bromide. Further, this effect is greatly improved in the presence of chloride, demonstrating that this ubiquitous halide take part in the detection of low concentrations of bromide. When the supporting electrolyte was formulated with different amounts of NaCl, an

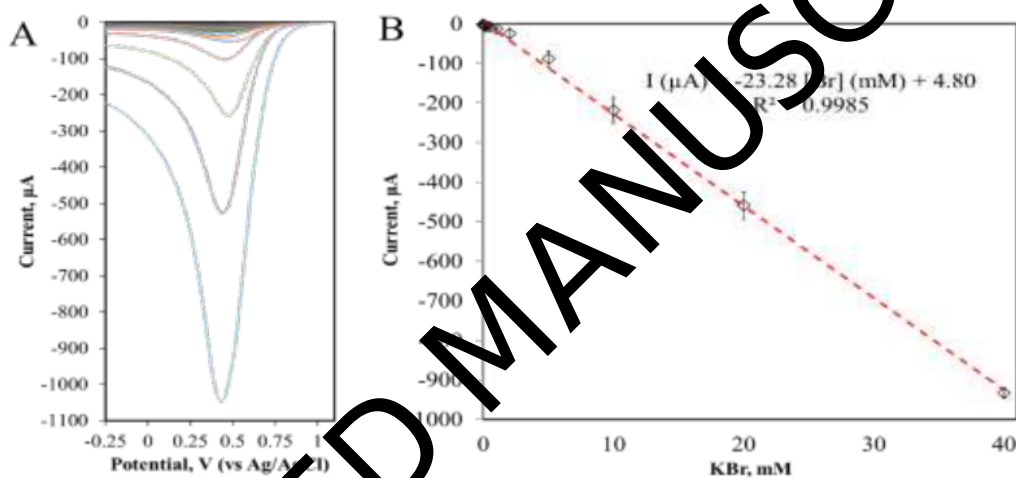
increase in the signal for bromide concentrations (< 1 mM) was observed. Additionally, this increase was more noticeable when the SPCE was modified with Rh-Nps, showing the synergetic effect of both elements (fig. S3 in Supplementary data).

The electrodeposited nanostructures of rhodium and the presence of chloride are both evidencing smaller concentrations of bromide, increasing the sensitivity of the device and improving the method limit of detection. In fact, this could be explained by the oxidative effect of the chlorine, also generated in the primary anodic stage. So, a 0.05 M PBS solution, supplemented with 0.05 M NaCl, was used as the supporting electrolyte, to avoid changes in the bromide peaks obtained in the real sample analysis, which can contain chloride concentrations.

The accuracy of the proposed method was established in terms of reproducibility. Using the optimum voltammetric conditions, and PBS 0.05 M with 0.05 M of NaCl as supporting electrolyte, several calibration curves for a bromide concentration range from 0 to 40 mM were performed. In table 1, the parameters of the calibration curves obtained for five replicas of different Rh/SPCE bromide sensors are shown. The sensor reproducibility value, determined in terms of the residual standard deviation (RSD %) associated with these calibration curves slopes, was 2.58 % (fig. 3). A limit of detection (LOD) of 39 μ M was obtained for the Rh/SPCE-based sensor, using the $LOD = 3 \frac{s}{m}$ equation, where, s is the estimated standard deviation of the blank, and m is the average slope of the five calibration curves [32,33].

Despite the disposable characteristics of the SPEs, repeatability studies were also performed using the same Rh/SPCE-based sensor. Over simultaneous measurements, the sensor displays a lack of stability of bromide determination, observable in the variation of the calibration slopes and in their linearity (fig. S4 in Supplementary data). Moreover, these repeated measurements led to peak deformation, increasing the blank signal, which affected the performance of the device when determining lower concentrations of bromide.

Rh/SPCE sensor	Slope ($\mu\text{A}/\text{mM}$)	R^2	Slopes average ($\mu\text{A}/\text{mM}$)	Deviation	RSD (%)	LOD (μM)
I	-23.09	0.996				
II	-23.57	0.999				
III	-24.08	0.998	-23.18	0.60	2.58	39
IV	-22.33	0.992				
V	-22.87	0.993				



The device selectivity in detecting bromide anions against the halides, F^- and I^- , and other anions, such as NO_3^- , CO_3^{2-} and SO_4^{2-} , was evaluated for 1 mM of bromide (table S1 in Supplementary data). Chloride, used in excess in the supporting electrolyte, was not considered in the interference study, as the presence of this anion improved bromide detection.

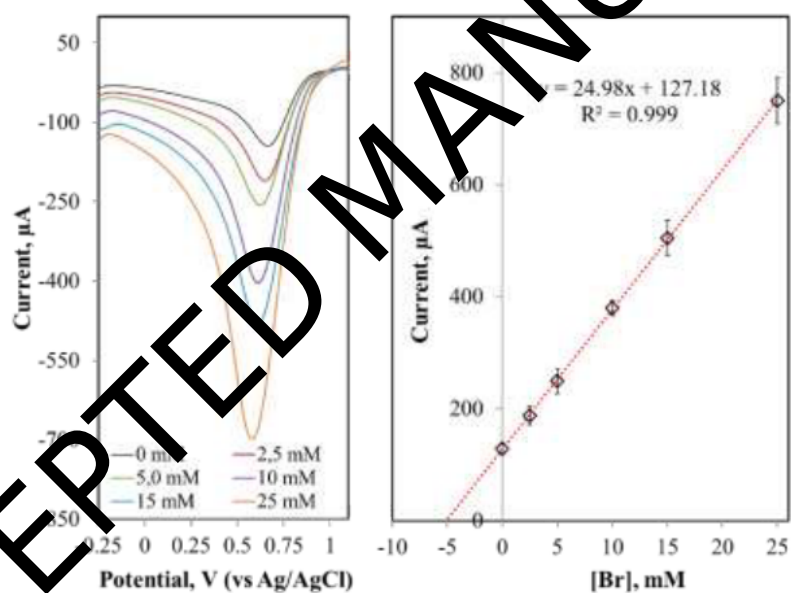
The current variation showed a very low interference effect for F^- , NO_3^- , CO_3^{2-} and SO_4^{2-} , with small variations in the bromide cathodic peak current, even for a 10-fold excess of the interfering anions. In contrast, the I^- effect was more noticeable, affecting the cathodic current of 1 mM of bromide. A variation in peak current was noted when the halides, I^- and Br^- , were both in the same concentration, since I^- cathodic peaks starts to rise, hindering the bromide process. The tested I^- concentrations of 0.20, 0.50 and 1 mM affected the sensor response for bromide at low concentrations. Even so, the sensor proved its capability to overpass this interference at higher bromide concentrations. Yet, the amount of I^- in the samples is often low and interference is negligible. Brines from hydraulic fracturing and oil and gas waste waters were found to contain iodide at concentrations of 2.2×10^{-4} M [34], and at even smaller concentrations in seawater (4.7×10^{-7} M) [35]. Hence, the selectivity of the Rh/SPCE-based sensor is still suitable in real sample analysis, as discussed later.

The effectiveness of the Rh/SPCE-based sensor for bromide determination was verified with several real-life samples. The analysis of bromide in seawater is first presented in this study. This matrix is of interest, as the brines from hydraulic fracturing contain higher amounts of dissolved salts than seawater [8]. No bromide content was detected in the raw sea-water sample. Thus, this sample was spiked with 2.5 and 5 mM of KBr, and evaluated by the standard addition method. The sensor demonstrated suitable correlations with the added amounts, determining 2.50 ± 0.08 mM and 5.07 ± 0.10 mM of bromide, recovering respectively 99.33 % and 100.45 % from the matrix (fig. 4).

Cetyltrimethylammonium bromide (CTAB), a quaternary ammonium surfactant and a component of a broad-spectrum antiseptic [5], was also analyzed to determine the amount of this halide present in a 6 mM synthetic solution, prepared on the supporting electrolyte. The Rh/SPCE-based sensor proved its capability to determine the expected bromide concentration (5.82 ± 0.18 mM), which can be related to the amount of tensioactive present in the solution.

The Rh/SPCE sensor was also applied to two commercial pharmaceutical formulations, dextromethorphan hydrobromide and ipratropium bromide, detecting 3.80 ± 0.08 mM and 0.66 ± 0.02 mM, respectively. The concentration determined in these samples closely correlated the bromide value, measured by the standard addition method, with the labeled values of 4.00 mM and 0.60 mM for dextromethorphan hydrobromide and for ipratropium bromide, respectively.

The results, summarized in table 2, demonstrate that the proposed sensor is applicable to real sample analysis, achieving high accuracy, as indicated by the RSD values.



			2.39		95.56	
2.50	2.50		2.50	2.50 ± 0.08	100.04	2.84
			2.56		102.40	
			5.07		101.48	
5.00	5.00		4.88	5.07 ± 0.12	97.50	2.09
			5.12		102.38	
			5.82			
-	6.00		6.13	5.82 ± 0.16	-	2.80
			5.75			
			3.90			
-	4.00 ^b		3.73	3.80 ± 0.08	-	1.80
			3.80			
			0.66			
-	0.60 ^b		0.63	0.66 ± 0.02	-	2.11
			0.66			

4. Conclusions

A simple method, capable of determining bromide in several real-life samples, by single drop analysis, has been developed. The proposed voltammetric Rh/SPCE-based sensor has proven its highly selective, precise and fast capability to determine bromide in different matrices, offering a very short analysis time (33 s for each measurement). Moreover, this disposable device, presents a low limit of detection of 39 μM , and highly accurate bromide determination (RSD % = 2.58). The linear range up to 40 mM is ideal for the detection of bromide concentrations that can be found in several types of samples, making this sensor a versatile analytical tool. The real-life samples were

analyzed with no pretreatment, except for the dextromethorphan hydrobromide formulation, resulting in an easy-to-use method for the evaluation of bromide in a broad range of samples.

5. Acknowledgements

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Biographies

Hugo Cunha-Silva is a PhD. Student at the Analytical Chemistry Department of the Burgos University since 2015. He obtained his degree in Biotechnology in 2012 and his Master's Degree in Biotechnology in 2014, from the University of Beira Interior (Portugal). He is funded by the Spanish Ministry of Economy and his research focuses on the application of screen electrodes for electroanalytical determinations.

M. Julia Arcos-Marnez received her PhD degree in 1987 in the University of Valladolid (Spain) in the study of electrochemical determinations of pharmaceutical compounds. She worked in the University of Valladolid until 1994 that joined the Burgos University where she worked in the Chemistry Department. Nowadays, her research focuses on the design and fabrication of screen-printed electrodes for electroanalytical determinations. She has published many referred papers in international journals on studies of electrochemical area.

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