

Article

Electrochemical Determination of Lead Using A Composite Sensor Obtained from Low-Cost Green Materials: Graphite/Cork

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Abstract: The purpose of this study was to develop an inexpensive, simple, and highly selective cork-modified carbon paste electrode for the determination of Pb(II) by differential pulse anodic stripping voltammetry (DPASV) and square-wave anodic stripping voltammetry (SWASV). Among the cork-graphite electrodes investigated, the one containing 70% w/w carbon showed the highest sensitivity for the determination of Pb(II) in aqueous solutions. Under SWASV conditions, its linear range and relative standard deviation are equal to 1–25 μM and 1.4%, respectively; the limit of detection complies with the value recommended by the World Health Organization. To optimize the operating conditions, the selectivity and accuracy of the analysis were further investigated by SWASV in acidic media. Finally, the electrode was successfully applied for the determination of Pb(II) in natural water samples, proving to be a sensitive electrochemical sensor that meets the stringent environmental control requirements.

Keywords: cork-graphite electrode; electrochemistry; lead; environmental application



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1. Introduction

Lead is a highly toxic heavy metal that causes serious environmental problems due to its non-biodegradability. It is commonly released into the environment because of mining activities, natural processes, and the development of new technological devices [1,2], being frequently used by the automotive, plastics, paints, and ceramics industries for its corrosion resistance [3].

Since the nitrate and chloride salts of lead show excellent solubility in water [4,5], lead is normally present in soil and aquatic ecosystems in ionic form, as Pb(II). According to the World Health Organization (WHO), a Pb(II) concentration as low as 0.24 $\mu\text{mol L}^{-1}$ can cause decreased intelligence in children, behavioral difficulties, and learning problems. For this reason, the concentration of lead in water and soils should always be below the WHO limit and, consequently, must be monitored.

Nowadays, several analytical methods are employed for lead detection, such as spectroscopy [6], optical colorimetry [7], inductively coupled plasma mass spectrometry (ICP-MS) [8], atomic absorption spectrometry (AAS) [9], and fluorescence spectrometry [10]. However, these analytical methods are expensive (they require trained operators, complex equipment, solvents or gases, and so on) and, in some cases, sample preparation procedures are required. In this context, electrochemical techniques have been investigated because of their significant advantages such as simplicity of operation, high sensitivity, low cost, and

easy handling [11–15]. In general, electrochemical sensors are rapid, portable, inexpensive, and highly sensitive and offer a low limit of detection, good reproducibility, good signal-to-noise ratio, and selective detection [12]. Consequently, electrochemical sensors have been applied for the determination of heavy metals in the environment, industrial products, food matrices, electronic waste, and clinical materials [16–18].

Among the electrochemical sensors used, graphite-modified electrodes have been extensively developed due to their higher selectivity, sensitivity, high specific area, unique electrical conductivity, self-assembly behavior, mechanical flexibility, extreme resistance to oxidation, natural origin, and low cost [19–22]. However, these properties can be improved by including other modifiers in their composition.

Recently, cork has emerged as a promising low-cost and efficient green material for various environmental applications (e.g., compound detection [13,23,24], soil and water remediation [25,26]). Cork is a natural organic polymeric material, which has modest electrical, magnetic, and optical properties and exhibits self-cleaning behavior and antibacterial activity. For raw cork (RAC), electrical conductivity (σ) values of approximately 1.2×10^{-10} and $1.67 \times 10^{-13} \text{ S m}^{-1}$ were registered at 25 and 50 °C, respectively [27]. Based on the existing literature, two types of cork are often used: raw cork (RAC) and regranulated cork (RGC). Their differences are mainly due to their composition, which depends on the thermal pretreatment applied to RAC to produce RGC.

In the present communication, cork–graphite composite electrodes to be used as electrochemical sensors for the detection of lead ions are discussed. The effects of the cork composition, the cork–graphite ratio, and the supporting electrolyte for detecting Pb(II) were investigated. The performance in Pb(II) detection of two voltammetric techniques (differential pulse adsorptive stripping voltammetry (DPASV) and square-wave adsorptive stripping voltammetry (SWASV)) was also evaluated. Finally, the applicability of the cork–graphite voltammetric device was successfully demonstrated by detecting Pb(II) in real water matrixes (groundwater, tap water, and “produced water”) as well as verifying the selectivity, repeatability, reproducibility, and stability of the sensors.

2. Materials and Methods

The highest quality commercially available chemicals were used. Graphite powder and $\text{Pb}(\text{NO}_3)_2$ were sourced from Sigma (Brazil); the former was used without further purification. Acetate buffer, NaNO_3 , CdCl_2 , H_2SO_4 , NaCl , FeCl_2 , KCl , CaCl_2 , MgSO_4 , ZnCl_2 , AlCl_3 , and MnSO_4 were sourced from Merck (Brazil). The raw cork (RAC) used in the experimental studies was provided by Corticeira Amorim S.G.P.S., S.A. (Portugal); the granules were washed twice with distilled water in cycles of 2 h at 60 °C to remove impurities and other water-extractable components that could interfere with the electrochemical analysis. Before use, the RAC was dried at 60 °C in an oven for 24 h [23]. Aqueous solutions were prepared using ultrapure water obtained from a Millipore Milli-Q direct-0.3 purification system.

2.1. Preparation of Cork-Modified Electrodes

The RAC granules were reduced in size using a ball mill and sieved to obtain the finest fractions. The fraction below 150 μm (designated as RAC powder) was selected for use in this work. The cork–graphite composite sensor (working electrode) was prepared by mechanical homogenization of RAC and graphite (Gr) in different proportions (10:90, 70:30, and 90:10 %w/w), using 0.3 mL of paraffin oil as a binder and mixing everything in an agate mortar for about 30 minutes, as previously reported [23]. The paste was packed in a polypropylene nozzle (model K31-200Y) used as a support, and the sensor surface was smoothed over a tissue paper. Before use, the sensor was electroactivated by cyclic voltammetry between -1.1 and 0 V (scan rate: 100 mV s^{-1}) in $0.5 \text{ M H}_2\text{SO}_4$. The different sensors are referred to as GrRAC-X, where X is the amount of cork (RAC) expressed as %w/w. The unmodified graphite sensor (Gr) was prepared as described for the GrRAC-X

sensors, but in the absence of RAC powder. Electrode stability was also determined by repetitive determinations of Pb (25 μ M) in 0.5 M H₂SO₄.

2.2. Electrochemical Measurements

The electrochemical tests were performed using an Autolab PGSTAT302N (Metrohm) controlled with NOVA 1.8 software, and a three-electrode cell including an Ag/AgCl (3.0 M KCl) reference electrode, a Pt wire auxiliary electrode, and one of the cork-graphite sensors (GrRAC) as the working electrode (geometrical area of approximately 0.45 mm²). Differential pulse anodic stripping voltammetry (DPASV) measurements were performed with different concentrations of Pb(II) ions in acetate buffer solutions (pH 4.5), 0.5 M NaNO₃, and 0.5 M H₂SO₄. The accumulation of Pb(II) ions on the surface of the composite sensor was achieved by applying a potential of -1.2 V (vs. Ag/AgCl) for different preconcentration times (40, 70, 100, 130, and 160 s), during which the stirring conditions were kept constant for 30, 60, 90, 120, and 150 s; the remaining 10 s were considered as an equilibration time, without stirring. Subsequently, the anodic stripping scan was performed at 50 mV s⁻¹, with a modulation amplitude of +0.05 V, and a modulation time of 0.04 s. Square-wave anodic stripping voltammetry (SWASV) measurements were performed in 0.5 M H₂SO₄. In this case, a preconcentration potential of -1.2 V was applied to the working electrode for 120 s under continuous magnetic stirring, with a scanning frequency of 80 Hz, an amplitude of 50 mV, and a step potential of 5 mV. All electrochemical studies were conducted without deaerating and performed at room temperature (25 ± 2 °C). Each measurement was performed in triplicate, and obtained data were subjected to statistical analysis and reported as mean $\pm$ standard deviation (SD). For the determination of Pb(II) in different water matrices (tap water, groundwater, and produced water), the water samples were spiked with a known quantity of a standard solution of Pb(II) and the determination of Pb(II) was performed using the standard addition method.

3. Results and Discussion

3.1. Effect of the Supporting Electrolyte

In order to evaluate the voltammetric response of the proposed modified sensor, the quantification of Pb(II) was carried out in different supporting electrolytes. Figure 1a–c show the DPASV response for the determination of Pb(II) using a GrRAC-70% sensor (this composition was selected for preliminary analysis based on the results reported in the literature) from solutions of 0.1 M acetate buffer (pH 4.5), 0.5 M NaNO₃, and 0.5 M H₂SO₄, respectively, using a preconcentration time of 30 s. The sulfuric acid solution proved to be the most suitable electrolytic solution because it provided a well-defined voltammetric signal and the response increased linearly without significant deviations (Figure 1). The limit of detection (LOD), for each of the supporting electrolytes used, was estimated by the equation $LOD = 3 \times S_{y/x}/b$, where $S_{y/x}$ is the residual standard deviation and b is the slope of the calibration plot, in accordance with IUPAC recommendations of the mean value for samples analyzed in triplicate. This approach allows the control of both false positive and negative errors ($\alpha = \beta = 0.05$), as recommended by IUPAC [28,29], and has been confirmed and recommended by experts in the field [30,31]. For the 0.1 M acetate buffer solution, no significant current response was obtained, resulting in an LOD of 4.8 μ M; a similar outcome was obtained in 0.01 M acetate buffer solution, where an LOD of approximately 3.2 μ M confirmed the poor performance of the sensor in acetate buffer solutions. Conversely, the analytical approach significantly improved when 0.5 M NaNO₃ and 0.5 M H₂SO₄ solutions were used, which resulted in LOD values of 2.8 (Figure 1b) and 1.6 μ M (Figure 1c). Comparing the values obtained with an unmodified graphite electrode and with the modified cork-graphite electrodes in H₂SO₄, the LOD is 3 times higher on graphite (≈ 4.8 μ M) than that obtained with the GrRAC-70% electrode. The best result obtained using the composite material shows that the cork-graphite mixture is able to influence the intensity of the current signals.

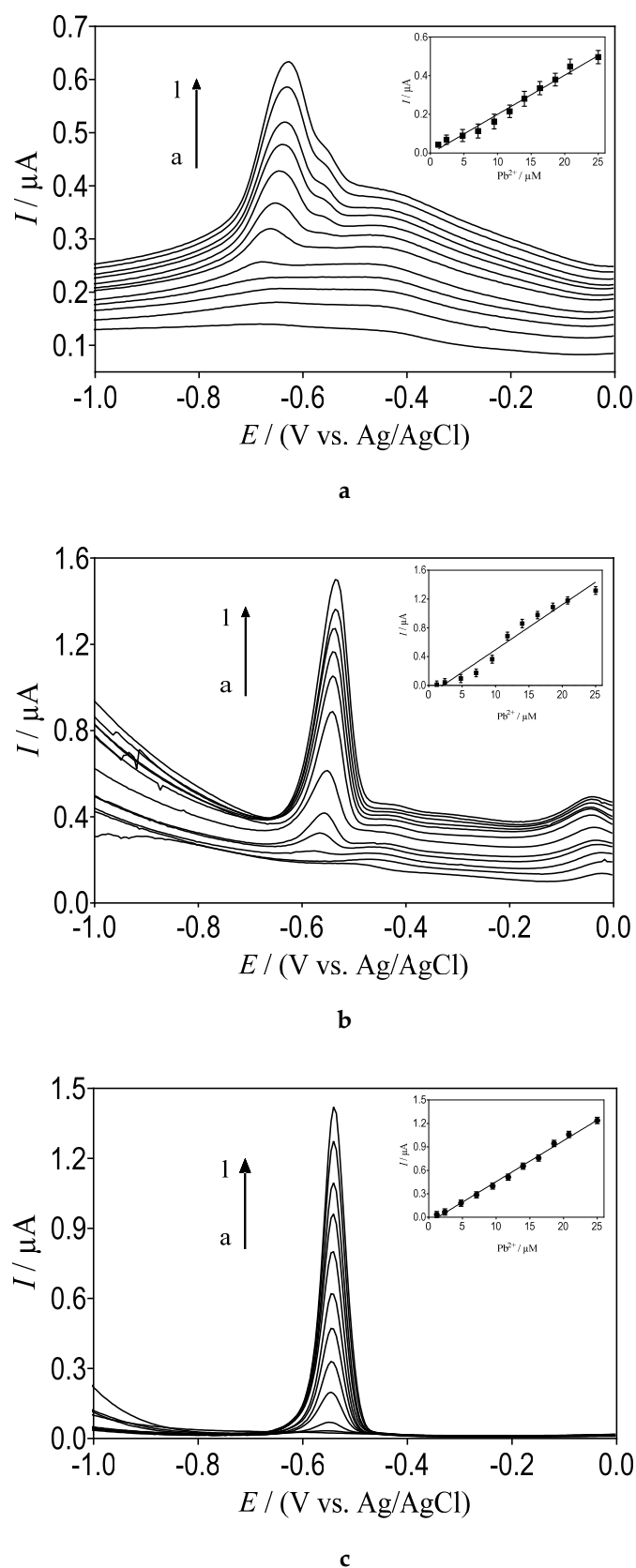


Figure 1. DPASV curves recorded for different concentrations of Pb(II) in (a) 0.1 M acetate buffer (pH 4.5), (b) 0.5 M NaNO_3 , and (c) 0.5 M H_2SO_4 . Lead concentrations: (a) 0, (b) 1.2, (c) 2.4, (d) 4.8, (e) 7.1, (f) 9.5, (g) 11.8, (h) 14.0, (i) 16.3, (j) 18.6, (k) 20.8, (l) 25 μM . Inserts: plots of the electrochemical response, in terms of current, as a function of the lead concentration.

According to the literature [32], cork has a great adsorption capacity, which is assumed to occur through a so-called biosorption mechanism consisting of an initial physical adsorption (rapid metal uptake) and then a slower chemisorption. The biosorption mechanism is the result of several kinds of interactions, such as complexation, coordination, chelation, ion exchange, inorganic microprecipitation, and hydrolysis products of metal ions; in the case of metal ion biosorption, ion exchange is usually the main mechanism. Hence, the type of cork, the pH conditions, and the contact time determine the interactions that can occur between the target compound and the cork surface. Depending on the cork used, specific active sites may predominate in its surface composition (phenolic, carboxylic, sulfonic, phosphate, and amino groups as well as coordination sites), in addition to the cork surface charge depending on pH conditions [33]. It is also important to consider that carbonaceous materials have micropores and mesopores, the accessibility of which will be increased following the inclusion of cork as a surface modifier. Thus, an improvement in voltammetric current signals can be achieved. Another important feature to consider is that the surface morphology of GrRAC-70% is more homogeneous, as evidenced by the SEM micrographs, which can positively influence its current response [34].

In the case of the acetate buffer as the supporting electrolyte, the formation of $\text{Pb}(\text{CH}_3\text{COO})_2$ can decrease the availability of $\text{Pb}(\text{II})$ in solution; in addition, the acetate ions can compete with $\text{Pb}(\text{II})$ ions for the active sites available on the graphite–cork surface. As a result, a poor current response is achieved, with limitations on the selectivity and sensitivity of the modified electrode. Indeed, lead concentrations below $10\text{ }\mu\text{M}$ (Figure 1a), which affect the LOD, cannot be efficiently detected. In the case of NaNO_3 , the lack of complexing activity by nitrate anions and the possibility of preferential interactions between the composite material (cork–graphite) and $\text{Pb}(\text{II})$ ions in solution allow significant improvements in the current response, with consequent benefits in terms of the linearity of the response, although superficial adsorption phenomena may be highlighted for lead concentrations below $10\text{ }\mu\text{M}$ (Figure 1b). Finally, well-defined voltammetric signals were observed at the GrRAC-70% electrode when H_2SO_4 was used (Figure 1c). Due to the acidic conditions, lead is present in solution in its cationic form, Pb^{2+} , and the cork surface is also completely protonated and positively charged. When the working electrode is negatively polarized, the lead ions compete with protons for surface sites; however, the surface accumulation of Pb ions is favored due to ion exchange mechanisms with active sites. In fact, the current response increased linearly without any significant deviations. Therefore, H_2SO_4 was selected as the supporting electrolyte for the subsequent experiments.

3.2. Influence of the Preconcentration Time

The effect of the preconcentration time (40, 70, 100, 130, and 160 s) on the voltammetric response for $\text{Pb}(\text{II})$ detection was studied in 15 mL of $0.5\text{ M H}_2\text{SO}_4$ by using the GrRAC-70% sensor. The results indicate that the peak current increased with the preconcentration time, from 40 to 160 s, as illustrated in Figure 2. For all tests, the initial potential was held constant at -1.2 V under stirring conditions for different times (30, 60, 90, 120, and 150 s), with an additional resting time of 10 s without stirring; subsequently, the stripping voltammetry was carried out at 50 mV s^{-1} . As seen in Figure 2, a decrease in current was achieved when the preconcentration time was extended to 160 s; thus, 130 s was chosen as the most suitable preconcentration time for further analysis. Ten replicates were considered in order to study the effect of preconcentration. According to Student's *t*-test at a confidence level of 95% (parameter denominated as *p*), there were no significant differences between the experimental value ($23.5\text{ }\mu\text{M}$ of Pb) and the theoretical value ($25\text{ }\mu\text{M}$ of Pb). The observed trend can be motivated by the high adsorption rate due to the porous structure of the cork [33]; for preconcentration times greater than 130 s (120 s under stirring conditions and 10 s in rest conditions), the GrRAC-70% sensor plausibly reached the maximum adsorption capacity on its surface.

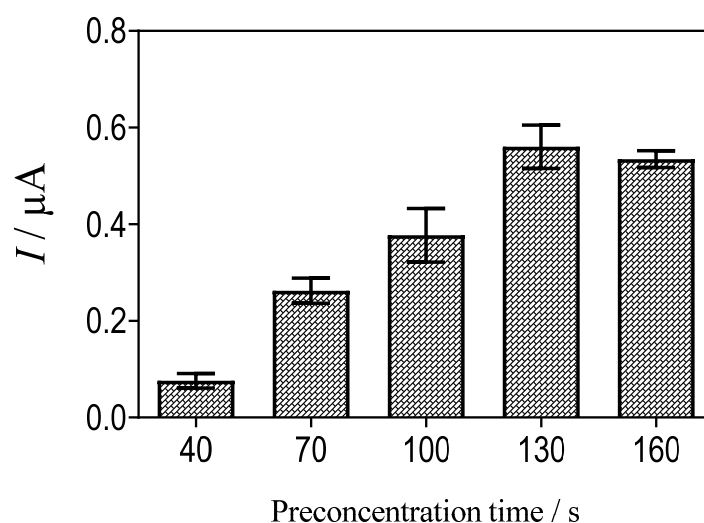


Figure 2. Effect of the preconcentration time on the quantification of Pb(II) ions by DPASV, using the GrRAC-70% composite sensor. Experimental conditions: 25 μM of Pb(II) ($n = 10$; $R^2 = 0.98$; $p = 95\%$). Reduction potential: -1.2 V (vs. Ag/AgCl); scan rate: 50 mV s^{-1} ; potential range: -1.0 to 0 V. Supporting electrolyte: 0.5 M H_2SO_4 .

3.3. Influence of the Cork Concentration

The performance of the composite electrode is affected by the amount of cork that is mixed with the graphite. In a previous work, we showed that the quantity of cork influences the electroactive area of the sensor as well as the electron transfer during the oxidation of caffeine [13]. In order to evaluate the effect of the quantity of cork on the detection of Pb(II) by DPASV, 0.5 M H_2SO_4 was used as the supporting electrolyte. As can be observed in Figure 3a–c, the peak current recorded on GrRAC depends on the amount of cork present in the composite sensor. In particular, a linear relationship between the peak current and the Pb(II) concentration was obtained in the Pb(II) concentration range from 1 to 25 μM in 0.5 M H_2SO_4 (inserts in Figure 3a–c), considering at least 11 different concentrations of the analyte. Pb(II) calibration curves were obtained for each of the prepared sensors. From the analytical curves obtained using GrRAC-10%, GrRAC-70%, and GrRAC-90% by DPASV, it can be seen that the stripping peak currents (I_p) increased linearly with the concentration of Pb(II) (inserts in Figure 3). The calculated correlation equations are

$$\text{GrRAC-10\%: } I_p (\mu\text{A}) = (0.05 \pm 0.03) \times C - (0.1 \pm 0.05); R^2 = 0.97$$

$$\text{GrRAC-70\%: } I_p (\mu\text{A}) = (0.08 \pm 0.04) \times C - (0.3 \pm 0.1); R^2 = 0.98$$

$$\text{GrRAC-90\%: } I_p (\mu\text{A}) = (0.11 \pm 0.09) \times C - (0.2 \pm 0.1); R^2 = 0.95$$

According to Figure 3, the best performing GrRAC sensor in terms of sensitivity, capable of providing an LOD for Pb(II) of only about 0.8 μM , was GrRAC-70%. In contrast, the GrRAC-10% and GrRAC-90% sensors provided higher LODs of approximately 1.5 and 1.2 μM , respectively. This difference in the LODs is attributable to the different degrees of dispersion of the surface active sites, as reported in our previous study on the determination of caffeine [23]. The highest peaks were obtained with GrRAC-70% and this cork–graphite ratio was used for detecting Pb(II). The results show that Pb(II) stripping signals with GrRAC-70% are superior to those obtained with the GrRAC-10% and GrRAC-90% electrodes. This can be attributed to the honeycomb macroporous structure of the cork granules, which favor the presence of propagation paths through the cork cells, forming macroporosity with textural properties. Based on our previous results, the surface morphology of GrRAC-70% appears particularly homogeneous because the graphite sheets are arranged in close contact within the porosities of the cork [23].

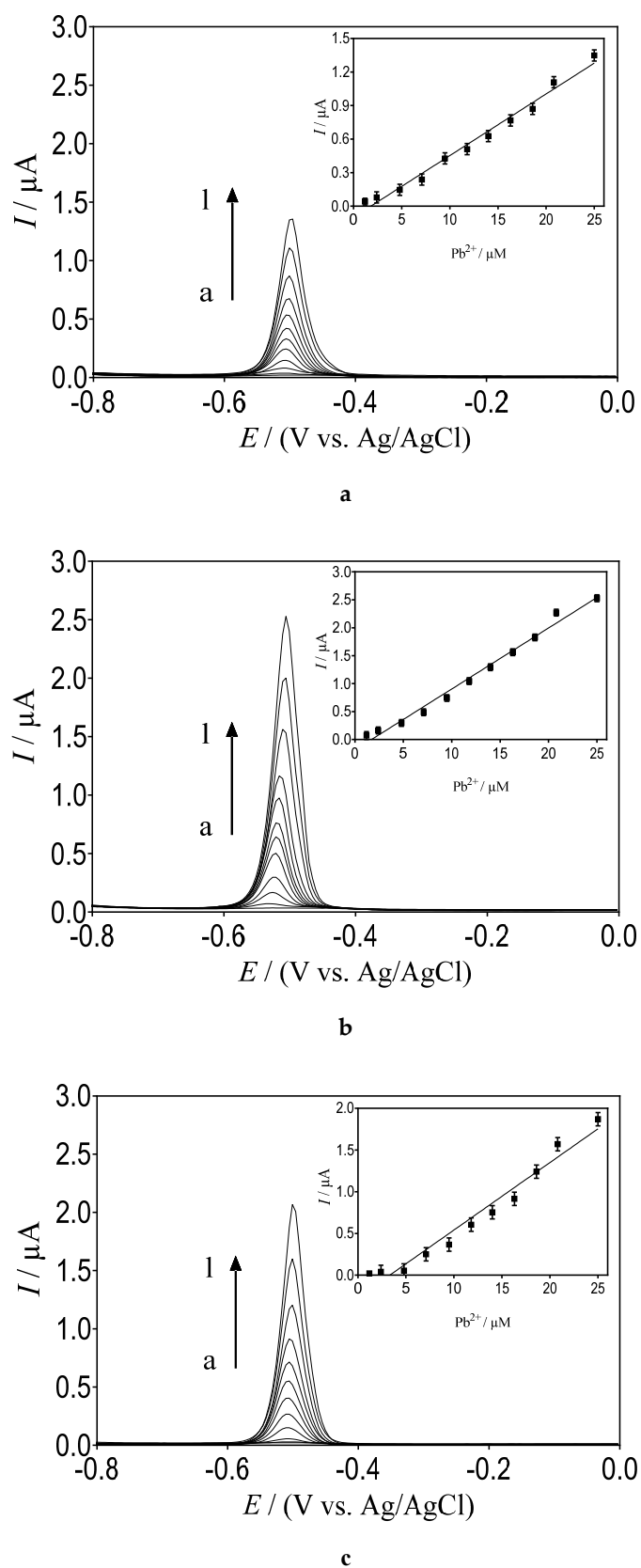


Figure 3. DPASV curves recorded for different concentrations of Pb(II) with (a) GrRAC-10%, (b) GrRAC-70%, and (c) GrRAC-90%. Lead concentrations: (a) 0, (b) 1.2, (c) 2.4, (d) 4.8, (e) 7.1, (f) 9.5, (g) 11.8, (h) 14.0, (i) 16.3, (j) 18.6, (k) 20.8, (l) 25 μM . Inserts: plots of the electrochemical response, in terms of current, as a function of the lead concentration.

3.4. SWASV Analysis

The GrRAC-70% composite sensor produced the best DPASV results for Pb(II) detection and was therefore chosen as the working electrode for evaluating Pb(II) traces by SWASV. Figure 4 shows the SWASV voltammetric responses of Pb(II) under pre-selected experimental conditions: 0.5 M H₂SO₄ as the supporting electrolyte, −1.2 V as the preconcentration potential, 120 s of preconcentration time plus 10 s of resting time. The stripping voltammetric peaks of Pb(II) ions appeared at −0.44 V for the GrRAC-70% sensor. The peak current (*I_p*) increased linearly with the concentration of Pb(II) in the range from 1 to 25 μM; the linear regression equation (*I_p* vs. *C*) was obtained as

$$I_p (\mu A) = (0.4 \pm 0.1) \times C - (0.8 \pm 0.2); R^2 = 0.98$$

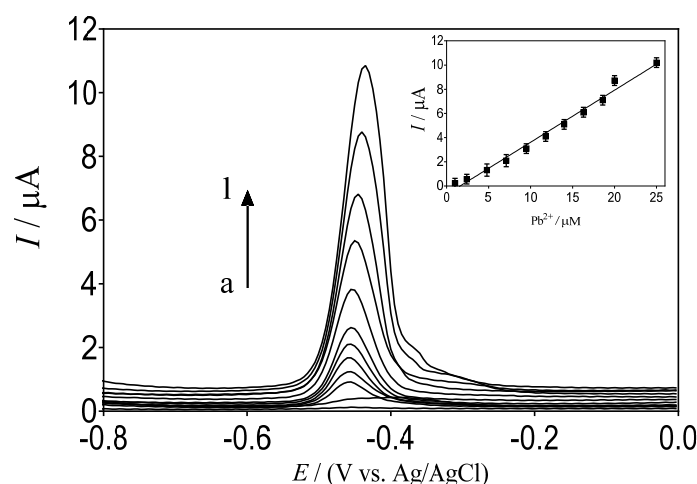


Figure 4. SWASV curves of GrRAC-70% recorded for different concentrations of Pb(II) in 0.5 M H₂SO₄: (a) 0, (b) 1.2, (c) 2.4, (d) 4.8, (e) 7.1, (f) 9.5, (g) 11.8, (h) 14.0, (i) 16.3, (j) 18.6, (k) 20.8, (l) 25 μM. Insets: plots of the electrochemical response, in terms of current, as a function of the lead concentration.

The LOD was found to be 0.3 μM. Compared with DPASV, SWASV produced much better results: the regression residuals are randomly distributed around zero and the linearity is practically perfect. Another important point is that no noticeable alterations were noted in the calibration curves recorded on different days, confirming the stability of the GrRAC-70% composite sensor. The GrRAC-70% sensor used in this work remained stable for at least two months of intensive use.

Table 1 collects the results available in the literature and relating to the analysis of Pb(II) with different electrodes and allows a comparison with the results obtained in this study. The ease of sensor preparation and the analytical protocol suggested here offer advantages over the other methods reported.

Table 1. Comparison of the analytical parameters of the sensors reported in the literature for the determination of Pb(II).

Electrodes	Method	Electrolyte	Linear Range μM	LOD/μM	Ref.
MTZ-PMO-S-S ¹	SWASV	0.2 M HCl	0.01–10	0.024	[35]
5-Br-PADAP/MWCNT ²	DPA	0.1 M acetate buffer	0.9–114	0.5	[36]
PPy/CNFs/CPE ³	SWASV	0.1 M acetate buffer	0.2–130	0.05	[37]
SRE ⁴	DPASV	0.01 M HNO ₃ + 0.01 M KCl	0.01–0.1	0.02	[38]
Glassy carbon	ADSV	0.5 M NaNO ₃		0.5	[12]
ErGO-MWNTs-L-cys ⁵	DPASV	0.1 M acetate buffer	0.2–40	0.05	[39]
CPE modified with IIP-MWCNTs ⁶	DPSV	0.1 M acetate buffer	3–55	0.5	[40]
IJP-MW-CNT ⁷	SWASV	0.1 M acetate buffer	5–20	0.05	[41]
GrRAC	SWASV	0.5 M H₂SO₄	1–25	0.3	This work

¹ Mercaptothiazoline-disulfide-bridged periodic mesoporous organosilica. ² 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol modified multi-walled carbon nanotube electrode. ³ Nanocomposite of polypyrrole (PPy) and carbon nanofibers (CNFs)-modified carbon paste electrode (CPE). ⁴ Silver ring electrode. ⁵ Electrochemically reduced graphene oxide–multiwalled carbon nanotubes–L-cysteine. ⁶ Carbon paste electrode (CPE) modified with ion-imprinted polymer nanoparticles and multiwalled carbon nanotubes. ⁷ Inkjet-printed multiwalled carbon nanotubes.

3.5. Study of the Interferences

In order to evaluate the specificity of the suggested approach, the sensor response in the presence of several potentially interfering species was investigated. In particular, the response to Pb(II) was evaluated in solutions containing 10 $\mu\text{mol/L}$ of the following cations: Fe^{2+} , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Al^{3+} , Mn^{2+} , Cu^{2+} , and Cd^{2+} . No additional signals were recorded when Fe^{2+} , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Al^{3+} , Mn^{2+} , or Cu^{2+} ions were present in solution during the determination of Pb at different concentrations (Figure 5). Conversely, a well-defined peak signal for Cd^{2+} was observed at -0.8 V. However, no changes in the Pb current peak were observed for the GrRAC-70% composite sensor in the presence of Cd^{2+} ions in solution (Figure 5). Therefore, the GrRAC-70% sensor can be used to detect Pb(II) even in the presence of other metals.

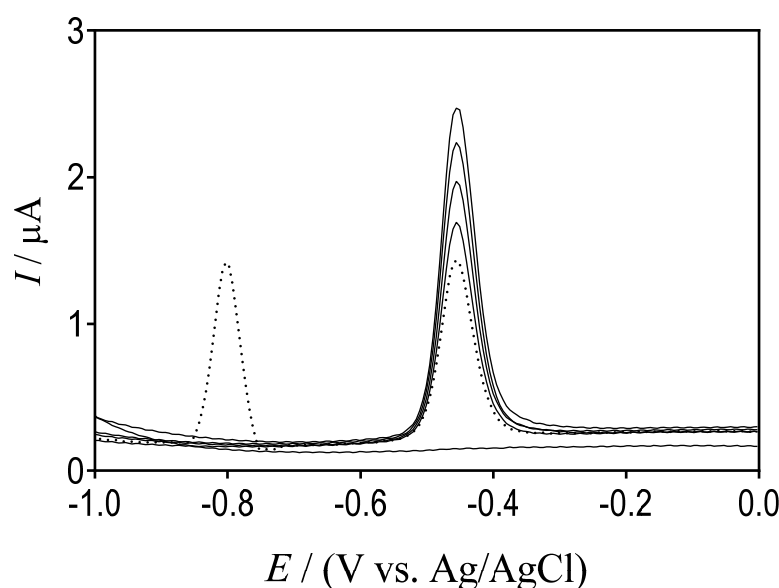


Figure 5. SWASV curves of GrRAC-70% recorded for different concentrations of Pb(II) in 0.5 M H_2SO_4 in the presence of a fixed concentration of interfering metal ions (10 $\mu\text{mol/L}$).

3.6. Stability

The stability of GrRAC was previously examined by determining caffeine, obtaining results of good consistency with a relative standard deviation (RSD) of 1.41% ($n = 3$); this outcome suggested that the cork-graphite composite sensor can be reused. A similar stability assessment was carried out in the case of Pb(II) by recording a series of voltammetric analyses over 10 days. No significant changes in the Pb peak current were observed after five measurements over that time period (Pb(II) = 15 μM ; RSD = 1.52%, $n = 5$). The cork-graphite composite sensor was washed and stored at 25 $^\circ\text{C}$ after each experiment.

3.7. Analytical Applications

The effectiveness of the proposed method, for the detection of Pb(II) in real samples, was also tested by analyzing tap water, groundwater, and “produced water” (a brackish water that is extracted as a by-product from underground during the process of oil and natural gas extraction). The electrochemical determination of Pb(II) was based on SWASV in acidic medium. For this, a quantity of Pb(II) was added to the water samples to obtain a well-known concentration between 10 and 50 μM for each sample. Then, the prepared samples were analyzed using the GrRAC-70% composite sensor under the optimized experimental conditions reported in Section 3.4. The validity of the proposed method for the determination of Pb(II) was evaluated using the standard addition method and recovery studies were conducted on the samples. As shown in Table 2, the recoveries ranged from 89 to 115 ($n = 3$), indicating that the proposed method can be efficiently applied for the

detection of Pb(II) in real water samples. In all cases, the relative standard deviation (RSD) values ranged from 0.3 to 2.1%, which confirms that the developed detection approach is potentially applicable.

Table 2. Pb(II) content in real water samples, measured with SWASV using the GrRAC-70% composite sensor.

Sample	Present Method ¹	Pb ²⁺ Added (μM)	Pb ²⁺ Found (μM) ¹	Recovery (%)
Groundwater	Not detected	10	11.5 ± 0.3	115
		50	52.1 ± 1.8	104
Tap water	Not detected	10	10.8 ± 0.5	108
		50	50.4 ± 1.5	100
Produced water	12.0 ± 0.4 μM	10	19.6 ± 0.5	89
		50	60.3 ± 2.1	97

¹ Mean of three determinations ± standard deviation.

4. Conclusions

Cork–graphite-based sensors offer a fast, reliable, cost-effective, and simple way to determine Pb(II) in real samples. The composite sensor exhibits higher sensitivity and reproducibility than conventional unmodified graphite sensors, and the low LOD allows for reduced matrix effects in dilute solutions. As for the materials tested, the affinity of the cork with the analyte allowed a substantial improvement in sensitivity. According to the results reported in this work, the sensor obtained by mixing 70% w/w of cork with 30% w/w of graphite allowed obtaining higher voltammetric responses and a rapid detection of Pb(II). The proposed approach is precise, with a limit of quantification of 0.3 μM, reproducible, and less expensive, both in terms of time and materials, compared to other analytical methods. The composite electrode can be applied effectively for the determination of Pb(II) in acidic media. As for the physical and chemical properties, which favor the interactions with the analytes to be detected or/and quantified, more experiments are needed to better understand the chemical and electrochemical processes that occur on the cork–graphite surface when the current is applied or when cork participates as a mediator.

Finally, even if the LOD reported in this work (0.3 μmol L^{−1}) is slightly above the limit established by the WHO (Pb: 0.24 μmol L^{−1}), there is room for improvement; for example, the size of the electrochemical sensor could be reduced, in order to approximate a micro-electrode, while the use of other carbon-based modifiers could allow improving the sensitivity.

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