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ELECTROCHEMICAL SENSOR TO MONITOR LEAD IN NATURAL WATER FOR PUBLIC SUPPLY

SENSOR ELETROQUÍMICO PARA MONITORAMENTO DE CHUMBO EM ÁGUA NATURAL DESTINADA AO ABASTECIMENTO PÚBLICO

SENSOR ELECTROQUÍMICO PARA EL CONTROL DEL PESO DEL AGUA NATURAL DESTINADA AL SUMINISTRO PÚBLICO

https://doi.org/10.56238/sevened2025.036-031

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ABSTRACT

Potentially toxic metals are capable of bio-accumulating in body tissues of living organisms and of having toxicological effects on both soil properties and the health of humans and animals. There are several methodologies available to quantify metals in aqueous matrices, however, these techniques are expensive, given their high cost and need of experts to manage the equipment. Accordingly, the present study introduces the application of an Au electrode, without surface modification, to analyze the presence of Pb2+ ions in surface water collected from Lanoso Brook, Uberaba City - MG, Brazil. The technique of anodic stripping voltammetry, without the need of sample preparation was employed. Volumetric parameters were optimized with the aid of central composite rotational design (CCRD) and method validation was carried out in atomic emission spectrophotometer. A detection limit (DL) of 0.04 ng L-1 and quantification limit (QL) of 0.13 ng L-1 were determined. Moreover, Pb2+ was found in real samples, and this finding highlighted the effectiveness of employing the Au electrode in this role.

Keywords: Environmental Electroanalyticals. Potentially Toxic Metals. Water Quality. Anodic Stripping Voltammetry.

RESUMO

Metais potencialmente tóxicos são capazes de bioacumular-se nos tecidos corporais de organismos vivos e de apresentar efeitos toxicológicos sobre as propriedades do solo e a saúde de humanos e animais. Existem diversas metodologias disponíveis para quantificar metais em matrizes aquosas; no entanto, essas técnicas são dispendiosas, devido ao seu alto custo e à necessidade de especialistas para operar os equipamentos. Assim, o presente estudo apresenta a aplicação de um eletrodo de ouro, sem modificação superficial, para

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analisar a presença de íons Pb^{2+} em água superficial coletada no Riacho Lanoso, cidade de Uberaba - MG, Brasil. A técnica de voltametria de redissolução anódica, sem necessidade de preparo da amostra, foi empregada. Os parâmetros volumétricos foram otimizados com o auxílio do planejamento composto central rotacional (CCRD) e a validação do método foi realizada em espectrofotômetro de emissão atômica. Foram determinados um limite de detecção (LD) de 0,04 ng L^{-1} e um limite de quantificação (LQ) de 0,13 ng L^{-1}. Além disso, a presença de Pb2+ foi detectada em amostras reais, e essa descoberta destacou a eficácia do uso do eletrodo de Au nessa função.

Palavras-chave: Eletroanálise Ambiental. Metais Potencialmente Tóxicos. Qualidade da Água. Voltametria de Redissolução Anódica.

RESUMEN

Los metales potencialmente tóxicos pueden bioacumularse en los tejidos de los organismos vivos y tener efectos toxicológicos tanto en las propiedades del suelo como en la salud humana y animal. Existen diversas metodologías para cuantificar metales en matrices acuosas; sin embargo, estas técnicas son costosas debido a su elevado precio y a la necesidad de personal especializado para su manejo. Por consiguiente, este estudio introduce la aplicación de un electrodo de oro (Au), sin modificación superficial, para analizar la presencia de iones Pb^{2+} en agua superficial recolectada del arroyo Lanoso, ciudad de Uberaba, Minas Gerais, Brasil. Se empleó la técnica de voltametría de redisolución anódica, sin necesidad de preparación de la muestra. Los parámetros volumétricos se optimizaron mediante un diseño compuesto central rotacional (DCCR) y la validación del método se realizó en un espectrofotómetro de emisión atómica. Se determinó un límite de detección (LD) de 0,04 ng L^{-1} y un límite de cuantificación (LC) de 0,13 ng L^{-1}. Además, se encontró Pb2+ en muestras reales, y este hallazgo destacó la eficacia del uso del electrodo de Au en esta función.

Palabras clave: Electroanálisis Ambiental. Metales Potencialmente Tóxicos. Calidad del Agua. Voltametría de Redisolución Anódica.

1 INTRODUCTION

Environmental contamination by potentially toxic metals is an increasingly pressing global concern, primarily driven by rapid industrialization and urban expansion. Among the various pollutants, lead (Pb) stands out due to its lack of any essential biological function and its ability to bioaccumulate in living organisms. This contaminant enters the environment through multiple anthropogenic sources, including industrial discharges, mining activities, fossil fuel combustion, and improper waste disposal. Furthermore, Pb can be present in pesticides and fertilizers, contributing to soil leaching and the contamination of both soil and water bodies. Its persistence and mobility significantly heighten environmental and public health risks.

In the environment, lead is found mainly in the form of Pb^{2+} ions or as chemically inert organic and inorganic species. Once absorbed by living organisms, Pb can cause significant biochemical disturbances, particularly affecting the nervous, hepatic, renal, and hematological systems. For this reason, monitoring Pb levels in environmental matrices is essential to prevent ecological damage and protect public health.

Given the need for sensitive and low-cost analytical techniques, electrochemical methods - especially anodic stripping voltammetry (ASV) - have shown great promise for detecting trace levels of Pb^{2+} in environmental samples. These techniques offer several advantages, including low operational cost, fast analysis, high sensitivity, and the possibility of in situ applications. In this context, the objective of this study was to evaluate the performance of an unmodified gold (Au) electrode for the electrochemical detection of Pb^{2+} ions in natural water samples intended for public supply.

2 THEORETICAL FRAMEWORK

Environmental pollution caused by potentially toxic metals is an issue of global concern. Accelerated population growth has led to several industries whose activities are the main source of release for potentially toxic metals (Latif *et al*., 2022; Hossaini-Zahed *et al*., 2022). Discharge of these elements into the environment can derive from such human activities as urban traffic, industrial activities, crop fertilizers and irrigation, mining, and, naturally, from soil erosion, weathering and rock cycles. Lead (Pb) stands out among possibly toxic metals as it is not an essential element and it can bio-accumulate in organisms and have permanent environmental effects (Balasubramanian *et al*., 2020; Latif *et al*., 2022; Chang *et al*., 2022; Cui *et al.,* 2023).

The availability of Pb availability in soils, sediments and waterbodies frequently occurs in the form of Pb^{2+} or in its inert form, as organic or inorganic species (Kumar *et al*., 2020). Pb can enter in contact with the environment via several pollution sources, such as smelting, mining, fossil fuels, besides inappropriate waste discharge including paint, gasoline and battery residues (Bahinting *et al*., 2021; Latif *et al*., 2022). Pesticides and phosphate fertilizers can also contain Pb in their formula, which can leach from soil to rivers and contaminate waterbodies (Ebrahimi *et al*., 2020).

When in contact with the organism, Pb can cause several biochemical changes in the nervous system, kidneys and liver, besides having carcinogenic and mutagenic properties (Gnonsoro *et al*., 2022; Nyamato *et al*., 2022). Given its interaction with iron, lead can compromise the hematological system and cause anemia, as well as weakness and fatigue (Barroso *et al*., 2021; Aniceto; Irazusta 2023). Symptoms attributed to exposure to lead can be light, such as burning eyes, irritation, vomiting, diarrhea, lung irritation, headaches and dizziness. However, sometimes, they can be severe and include allergic dermatitis, Painters syndrome, lung cancer, reproductive harm, kidney and liver damage (Balasubramanian *et al*., 2020).

Lead determination in real samples is most often carried out through atomic absorption spectrometry (AAS), Microwave Plasma Atomic Emission Spectrometry (MP-AES), plasma source mass spectroscopy (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and micro-solid-phase extraction (μ-SPE) in combination with gas chromatography–mass spectrometry (Boleji *et al*., 2021). However, such traditional techniques require sophisticated sample preparation, longer analysis times analyses, trained technicians and high-cost equipment (Guenang *et al*., 2020; Bahinting *et al*., 2021). Electrochemical techniques are promising for analysis of pollutants as it is possible to reduce many of the costs. Voltammetry is an electroanalytical technique capable of providing high sensitivity in several environmental matrices in order to monitor traces of potentially toxic metals. In addition, the pre-concentration stage in anodic stripping voltammetry, can significantly increases sensitivity levels and analyte detection limits (Jovanovsk; Hrastnik 2019; Sánchez-Calvo; Blanco-López; Costa-García 2020).

Electrochemistry is an important tool to analyze reactions involving electron transfer, and a set of analytical methods based on the electric properties of analytes in the solution are available (Elgrishi *et al*., 2018). Such techniques have been gradually more widely used due to their low operational cost, high selectivity and sensitivity to detect and quantify harmful substances found in water bodies. Moreover, they can help studies on the formation of intermediate toxic products to both humans and the environment. Such analyses are fast, and they can be carried out in situ (Monteiro; Dos Santos Júnior; Sussuchi, 2020; Zier; Bouafia-Chergui; Chabani, 2021).

Anodic stripping voltammetry (ASV) is one of the most often used techniques to detect potentially toxic elements at low concentrations, based on using the electrochemical sensor. This device can measure the concentrations of certain molecules or analytes through redox reactions, in which electrons are transferred between analyte molecules and the electrode and consequently, a current proportional to the analyte's concentration is generated at the sensor (Nourbakhsh *et al*., 2022).

Thus, it is worth noting that the use of unmodified gold (Au) electrodes for metal detection remains relatively unexplored in the scientific literature. Most available studies report comparatively high detection limits when measured against conventional analytical methods, which limits their applicability for trace-level environmental analysis. Therefore, investigations assessing the performance of these electrodes under real sample conditions are highly relevant, particularly when considering their simplicity, reproducibility, and potential for use in low-cost monitoring systems.

3 METHODOLOGY

3.1 REAGENT

Lead (II) chloride (Cinética, 99%) was used as the source of Pb(II) for all assays performed. All other reagents were provided by Sigma Aldrich® at analytical grade and used without further purification. Ultra-pure water (Milli-Q®) was used for solution preparation purposes (resistivity ~ 18 MΩcm). Experiments were conducted at room temperature (25ºC). Hydrochloric acid solution (HCl) at a concentration of 1 mol L^{-1} was adopted as supporting electrolyte. Lead (II) chloride stock solution ($PbCl_2$ - 1,000 µg L^{-1}) was prepared by diluting its solid standard in a solution of the supporting electrolyte. Solutions of sodium hydroxide (NaOH - 5.0 mol L^{-1}) and standard hydrochloric acid solutions (37 %) were used for pH adjustment purposes.

3.2 ELECTRODES

Electrodes used in the experiments were provided by Lab Solutions®. The Au electrode disc (ϕ = 1.6 mm) was pretreated by performing 15 potential sweeps in 0.1 mol L^{-1} sulfuric acid in the solution at range of 0.15 to 0.6 V (vs. Ag/AgCl) at a sweep-rate of 0.05 V s^{-1}. The Au electrode was also polished with suspended alumina (0.3 µm) and washed in ultra-pure water for a mirror finish. A potential of 0.33 V per 200 s was applied for cleaning after each sweep, to make sure that the metal ions were re-oxidized. A Platinum (Pt) wire (5 cm) was the auxiliary electrode and Ag/AgCl in 3 mol L^{-1} KCl solution was the reference electrode.

3.3 EQUIPMENT

Autolab® potentiostat/galvanostat model PGSTAT 320N, controlled using NOVA 2.1 (Metrohm) software, was used for voltammetry procedures. Fisatom magnetic stirrer model 752A 115 V and a stirring bar (9 mm in diameter x 8 mm in height) by Merck were used in ASV. A Tecnopon pH meter, model MPA-210, was employed to determine pH values. OriginPro® 2019b by OriginLab was used to treat the results and to plot the graphics. Method validation was made in MP-AES 4200 Microwave Induced Plasma Atomic Emission Spectrometer, Agilent Technologies. Statistica software was used for the experimental design procedure.

3.4 CENTRAL COMPOSITE ROTATIONAL DESIGN

A Central Composite Rotational Design (CCRD) was used to optimize the parameters under study. In total, 17 experiments were carried out through CCRD 23, with 6 axial points and 3 repetitions, at the central point. Table 1 presents the codified values and the real independent variables of the CCRD.

Table 1

Codified and real values recorded for the independent variables

Variables	Code	- α	-1	0	+1	+ α
Deposition time (s)	X_1	34	100	200	300	366
Frequency (Hz)	X_2	13.5	30	55	80	96.5
Amplitude (mV)	X_3	6.9	30	65	100	123.1

Source: Developed by the authors.

3.5 VOLTAMMETRY ANALYSES

The analysis limit applied to deposition time, frequency and amplitude was established based on the proposed experimental design. After assessing studies available in the literature, the value of 04 mV was established for scan increment. The pH was varied in the range of 0.0 to 4.0, at a 0.5 increase.

3.6 ANALYSES APPLIED TO NATURAL SAMPLES

Lanoso Brook is in the Triângulo Mineiro region, inside an environmental protection area. It is one of Uberaba River's main tributaries. Surface water samples were collected from September 2022 to February 2023, as this is the rainy period, which possibly allows more Pb2+ ions to leach into surface water. All samples were stored in plastic containers and kept in the dark and under refrigeration, to avoid degradation and composition changes. This process made the samples integrated over the whole collection period.

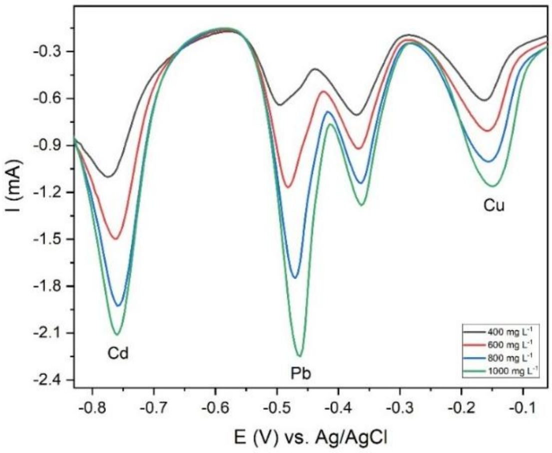
4 RESULTS AND DISCUSSIONS

4.1 EAU APPLICABILITY IN METALLIC ION ANALYSIS

Preliminary analysis of lead, cadmium and copper at an Au electrode was performed with the aim of assessing the possibility of simultaneous detection. Square wave voltammetry (SWV) was applied to at concentrations of 400, 600, 800 and 1.000 mg L-1, using HCl (0.1 mol L-1) as the supporting electrolyte, according to the following parameters: pulse amplitude: 50 mV, frequency: 60 Hz and scan increment: 04 mV. Figure 1 presents the voltammograms obtained during the analyses.

Figure 1

Square wave voltammogram of simultaneous detection of Pb, Cd and Cu, at concentrations of 400; 600; 800 and 1.000 mg L-1 in HCl (0.1 mol L-1) and pH 0.5. f = 60 Hz, a = 50 mV, s = 04 mV, f = 60 Hz, a = 50 mV, s = 04 mV



Source: Developed by the authors.

From Figure 1 it can be observed that the voltammogram presented characteristic reduction peaks for the analyzed metals with a satisfactory response to the concentration gradient. The r^2 values learned from analytical curves were 0.999, 0.995 and 0.998 for lead, cadmium and copper, respectively. Thus, it was possible to observe that, under the conditions employed, that the Au electrode was able to simultaneously determine multiple metals in solution during SWV. This finding demonstrates the potential of Au to be used in multi-elementary analysis.

4.2 CENTRAL COMPOSITE ROTATIONAL DESIGN

The Central Composite Rotational Design (CCRD) was employed to optimize three experimental variables: deposition time (34 to 366 s), frequency (13.5 to 96.5 Hz), and amplitude (6.9 to 123.1 mV). A total of 17 experiments were conducted using a Pb^{2+} concentration of 1,000 µg L^{-1} and pH 0.0. The optimized parameters obtained were a deposition time of 200 s, frequency of 81 Hz, and amplitude of 98 mV. Response surface analyses revealed that the highest current signals occurred at deposition times close to 200 s and frequencies ranging from 60 to 85 Hz, highlighting the importance of deposition time for the preconcentration of Pb^{2+} ions on the Au electrode and the consequent enhancement in detection limits.

Statistical analysis, with 95% confidence, confirmed that the optimal amplitude range was between 80 and 100 mV, and that the best analytical signals were obtained with frequencies between 60 and 100 Hz. The proposed mathematical model (Eq. 1) showed that amplitude (X_3) was the most influential variable—nearly five times more relevant than deposition time (X_1).

$$I(uA) = -149.20 + 0.71.X_1 - 0.002X_1^2 + 4.62.X_2 - 0.03\,X_2^2 + 3.70.X_3 - 0.022\,X_3^2 + 0.001.X_1.X_2 + 0.002X_1.X_3 - 0.019.X_2.X_3 \quad (1)$$

Where:

X_1 is deposition time

X_2 is frequency

X_3 is amplitude.

Additionally, it was observed that increasing frequency had a greater impact on current signal intensity compared to the other two variables, which aligns with findings by Vasconcellos *et al*. (2020).

4.3 EFFECT OF PH

The release of cations increases at lower pH values and alters the voltammetric profiles (Sun *et al*., 2020; Król; Mizerna; Bożym, 2020). Thus, a pH study was conducted to analyze the best analytical results. After studying the literature, the following pH range was set: 0.0 to 4.0, with a 0.5 step increase.

The highest current intensity was recorded at pH 0.0, which led to the most satisfactory analytical signal. Therefore, this value was used as the standard pH for the analyses applied to natural samples to obtain the highest sensitivity for the electroanalytical method.

4.4 LEAD ANALYTICAL CURVE

After assessing several articles and analyzing the laboratory conditions adopted in the studies by Munoz & Angnes (2004), Zhu *et al.* (2014), Vasconcellos (2020), Yaman *et al.* (2021), it was possible to observe that the best scan increase for the present study was 4 mV. Accordingly, parameters were established to find the best analytical signal for the Pb^{2+} analytical curve.

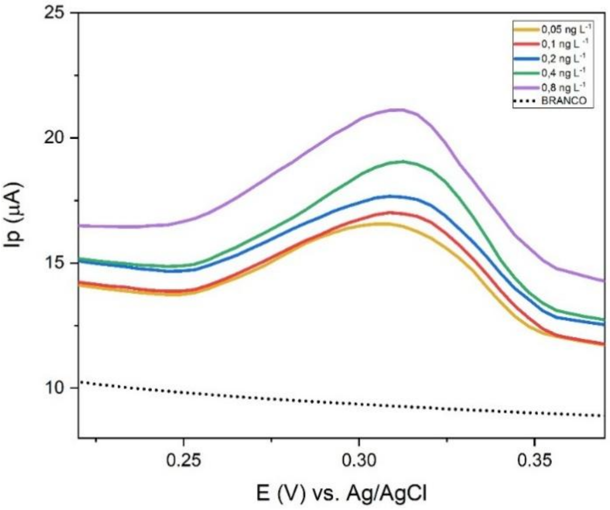
All assays used hydrochloric acid (HCl 1 M) as supporting electrolyte. Thus, some exploratory voltammograms were performed to determine the oxidation potential of Pb under the conditions set for these analyses. Pd undergoes oxidation at values close to 0.33 V. Therefore, during the analyte pre-concentration stage at the Au electrode, a potential of -0.33 V, for 200 s, was applied.

Equation 2 shows the reaction taking place at deposition stage, which involves Pb^{2+} reduction to metallic lead (Pb^0) at the working electrode after applying a potential of -0.3 V. Subsequently, anodic stripping occurs, which makes the lead deposit at the electrode oxidize and form Pb^{2+} (Eq.3) in solution. Thus, a positive scan was performed, and resulted in Pb oxidation at concentrations 0.05, 0.1, 0.2, 0.4 and 0.8 ng L^{-1}, as depicted in Figure 2.

$$Pb^{2+} + 2e- \rightarrow Pb^{0} \qquad (2)$$
$$Pb^{0} \rightarrow Pb^{2+} + 2e- \qquad (3)$$

Figure 2

Anodic stripping voltammogram at concentrations 0.1, 0.2, 0.4 and 0.8 ng L^{-1} Pb^{2+} *in HCl (1 mol* L^{-1}*) and pH 0.0. Deposition time = 200 s, f = 81 Hz, a = 98 mV, s = 04 mV*



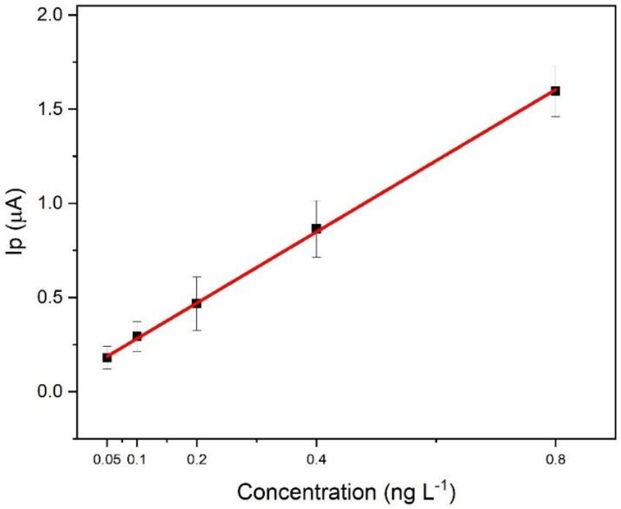
Source: Developed by the authors.

Linearity, in the analytical method, is an intrinsic property that allows analytical responses to be directly proportional to the concentration of the analyte in the study (Ribani *et al*., 2004). Therefore, it is possible to observe (Figure 2) the Pb analyses at different concentrations conducted in triplicate, as well as the gradual increase in peak current as analyte concentration increases.

Based on Figure 3, the analytical curve displays satisfactory association between Pb2+ concentration and current peak. The current increased as concentration also increased. Thus, the linear equation is given by Ip (µA) = $1.88952 \cdot 10^{-6} + 9.27194^{-8} * C_{lead}$.

Figure 3

Ip association with Pb2+ concentration (0.05, 0.1, 0.2, 0.4 and 0.8 ng L-1). Deposition time = 200 s, f = 81 Hz, a = 98 mV, s = 04 mV



Source: Developed by the authors.

The results display a satisfactory linear response between concentration and peak current (r² = 0.999). The proposed method, based on the application of an Au electrode, and ASV, presented a detection limit (DL) of 0.04 ng L^{-1} and quantification limit (QL) of 0.13 ng L^{-1}.

4.5 ELECTROANALYTICAL DETERMINATION OF LEAD (II) IONS IN NATURAL WATER

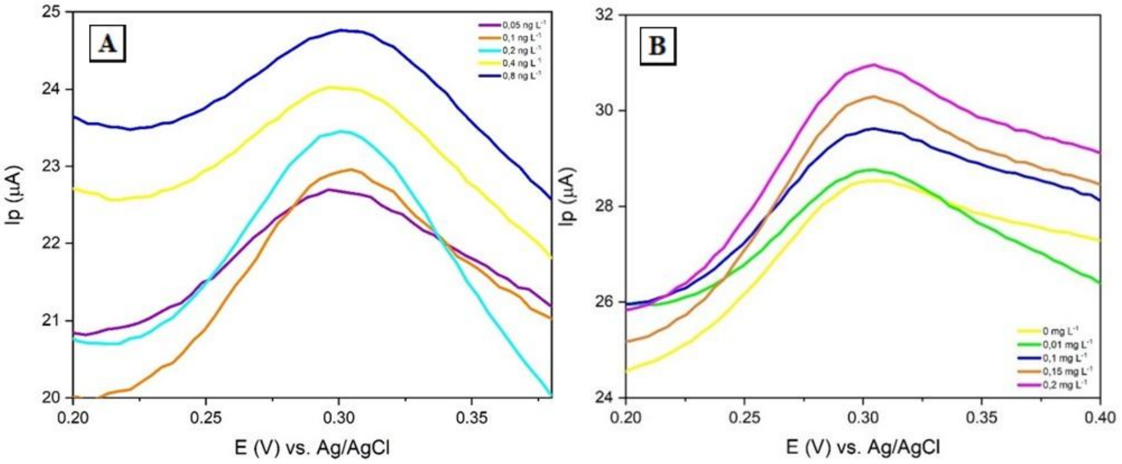
Tests were performed with surface water samples collected from the Lanoso Brook, Uberaba City – MG, Brazil. Figure 4a presents the characteristic voltammogram of analyses applied to concentrations 0.05, 0.1, 0.2, 0.4 and 0.8 ng L^{-1} adopted to compare the analyses performed under laboratory conditions. The process was performed for concentrations of 0.0, 0.01, 0.1, 0.15 and 0.2 mg L^{-1} (Figure 4b), which is in the detection range of microwave induced plasma atomic emission spectroscopy.

Characteristic current peaks were observed at 0.3 V, without significant peak displacement and with variations in anodic stripping voltammetry, based on voltammograms of Pb^{2+} oxidation in natural samples, at the two concentration limits. These fluctuations likely occur due to the presence of organic pollutants, organic matter and dissolved inorganic matter, because these are complex samples; this process could lead to slight changes (Kobielska *et al*., 2018; Nourbakhsh *et al.*, 2022).

Nevertheless, interaction with organic matter can form stable complexes with metallic ions and compete for electrode surface sites in deposition or redissolution. This reduces signal intensity or allows the presence of interfering signals (Monteiro *et al.*, 2018).

Figure 4

Anodic stripping voltammetry applied to natural samples at different Pb2+ concentrations, expressed in HCl 1 mol L-1 (pH 0.0). Concentrations were A) 0.05, 0.1, 0.2, 0.4 and 0.8 ng L-1 and B) 0.0; 0.01; 0.1; 0.15 and 0.2 mg L-1. Deposition time = 200 s, f = 81 Hz, a = 98 mV, s = 04 mV



Source: Developed by the authors.

4.6 ELECTROCHEMICAL METHOD VALIDATION

Microwave Plasma Atomic Emission Spectrometry (MP-AES) was applied to validate the proposed method adopted to detect Pb^{2+} ions in natural samples. Table 2 presents the comparison between MP-AES and ASV in natural water samples for lead detection purposes. These results show similarities between the two techniques employed to detect Pb^{2+} ions. Interestingly, the ASV technique was capable of detecting Pb^{2+} in natural water samples.

Table 2

Comparison of results recorded for natural water samples

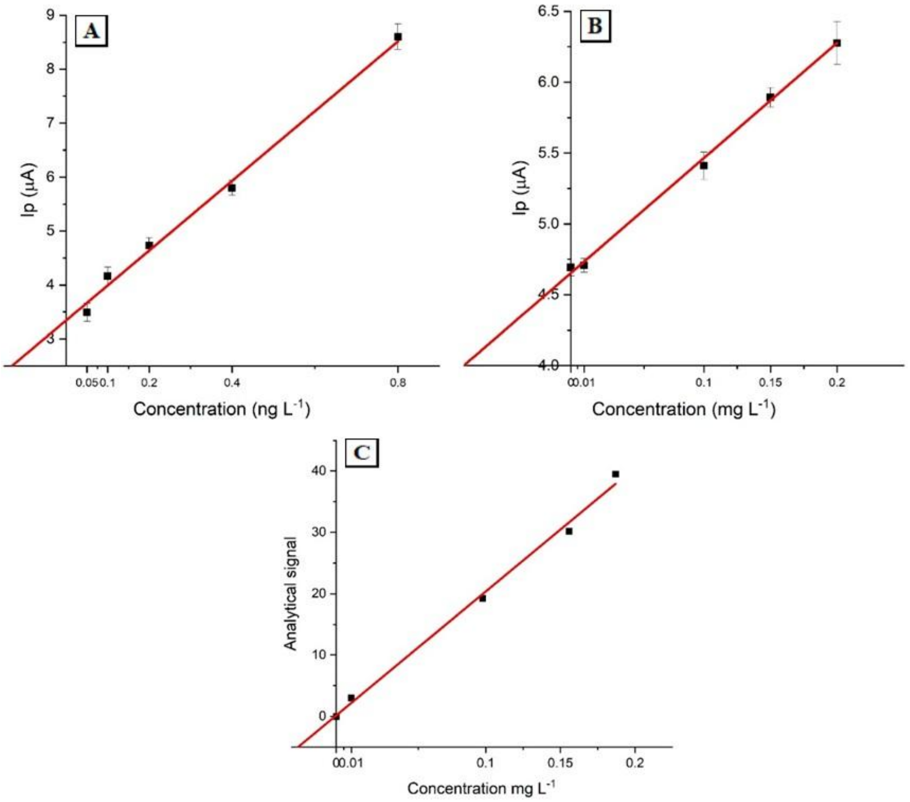
Added concentration (mg L^{-1})	Concentration found in MP-AES (mg L^{-1})	Concentration found in ASV (mg L^{-1})
0.000	< QL	0.005 ± 0.062
0.010	0.010 ± 0.001	0.007 ± 0.090
0.100	0.098 ± 0.002	0.093 ± 0.031
0.150	0.156 ± 0.010	0.153 ± 0.044
0.200	0.187 ± 0.020	0.199 ± 0.093

Source: Developed by the authors.

Figure 5 (a and b) depicts the concentration curves plotted for concentrations expressed in ng L^{-1} using ASV at the concentration of ng L^{-1} ($r^2 = 0.990$) and at mg L^{-1} ($r^2 = 0.996$), respectively. Figure 5(c) contains the data obtained using MP-AES analysis ($r^2 = 0.995$).

Figure 5

Analytical curve plotted for lead in natural samples expessed in A) and B) ASV concentrations ng L-1 and mg L-1, respectively. Deposition time = 200 s, f = 81 Hz, a = 98 mV, s = 04 mV and C) MP-AES 4200 analysis



Source: Developed by the authors.

The t test was performed to statistically compare results recorded through MP-AES analysis and ASV, at concentrations expressed in mg L^{-1}. The value obtained was -0.02386 and indicated a lack of evidence of significant differences between the observed results.

4.7 RECOVERY TEST

Recovery values recorded for both electrochemical techniques employed for lead detection purposes were calculated and they are given in Table 3. This was done to assess the accuracy of the analyses carried out with natural water samples.

Table 3

Total lead recovery in natural water

Analytical method	Total recovered concentration (mg L^{-1})	% Recovery
MP-AES	0.451	98
ASV	0.457	99

Source: Developed by the authors.

The standard addition method was chosen to minimize the matrix effect. The matrix effect, in its turn, can interfere with the analyses (Ribani *et al*., 2004). These results recorded 98% recovery through MP-AES and 99% recovery through ASV. The t value was 0.79046, at a 95% significance level. This finding shows that there is no evidence of significant differences between results provided by ASV, based on the use of Au electrodes, and MP-AES.

The Au electrode was effective both in terms of costs and of detection and quantification limits obtained in the analyses. The Au electrode does not need pre-treatment of its surface and reached detection levels of ng L^{-1}. Thus, the proposed method, in combination with the electrode, emerged as an efficient alternative to quickly detect low Pb^{2+} concentrations in natural water samples.

5 CONCLUSION

The Au electrode proved itself to be effective and promising for detection of Pb^{2+} without any surface modification or pre-treatment, through ASV, applied to natural water samples collected from Lanoso Brook, Uberaba City – MG, Brazil. The methods were validated through MP-AES and ASV with $r^2 = 0.995$ and $r^2 = 0.996$, at recovery rate of 98% and 99%, respectively. This result was statistically confirmed through the t test, which demonstrated the lack of substantial differences between the analytical procedures.

It was possible to that any future application of the methodology proposed would employ printed electrodes. This would be required to reduce the time of electrode cleaning. Therefore, the electrochemical method proposed here, based on using Au electrodes without pre-treatment, has emerged as feasible alternative for Pb^{2+} detection in natural water samples. The methodology makes in situ analysis feasible and allows for real-time analyses to assess and monitor surface water used for public supply.

ACKNOWLEDGEMENTS

Thanks to CAPES, CNPq and FAPEMIG for the financial resources that made this research possible. We also extend our special thanks to Professor Dr. Geoffroy for his invaluable support throughout the development of this work.

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