Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2022.29023

280 (2022) 251–261
December

Investigation on square wave and cyclic voltammetry approaches of the Pb^{2+}, Cd^{2+}, Co^{2+} and Hg^{2+} in tap water of Beni Mellal City (Morocco)

Charaf Laghlimi[a,*], Abdelaziz Moutcine[b], Morad Elamrani[b], Abdelilah Chtaini[b], Jalal Isaad[a], Hamza Belkhanchi[c], Younes Ziat[c]

[a]*ERCI2A, FSTH, Abdelmalek Essaadi University, Tetouan, Morocco, email: Charaf.cac.fbs@gmail.com*
[b]*Molecular Electrochemistry and Inorganic Materials Team, Faculty of Science and Technology of Beni Mellal, Sultan Moulay Slimane University*
[c]*Laboratory of Engineering and Applied Technologies, Higher School of Technology, Sultan Moulay Slimane University, Beni Mellal, Morocco*

Received 4 May 2021; Accepted 11 October 2022

ABSTRACT

A sensitive sensor has been prepared to detect and quantify electrochemically Pb^{2+}, Cu^{2+} and Co^{2+} in drinking water. The objective of this work is to qualify the trueness and preciseness of two electrochemical methods which are the square wave (SWV) and the cyclic voltammetry (CV) with regard to the detection of lead, copper and cobalt ions in tap water. The electrode used for this purpose is modified with an organic molecule EDTA (ethylenediaminetetraacetic acid) of chemical formula ($C_{10}H_{16}N_2O_8$) that we added to a specific amount of graphite carbon powder (CP). The formed paste is introduced into a cylindrical plastic cavity. This formed entity is attached to a carbon graphite rod to ensure the passage of the current. The detection limit and quantification limit of carbon-paste electrode CPE-1% EDTA for the reduction peak ($CV_{\text{Pic-red}}$) are the lowest, they are respectively 9.31×10^{-10} mM and 3.1×10^{-9} mM. The coefficient of variation (CV*) and repeatability uncertainty for measurements made by the SWV are lower compared to the CV. The SWV gives more accurate but not correct results while the $CV_{\text{Pic-red}}$ gives correct but not accurate results. For all studied metals, the method is linear in the concentration range (0.6–2.1 mM), except for mercury it is linear in the range (0.3–2.1 mM). Cadmium has a low systematic error (SE = 0.009 mA/cm^2) followed by lead (0.013 mA/cm^2) then mercury.

Keywords: Precision; Accuracy; Regression; Square wave (SWV); Cyclic voltammetry (CV); Drinking water

1. Introduction

Consumption of products contaminated with lead, cadmium and mercury presents an increased danger to human health [1]. Controlling the quality of food and drinking water has become a major priority issue [2–5]. Very interesting methods have been used to detect some heavy metals such as an inductively coupled plasma mass spectrometry (ICP-MS) [6], atomic absorption/emission spectroscopy [7], surface-enhanced resonance Raman scattering [8] and fluorescence resonance energy transfer [9].

Ultrasensitive fluorometric biosensors based on Ti_3C_2 MXenes [2] and silver hairpin DNA nanoclusters [3] are methods used to analyze mercuric ions in contaminated waters These biosensors have proven high reproducibility, good specificity and low cost. Qiu et al. [4] developed an inexpensive sensor coupled with thymine-Hg2þ-thymine (T-Hg2þ-T) coordination chemistry and invertase-functionalized gold

---

* Corresponding author.

dendrimer nanospheres for signal amplification with glucometer reading dedicated to mercury(II) detection. The realized sensor has several advantages namely cost effectiveness, simplicity, portability and convenience. In the same sense, a DNA-based biosensor was used for the detection of Hg(II) in contaminated drinking water samples [5]. The detection is performed impedimetrically based on the formation triggered by a specific enzyme. This strategy has a high specificity, high selectivity and good repeatability.

Electrochemical techniques are widely used in the agricultural, ecological, medical and industrial fields [10–12]. The excessive use of these techniques is due to their high efficiency, selectivity, low cost, low maintenance and time saving [13,14]. In 1958, Adams [15] used carbon paste as an electrode material, and since then, carbon-paste electrodes (CPE) have been over-used because of their ease of renewal, stable response and low ohmic resistance [16,17].

Recently very interesting research has been carried out to quantify the traces of Pb^{2+} ions using modified carbon-paste electrodes [18–22]. Modified carbon-paste electrodes have very important advantages such as absence of toxicity, low cost, ease of fabrication and very good selectivity [18–25].

The analysis of samples using such methods requires a lot of time, pre-treatment, high cost, qualified personnel, and accredited laboratories, etc. Analytical methods are undertaken with the aim to exactly determine the quantity of existing elements in a sample which has unknown concentration. On the other hand, the validation of an analytical method is a procedure which enables to confirm, through experimental studies, that the performance criteria of the method allow to meet the requirements of intended use [26–28].

The ethylenediaminetetraacetic acid (EDTA) molecule is characterized by the presence of six basic sites which are ligand centers. EDTA has a strong chelating (or complexing) power which gives it the possibility to form very stable metal complexes [29]. In the present study, we developed an EDTA-modified sensor for the detection and quantification of heavy metals. The fabricated sensor is characterized by its simplicity, sensitivity and low cost. The performance of the electrode is evaluated by electrochemical methods such as square wave (SWV) and cyclic voltammetry (CV). In this framework, we will answer the following question:

Which method (SWV or CV) gives precise and accurate results concerning the detection and quantification of lead in the tap water of our laboratory via the developed sensor (CPE-EDTA).

2. Material and methods

Modified carbon paste is prepared by adding a specific amount of disodium ethylenediaminetetraacetic acid molecule ($C_{10}H_{16}N_2O_8$) to a specific amount of graphite carbon powder (CP). The formed paste is introduced into a cylindrical plastic cavity. This formed entity is attached to a carbon graphite rod to ensure the passage of the current. Three modified electrodes with ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$) were prepared (CPE-1% EDTA, CPE-5% EDTA and CPE-10% EDTA). These electrodes are rinsed with double-distilled water and then immersed in an electrolytic solution containing 0.1 M NaCl. The electrode having the highest performance is used to validate the proposed electrochemical method. The chosen concentrations are ranging from 0.3 mM Pb^{2+} to 2.1 mM Pb^{2+}. Each concentration is repeated 10 times and the electrochemical potential occurred between (–1.5 V and +1.5 V). The same procedure was conducted for the study of mercury, cobalt and cadmium in tap water.

3. Results and discussion

3.1. Optimization of detection parameters

The cyclic voltammograms of CPE-EDTA at different EDTA contents is exhibited in Fig. 1. The intensity of oxidation

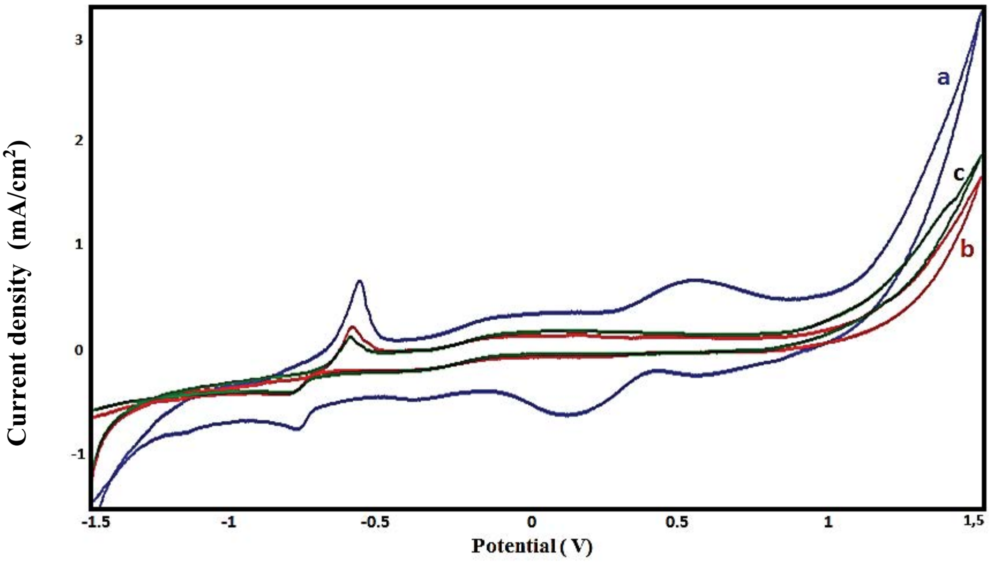

Fig. 1. Cyclic voltammograms of CPE-EDTA at 0.3 mM Pb^{2+} in 0.1 M NaCl, pH = 2, scan rate 100 mV/s, t_p = 10 min at (a) 1%, (b) 5% and (c) 10% EDTA in carbon paste (w/w).

peak is around the value of –0.58 V for 1% EDTA. Here, it is stated that is six times greater than that observed for 10% EDTA. Similar observations are noted for the reduction peaks at –0.79 V, the peak intensity is around –0.755 mA/cm^2 for CPE-1% EDTA and –0.4067 mA/cm^2 for the CPE-10% electrode. 1% EDTA will be used to modify the electrode.

The ongoing investigations will be based on the listed parameters in Table 1.

3.2. *Verification of the precision and trueness of the square wave and cyclic voltammetry*

3.2.1. *Calculation of detection limit and quantification limit*

The cyclic voltammetry (CV) and SWV of CPE-1% EDTA at different concentrations of Pb^{2+} in 0.1 M NaCl are plotted in Figs. 2 and 3, respectively.

In order to design an appropriate equation to calculate "the limit of detection" and "the limit of quantification" of Pb^{2+}, the manipulation was similarly repeated 10 times with two different operators during two months. We calculated the average of the current intensities found for each concentration from 0.3 to 2.1 mM Pb^{2+} (each concentration is repeated ten times).

The analytical general regression curves connected to SWV method (Fig. 4) and CV method (Fig. 5) were plotted taking into account the calculated averages. Note that the analytical regression curves are linear over the aforementioned concentration range (from 0.3 to 2.1 mM Pb^{2+}) (cf. Figs. 4 and 5). The linear regression line equations for each method are compiled in Table 2. The limit of detection and quantification are calculated using the following equations [26–28]:

$$\text{SD} = \frac{1}{(n-2)} \sum_{j=0}^{n} \left(i_j - I_j\right)^2 \tag{1}$$

$$\text{LOD} = \frac{(3 \times \text{SD})}{\text{slope}} \tag{2}$$

$$\text{LOQ} = \frac{(10 \times \text{SD})}{\text{slope}} \tag{3}$$

where i_j: is the experimental value of the current calculated at manipulation j. I_j: is the corresponding value recalculated at the same concentration using the calibration equation. $n = 7$: number of experiments.

From Table 2, the predictive power of the regression line equation for the reduction peak obtained by the CV method is stronger than the one obtained by SWV method. This equation is able to determine 99.74% of distribution

Table 1
Optimal settings for Pb^{2+} analysis

Settings	EDTA content	pH	Preconcentration time	Scan rate	Interval of potential	Electrolytic medium
	1%	2	10 min	100 mV/s (CV) 20 mV/s (SWV)	–1.5 V; +1.5 V	0.1 M NaCl

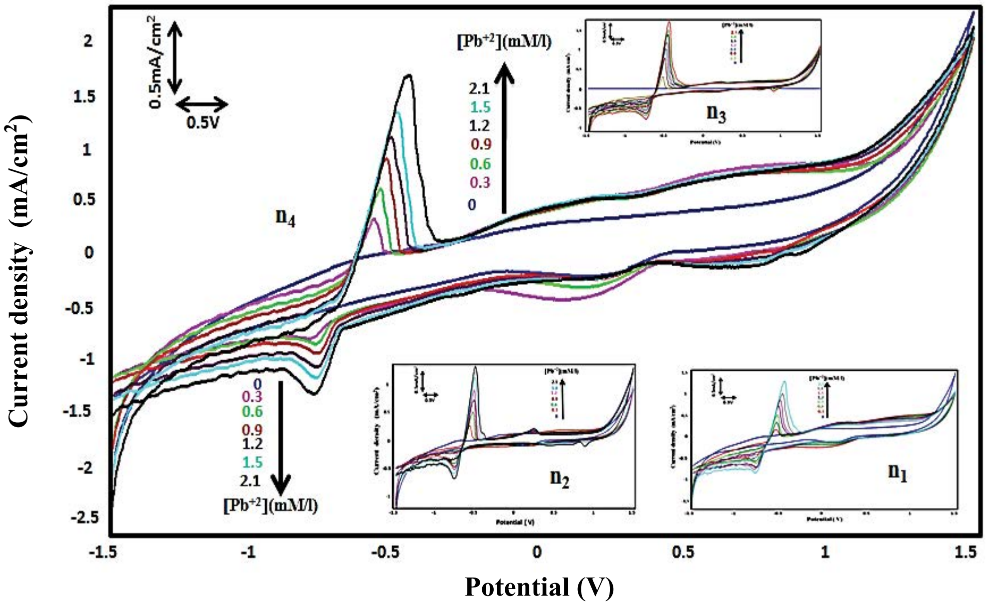

Fig. 2. Cyclic voltammograms of CPE-1% EDTA at different concentrations of Pb^{2+} in 0.1 M NaCl, pH = 2, scan rate 100 mV/s, t_p = 10 min. The manipulation is repeated 10 times in the same way with the same operator. Four manipulations are shown (n_1, n_2, n_3 and n_4).

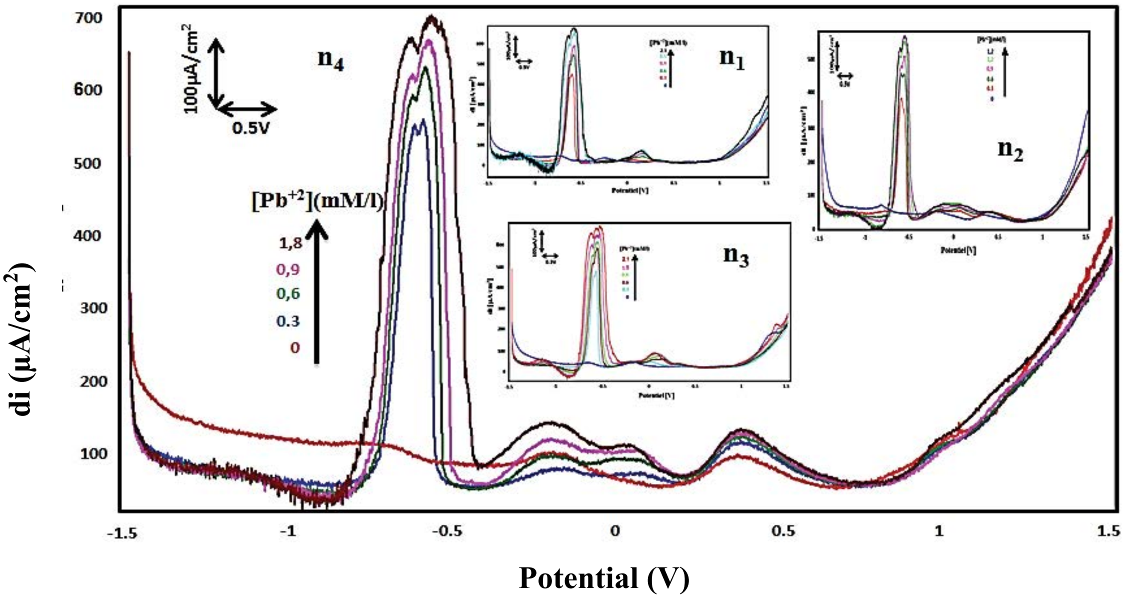

Fig. 3. Square wave voltammograms of CPE-1% EDTA at different concentrations of Pb^{2+} in 0.1 M NaCl, pH = 2, scan rate 100 mV/s, t_p = 10 min. The manipulation is repeated 10 times in the same way with the same operator. Four manipulations are shown (n_1, n_2, n_3 and n_4).

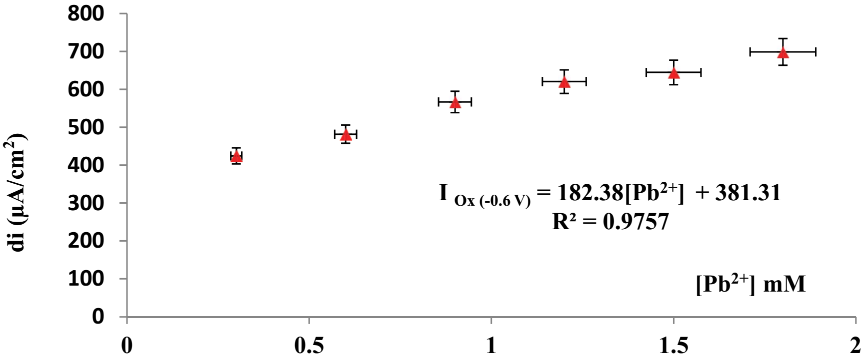

Fig. 4. Effect of concentration on the oxidation peak of CPE-1% EDTA obtained by SWV in 0.1 M NaCl, pH = 2, t_p = 10 min, scan rate 20 mV/s.

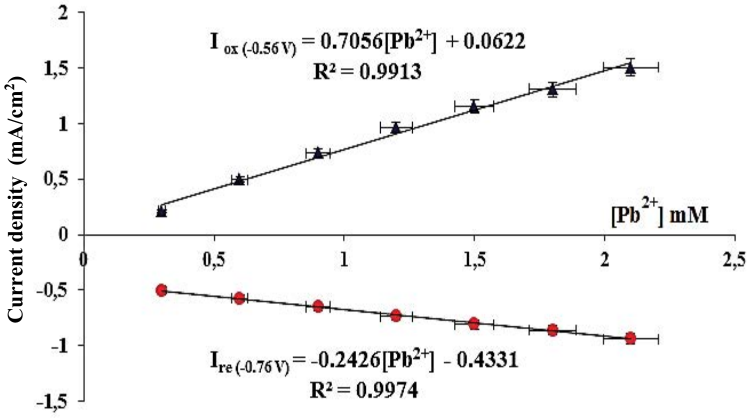

Fig. 5. Effect of concentration on redox peaks of CPE-1% EDTA obtained by CV in 0.1 M NaCl, pH = 2, t_p = 10 min, scan rate 100 mV/s.

Table 2
Representation of the equation of the regression line, the coefficient of determination, standard deviation (SD), LOD and LOQ of SWV and CV

Method		Equation of the regression line I en µA/cm^2	Coefficient of determination	SD (µA/cm^2)^2	LOD (10^{-9} mM)	LOQ (10^{-9} mM)
SWV		$I_{\text{ox }(-0.6\text{V})} = 182.38[\text{Pb}^{2+}] + 381.31$	$R^2 = 0.9757$	260.604	4.286	14.28
CV	Pic-ox	$I_{\text{ox }(-0.56\text{V})} = 0.7056[\text{Pb}^{2+}] + 0.0622$	$R^2 = 0.9913$	0.001875	7.973	26.57
	Pic Red	$I_{\text{red }(-0.79\text{V})} = -0.2426[\text{Pb}^{2+}] - 0.4331$	$R^2 = 0.9974$	7.53×10^{-5}	0.931	3.102

Concentrations are expressed in mmol/L.

points vs. 97.57% for the equation obtained by the SWV. The detection and the quantification limits of CPE-1% EDTA for the reduction peak are the lowest, they are respectively 9.31×10^{-10} mM and 3.102×10^{-9} mM.

3.2.2. Fidelity

Precision at a given level reflects the degree of agreement between the values found by applying an analytical procedure several times (n = 10 replicates) under specified conditions. Depending on the conditions under which the test is carried out, this characteristic is expressed in the form of replicability, repeatability or reproducibility for a method.

3.2.2.1. Repeatability

Here the repeatability is defined as the degree of agreement between individual results obtained for the same sample tested in the same laboratory "Laboratory of the Molecular Electrochemistry and Inorganic Materials Team, Faculty of Sciences and Techniques of Béni Mellal, Morocco" and for which the analyst is different. In the literature, the term "inter-technician precision" is often used. This validation parameter was determined from the following equation [26–28]:

$$\frac{t_{(0,975;n-1)}}{\sqrt{n}} \times S_2 \tag{4}$$

where S_2: standard deviation of a series of measurements referring to repeatability; $t_{(0.975;n-1)}$: student test at a 95% confidence level, corresponding to the probability of bilateral exceedance. The value of $t_{(0.975;n-1)}$ is obtained from Table 4. n = number of replicates.

3.2.2.2. Replicability

Replicability is the degree of the agreement between successive individual results obtained for the same sample tested in the same laboratory and under the same conditions.

This validation parameter was determined from Eq. (5) [26–28]:

$$\frac{t_{(0,975;n-1)}}{\sqrt{n}} \times S_2 \tag{5}$$

3.2.2.3. Reproducibility

Reproducibility is the degree of the agreement between individual results obtained for the same sample tested in different laboratories and under the following conditions: different analyst, different device and the same day.

3.2.2.4. Method of calculating repeatability, replicability and reproducibility

The repeatability, replicability and reproducibility terms are related to precision and expressed using a confidence interval at a given concentration, as a function of the standard deviation ($s(n)$), at a specified confidence level, usually 95%, and for a given number of determinations (n = 10 replicates).The two-sided confidence interval of the arithmetic mean of a series of measurements at a 95% confidence level is defined by the following double inequality [26–28]:

$$\bar{x} \mp \frac{t_{(0,975;n-1)}}{\sqrt{n}} \times S_2 \tag{6}$$

The coefficient of variation (CV*) is the ratio of the standard deviation to the mean. The higher the value of the coefficient of variation, the greater the dispersion above the mean. It is usually expressed as a percentage. However, the lower value of the coefficient of variation results in an accurate estimate [26–28].

$$\text{CV*} = \frac{S_2}{\text{I}_\text{m}} \times 100 \tag{7}$$

where I_m is the average current intensity observed.

The calculated values are shown in Table 3.

Generally the coefficient of variation (CV*) decreases with the increase in concentration for both used methods. However, this coefficient is even lower for the measurements made by the SWV, and indicating that the measurements are precise. The latter method has a lower repeatability uncertainty (RU) than the CV. Also, it is noticed that the repeatability uncertainty (RU) remains constant for all the measurements made by the $\text{CV}_{\text{Pic-red}}$. The percentage of measurements outside the confidence interval is 37.2% for the SWV, it is the lowest in comparison with the $\text{CV}_{\text{Pic-red}}$ (46.03%) and the $\text{CV}_{\text{Pic-ox}}$ (50%). This means that the SWV gives more faithful results than the CV.

3.2.3. Calculating accuracy and errors

The accuracy reflects the closeness of agreement between the standard value and an average value found

Table 3
Calculation of the mean observed current intensity (I_m), standard deviation (S_2), t_s (test student, the value is found using Table 4), repeatability uncertainty (RU), confidence interval (CI) = [lower estimate (LE), upper estimate (UE)] and coefficient of variation (CV*) or relative standard deviation (RSD), NM = number of measurements made, RM = the percentage of measurements rejected (outside the confidence interval)

Concentration (mM)			0.3	0.6	0.9	1.2	1.5	1.8	2.1
SWV	I_m (µA/cm^2)		424.3714	481.7286	566.7375	620.5	644.7	698.8286	–
	S_2		132.6716	83.40351	89.78901	55.71514	55.45106	67.9409	–
	t_s*		2.447	2.447	2.365	2.447	2.447	2.447	–
	RU (µA/cm^2)		122.7052	77.13816	75.07742	51.52977	51.28552	62.83711	–
	CI (µA/cm^2)	LE	301.6662	404.5904	491.6601	568.9702	593.4145	635.9915	–
		UE	547.0767	558.8667	641.8149	672.0298	695.9855	761.6657	–
	NM		7	7	8	7	7	7	–
	RM (%)		57.14	28.57	37.5	42.85	28.57	28.57	–
	RSD (%) (CV*)		31.2631	17.31338	15.84314	8.979071	8.601064	9.722112	–
CV$_{\text{Pic-ox}}$	I_m (mA/cm^2)		0.213222	0.491556	0.729667	0.962667	1.15375	1.307333	1.503556
	S_2		0.093615	0.186247	0.198836	0.206118	0.230077	0.27866	0.245669
	t_s*		2.306	2.306	2.306	2.306	2.365	2.306	2.306
	RU (mA/cm^2)		0.071958	0.143162	0.152839	0.158436	0.19238	0.214196	0.188838
	CI (mA/cm^2)	LE	0.141264	0.348394	0.576828	0.804231	0.96137	1.093137	1.314718
		UE	0.285181	0.634717	0.882505	1.121102	1.34613	1.52153	1.692393
	NM		9	9	9	9	8	9	9
	RM (%)		55.55	55.55	44.44	55.55	37.5	55.55	44.44
	RSD (%) (CV*)		43.90471	37.88922	27.25025	21.41112	19.94166	21.31513	16.33921
CV$_{\text{Pic-red}}$	I_m (mA/cm^2)		–0.50172	–0.57489	–0.651	–0.73522	–0.80811	–0.85978	–0.93874
	S_2		0.15749	0.148662	0.166389	0.192334	0.200486	0.214848	0.221195
	t_s*		2.306	2.306	2.306	2.306	2.306	2.306	2.306
	RU (mA/cm^2)		0.121058	0.114271	0.127898	0.147841	0.154107	0.165147	0.170025
	CI (mA/cm^2)	LE	–0.62278	–0.68916	–0.7789	–0.88306	–0.96222	–1.02492	–1.10877
		UE	–0.38066	–0.46062	–0.5231	–0.58738	–0.654	–0.69463	–0.76872
	NM		9	9	9	9	9	9	9
	RM (%)		55.55	44.44	44.44	55.55	55.55	33.33	33.33
	RSD (%) (CV*)		31.3899	25.8592	25.559	26.16	24.8092	24.9888	23.5628

by applying an analytical procedure several times [26–28]. The accuracy is verifies by the following equations [26–28]:

$$\text{Accuracy}(\%) = 100 - \left|\text{Relative error}\right| \tag{8}$$

$$\text{Relative error}(\%) = \frac{V_0 - V_S}{V_S} \times 100 \tag{9}$$

where V_S: certified value; V_0: average of observed values.

The systematic error or bias is the difference between the target value (I_{target}) and the observed mean value (I_m). The random error is calculated by the following equation [26–28]:

$$\text{RE}^* = \frac{S_2}{\sqrt{n}} \tag{10}$$

The results obtained are shown in Table 5. The systematic error (SE) and the relative error (RE) are the lowest in the case of CV$_{\text{Pic-red}}$. The accuracy of CV$_{\text{Pic-red}}$ is tending to 100% compared to the other methods. SWV has the lowest random error (RE*).

3.2.4. Test of χ^2

The χ^2 test (chi-square or chi-square) provides a method for determining the nature of a distribution. Our goal is to determine the uniform method.

χ^2 is calculated by the following equation:

The χ^2 test (chi-square) provides a method to determine the nature of the distribution. The current work aims to determine the uniform method. The χ^2 is expressed by [26–28]:

$$\chi^2 = \sum_{i=1}^{n} \frac{\left(\text{I}_{\text{m}} - I_{\text{target}}\right)^2}{I_{\text{target}}} \tag{11}$$

Based on Eq. (11), the values of χ^2 would be accepted unless the $\chi^2 > \chi^2$ (theoretical) (cf. Table 6), where n is large enough at this point the hypothesis is verified and the theoretical distribution is rejected with probability error of 5%.

From the results obtained it can be concluded that the methods used are uniform.

3.3. Interference

The "CPE-1% EDTA" occurred to simultaneously analyze the studied elements (lead, mercury, cadmium and cobalt) in an electrolytic solution of "0.1 M NaCl and pH = 2 with 100 mV/s".

To reveal the interference of Hg^{2+}, Cd^{2+} and Co^{2+} in the quantification of Pb^{2+}, we constantly increased the concentration of these four elements simultaneously in the solution. Seven concentrations have been tested in the following range (from 0.3 to 2.1 mM).

Each concentration is repeated 10 times ($n = 10$). The cyclic voltammograms for $n = 1$ is depicted in Fig. 6. From the obtained voltammograms, it is clear that the four studied elements are perfectly distinguishable. Each element keeps its own electrochemical identity in the absence and in the presence of the other studied elements. For instance, mercury is characterized by two oxidation peaks in the presence of other elements in the potential interval ranging from 0.1 to 0.5 V and two reduction peaks in the potential interval extended from 0 to –0.5 V. The same peaks are observed in the absence of other heavy metals (Fig. 8). The cobalt exhibits a single oxidation peak observed at –0.3 V in the absence and in the presence of other elements (Figs. 9 and 6). Here, it is worthy to mention that the prepared electrode is selective and able to simultaneously determine Pb^{2+}, Hg^{2+}, Cd^{2+} and Co^{2+}. The potentials of the redox peaks of cadmium, mercury, cobalt and lead are determined respectively from Figs. 7–10.

Table 4
Student's *t*-value for a bilateral interval at a 95% confidence level [26–28]

Degree of freedom	*t*(0.975)
1	12.706
2	4.303
3	3.182
4	2.776
5	2.571
6	2.447
7	2.365
8	2.306

Similar research [20,21] has shown that Pb(II) ions initially complex on the electrode surface during the preconcentration moment. Pb(II) ions reduce in the electrolyte solution after the application of a voltage of 0.398V(P3). In the anodic sweep direction, we note that there are two peaks,

Table 6
Calculation of χ^2

	SWV	$CV_{Pic\text{-}ox}$	$CV_{Pic\text{-}red}$
χ^2	2.317951	0.019642	–0.0005
χ^2 (theoretical)	12.592	15.507	15.507
Hypothesis	Accepted	Accepted	Accepted

Table 5
Calculation of mean observed current strength (I_m), target peak strength (I_{target}), systematic error (SE), relative error (RE), recovery rate (RR), accuracy (A), and random error (RE*)

Concentration (mM)		0.3	0.6	0.9	1.5	1.8	2.1
SWV	I_m (μA/cm^2)	424.3714	481.7286	566.7375	644.7	698.8286	–
	I_{target} (μA/cm^2)	436.024	490.738	545.452	654.88	709.594	–
	SE (μA/cm^2)	–11.6526	–9.00943	21.2855	–10.18	–10.7654	–
	RE (%)	–2.67246	–1.83589	3.90236	–1.55448	–1.51713	–
	RR (%)	78.70276	91.7668	112.9677	96.27883	96.7207	–
	A (%)	97.32754	98.16411	96.09764	98.44552	98.48287	–
	RE* (μA/cm^2)	50.14517	31.52356	31.74521	20.95853	25.67925	–
$CV_{Pic\text{-}ox}$	I_m (mA/cm^2)	0.213222	0.491556	0.729667	1.15375	1.307333	1.503556
	I_{target} (mA/cm^2)	0.27388	0.48556	0.69724	1.1206	1.33228	1.54396
	SE (mA/cm^2)	–0.06066	0.005996	0.032427	0.03315	–0.02495	–0.0404
	RE (%)	–22.1476	1.234771	4.650718	2.958237	–1.87248	–2.61694
	RR (%)	71.34459	101.4162	105.1062	103.1321	98.03582	97.27321
	A (%)	77.85243	98.76523	95.34928	97.04176	98.12752	97.38306
	RE* (mA/cm^2)	0.031205	0.062082	0.066279	0.081344	0.092887	0.08189
$CV_{Pic\text{-}red}$	I_m (mA/cm^2)	–0.50172	–0.57489	–0.651	–0.80811	–0.85978	–0.93874
	I_{target} (mA/cm^2)	–0.50588	–0.57866	–0.65144	–0.797	–0.86978	–0.94256
	SE (mA/cm^2)	0.004158	0.003771	0.00044	–0.01111	0.010002	0.003816
	RE (%)	–0.82189	–0.6517	–0.06754	1.394117	–1.14997	–0.40481
	RR (%)	94.2872	97.40924	99.79848	103.0533	97.70948	99.25106
	A (%)	99.17	99.34	99.93	98.60	98.85	99.59
	RE* (mA/cm^2)	0.05249	0.04955	0.05546	0.06682	0.07161	0.07373

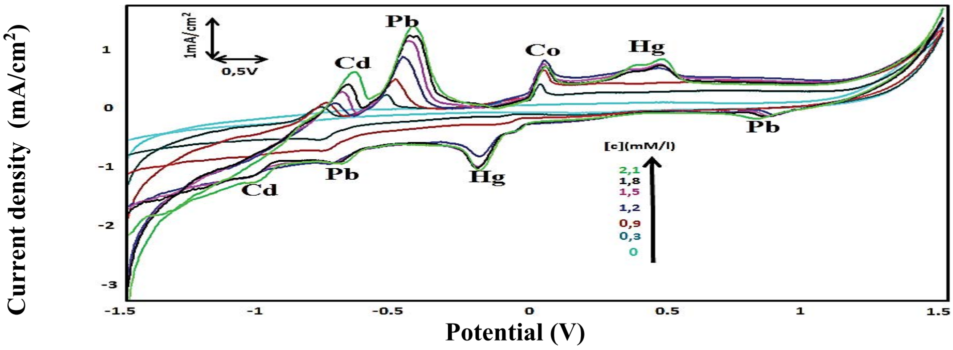

Fig. 6. Cyclic voltammograms of CPE-EDTA in 0.1 M NaCl at 100 mV/s, pH = 2 and 1% (w/w) EDTA/carbon graphite after 10 min preconcentration at different concentrations of Pb^{2+}, Hg^{2+}, Cd^{2+} and Co^{2+}.

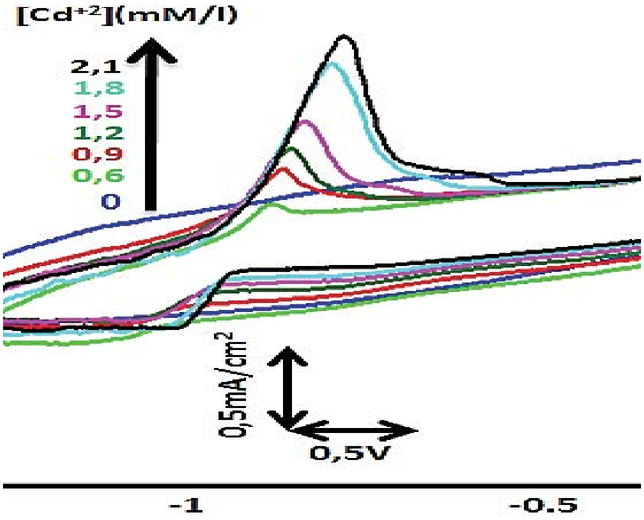

Fig. 7. Cyclic voltammograms of CPE-1% EDTA at various cadmium concentrations under the conditions listed in Table 1.

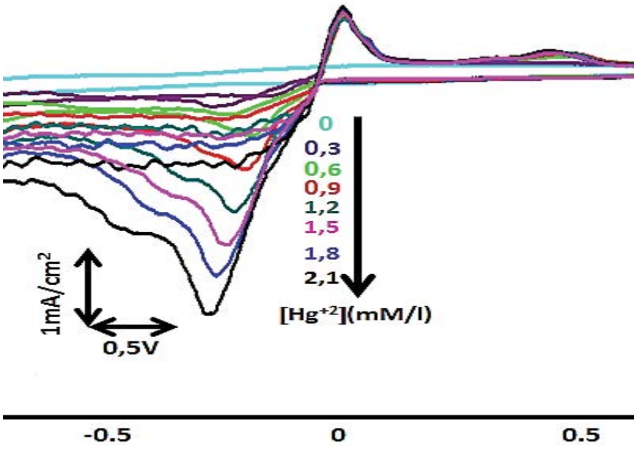

Fig. 8. Cyclic voltammograms of CPE-1% EDTA at various concentrations of mercury under the conditions listed in Table 1.

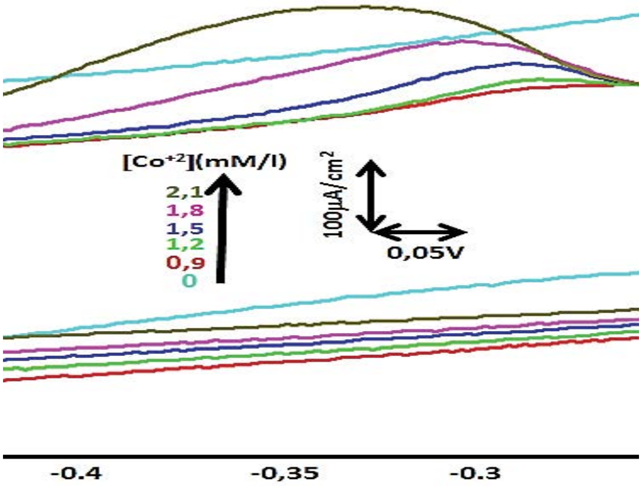

Fig. 9. Cyclic voltammograms of CPE-1% EDTA at various cobalt concentrations under the conditions listed in Table 1.

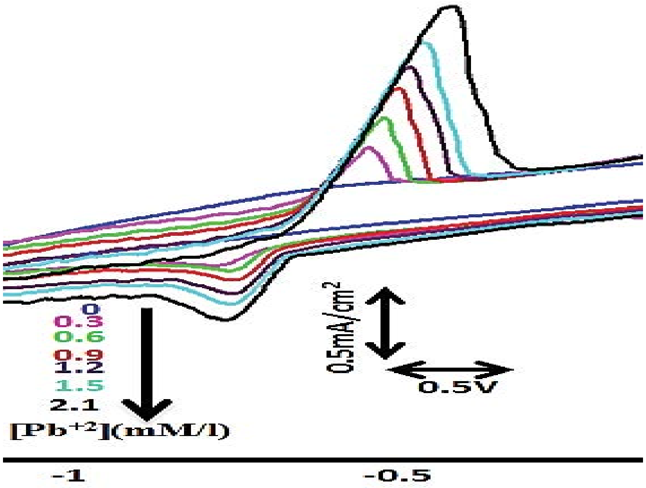

Fig. 10. Cyclic voltammograms of CPE-1% EDTA at various lead concentrations under the conditions listed in Table 1.

P1 and P2, respectively at 0.7 and 0.53 V which corresponds to the oxidation of the lead metal in the solution or in the organic matrix [20,21]. The same reaction mechanism can be attributed to other ions (Cd(II), Co(II) and Hg(II)).

The results of the statistical study of the simultaneous determination of these heavy metals are listed in Table 7. In the presence of heavy metals in the solution, a slight decrease in the slope of the calibration curve for the determination of lead is noted and a slight increase in reduction peaks is observed, as well as a decrease in the value of R^2 (from 0.997 to 0.975) is occurred. The detection limit value is increased from 0.931×10^{-9} to 5.59×10^{-9} mol/L. The presence of heavy metals resulted in a significant decrease in the coefficient of variation (CV*), it is going from 25.55% to 12% for the concentration of 0.9 mM and from 24.98% to 6.73% for the concentration of 1.8 mM. The relative error (RE) increased from –0.067% to –0.86% for 0.9 mM and from 1.51% to 1.86% for 1.2 mM. The method is linear in the concentration range between 0.6 and 2.1 mM. The accuracy of the lead determination is around 100% compared to the determination accuracy of other elements, the average accuracy of all measurements is about 98.23% vs. 98.82% associated to cadmium, 94.54% for mercury and 97.13% for cobalt. All these results show that heavy metals slightly affect the determination of lead in solution. The lowest detection limit is that of cobalt (1.2×10^{-9} mol/L) followed by cadmium, mercury and finally lead. For all studied metals, the method is linear in the concentration range (0.6–2.1 mM), except for mercury it is linear in the range (0.3–2.1 mM). Cadmium has a low systematic error (SE = 0.009 mA/cm^2) followed by lead (0.013 mA/cm^2) then mercury. Regarding the relative error, cadmium also shows a lower value of 1.70% followed by lead with 1.7%, cobalt and mercury. These observations are due to the interactions of metal ions with EDTA. The change in the electrochemical behavior of lead in the presence of different concentrations of mercury, cadmium and cobalt is explained by the competition between these elements at the active sites of the modified electrode.

3.4. Application: tap water

The elaborated electrode is tested in tap water from laboratory at the Faculty of Sciences and Techniques of Béni Mellal. Lead is added to the sample, and the peak observed for each concentration is used to find the added concentration based on the general equation given in Table 2. The analysis results of lead in drinking water are summarized in Table 8. Note that in the case of CV$_{\text{Pic-red}}$, the determined concentrations by the equation is almost the same as the added concentrations with a recovery rate equal to 100%. The found concentrations are very far from those added for CV$_{\text{Pic-ox}}$ and SWV. It is noted that some of the metallic lead oxidizes in the solution and some oxidizes in the organic matrix [20,21]. Thus to measure the amount of lead in the

Table 7
Statistical study of the simultaneous detection of heavy metals by CPE-1% EDTA

	Concentration (mM)	0.3	0.6	0.9	1.2	1.5	1.8	2.1
Lead	Systematic error (SE) in mA/cm^2	–	–0.021	0.006	0.014	0.019	–0.004	–0.015
	Relative error (RE) in %	–	3.07	–0.86	–1.86	–2.32	0.50	1.61
	Accuracy in %	–	96.9	99.1	98.1	97.6	99.4	98.3
	Coefficient of variation (CV*) in %	–	2.12	10.8	12.0	8.20	6.73	11.95
	LOD/LOQ	5.59×10^{-9} mol/L			1.8×10^{-8} mol/L			
	Linearity interval	(0.6–2.1) mmol/L						
Cadmium	Systematic error (SE) in mA/cm^2	–	0.016	0.0005	–0.03	0.003	0.001	0.008
	Relative error (RE) in %	–	–2.10	–0.06	3.35	–0.37	–0.17	–0.76
	Accuracy in %	–	97.8	99.9	96.6	99.6	99.82	99.2
	Coefficient of variation (CV*) in %	–	35.87	34.89	38.63	38.98	36.96	40.18
	LOD/LOQ	4.13×10^{-9} mol/L			1.37×10^{-8} mol/L			
	Linearity interval	(0.6–2.1) mmol/L						
Mercury	Systematic error (SE) in mA/cm^2	–0.017	0.034	–0.001	–0.033	0.017	–	–
	Relative error (RE) in %	9.98	–10.05	0.20	4.89	–1.96	–	–
	Accuracy in %	90.0	89.9	99.7	95.1	98.0	–	–
	Coefficient of variation (CV*) in %	116.02	44.04	73.52	72.51	75.63	–	–
	LOD/LOQ	5.08×10^{-9} mol/L			1.69×10^{-8} mol/L			
	Linearity interval	(0.3–1.5) mmol/L						
Cobalt	Systematic error (SE) in	–	2.490	0.219	–2.425	1.871	–9.730	7.610
	Relative error (RE) in %	–	6.50	0.31	–2.40	1.41	–5.94	3.90
	Accuracy in %	–	93.4	99.6	97.5	98.5	94.05	96.0
	Coefficient of variation (CV*) in %	–	63.18	63.92	66.74	67.00	63.70	71.09
	LOD/LOQ	1.20×10^{-9} mol/L				4.02×10^{-9} mol/L		
	Linearity interval	(0.6–2.1) mmol/L						

Table 8
Results of the determination of lead in tap water by the different electrochemical methods

Concentration of lead added	Method used to quantify lead					
	CV_{Pic-ox}		SWV		$CV_{Pic-red}$	
	Found	RR %	Found	RR %	Found	RR %
0 Mm	–0.06901	–	–1.9642	–	–1.7848	–
0.6 Mm	0.205	34.20	0.826	137.67	0.55234955	92.05
0.92 Mm	0.290	31.54	0.7273	79.05	0.94394064	102.60
1.22 Mm	0.485	39.82	0.6657	54.56	1.26957955	104.06

Recovery rate (RR)

Table 9
Detection limit of some prepared electrodes

Modified	Detection limit	References
NP-Al_2O_3/CPE	0.75×10^{-9} M	[18]
CA-RGO/GCE	2.0×10^{-11} M	[31]
ETO/GC	5.0×10^{-10} M	[32]
MMT-Ca/CPE	105×10^{-9} M	[33]
AuNP-GCE	10×10^{-9} M	[34]
CPE-EDTA	0.93×10^{-12} M	The present work

sample it is necessary to use both oxidation peaks and not just one. The SWV essentially takes into account the faradaic current that results from the redox reactions of the elements to be analyzed at the electrode-solution interface [30], so the SWV does not allow to give precise and accurate results since lead does not oxidize only in the organic matrix of the electrode. All used methods are able to confirm the non-presence of lead, since the negative value is always found in the case of a concentration of 0 mM Pb^{2+}.

The prepared electrode (CPE-EDTA) has a low detection limit (0.93×10^{-9} M) compared to the other sensors performed the work mentioned in Table 9.

4. Conclusion

The 1% EDTA modified carbon-paste electrode is capable of determining Pb^{2+}, Hg^{2+}, Cd^{2+} and Co^{2+} in tap water of our laboratory. The electrochemical responses obtained by $CV_{Pic-red}$ allowed determining a general equation for the analysis of Pb^{2+} in tap water, the predictive power of this method is greater than that of SWV with a recovery rate of 100%. The coefficient of variation (CV*) and repeatability uncertainty (RU) for measurements made by the SWV are lower compared to the CV which means that this method is faithful. The $CV_{Pic-red}$ specific SE and RE* are the lowest of all the used methods, indicating that this method is more accurate. The determination of lead is slightly affected by the presence of heavy metals. The simultaneous analysis of heavy metals showed that cadmium and lead have the lowest limit of detection, RE and SE. The use of the general equation for the analysis of lead does not apply to the analysis in a sample containing Hg^{2+}, Co^{2+} and Cd^{2+}. Thus, we have to find another equation that takes into account the interference with the other elements.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors would like to thank professor Ghizlane Laghlimi from "Faculty of Science and Technology of Béni Mellal, Sultan Moulay sliman University, Morocco", section "Analysis Techniques and Quality Control in the Agrifood Industry" for the fruitful discussion. We are grateful to Mr. Anas Laghlimi and Mrs. Fatna NÂna for their encouragement and support and Mrs. Ikram Ait Lebbad from "Lycée Ibnou Tofayl, Oulad yaich, Direction Provinciale du Ministère de l'Education Nationale, de la Formation Professionnelle, de l'Enseignement Supérieure et de la Recherche Scientifique de Béni Mellal, Maroc", section "Life and Earth Sciences" to accept the language revision. Also, we acknowledge the support of Catedra CONACYT project number 746, and the ECOSUR Chetumal for the SEM images, Mexico.

References

[1] M. Keshvari, R. Nedaeinia, M. Nedaeinia, G.A. Ferns, S.N. Nia, S. Asgary, Assessment of heavy metal contamination in herbal medicinal products consumed in the Iranian market, Environ. Sci. Pollut. Res., 28 (2021) 33208–33218.

[2] L. Lu, X. Han, J. Lin, Y. Zhang, M. Qiu, Y. Chen, D. Tang, Ultrasensitive fluorometric biosensor based on Ti_3C_2 MXenes with Hg^{2+}-triggered exonuclease III-assisted recycling amplification, Analyst, 146 (2021) 2664–2669.

[3] M. Xu, Z. Gao, Q. Wei, G. Chen, D. Tang, Label-free hairpin DNA-scaffolded silver nanoclusters for fluorescent detection of Hg^{2+} using exonuclease III-assisted target recycling amplification, Biosens. Bioelectron., 79 (2016) 411–415.

[4] Z. Qiu, J. Shu, G. Jin, M. Xu, Q. Wei, G. Chen, D. Tang, Invertase-labeling gold-dendrimer for in situ amplified detection mercury(II) with glucometer readout and thymine–Hg^{2+}–thymine coordination chemistry, Biosens. Bioelectron., 77 (2016) 681–686.

[5] Z. Qiu, D. Tang, J. Shu, G. Chen, D. Tang, Enzyme-triggered formation of enzyme-tyramine concatamers on nanogold-functionalized dendrimer for impedimetric detection of Hg(II) with sensitivity enhancement, Biosens. Bioelectron., 75 (2016) 108–115.

[6] N. Yan, Z. Zhu, L. Jin, W. Guo, Y. Gan, S. Hu, Quantitative characterization of gold nanoparticles by coupling thin layer chromatography with laser ablation inductively coupled plasma mass spectrometry, Anal. Chem., 87 (2015) 6079–6087.

[7] K.E. Kristian, S. Friedbauer, D. Kabashi, K.M. Ferencz, J.C. Barajas, K. O'Brien, A simplified digestion protocol for the analysis of Hg in fish by cold vapor atomic absorption spectroscopy, J. Chem. Educ., 92 (2015) 698–702.

[8] Y. Zhu, Y. Cai, Y. Zhu, L. Zheng, J. Ding, Y. Quan,. B. Qi, Highly sensitive colorimetric sensor for Hg^{2+} detection based on cationic polymer/DNA interaction, Biosens. Bioelectron., 69 (2015) 174–178.

[9] H.R. Cheng, Y. Qian, Intramolecular fluorescence resonance energy transfer in a novel PDI–BODIPY dendritic structure: synthesis, Hg^{2+} sensor and living cell imaging, Sens. Actuators, B, 219 (2015) 57–64.

[10] L. Fernández, I. Ledezma, C. Borrás, L.A. Martínez, H. Carrero, Horseradish peroxidase modified electrode based on a film of Co–Al layered double hydroxide modified with sodium dodecylbenzenesulfonate for determination of 2-chlorophenol, Sens. Actuators, B, 182 (2013) 625–632.

[11] F.C.M. de Oliveira, S.H.P. Serrano, Electrochemically active L-cysteine gold modified electrodes, Electrochim. Acta, 125 (2014) 566–572.

[12] M. Asadollahi-Baboli, A. Mani-Varnosfaderani, Rapid and simultaneous determination of tetracycline and cefixime antibiotics by mean of gold nanoparticles-screen printed gold electrode and chemometrics tools, Measurement, 47 (2014) 145–149.

[13] H. Beitollahi, A. Mohadesi, S. Mohammadi, A. Akbari, Electrochemical behavior of a carbon-paste electrode modified with 5-amino-3′,4′-dimethylbiphenyl-2-ol/carbon nanotube and its application for simultaneous determination of isoproterenol, acetaminophen and N-acetylcysteine, Electrochim. Acta, 68 (2012) 220–226.

[14] H. Bagheri, A. Afkhami, Y. Panahi, H. Khoshsafar, A. Shirzadmehr, Facile stripping voltammetric determination of haloperidol using a high performance magnetite/carbon nanotube paste electrode in pharmaceutical and biological samples, Mater. Sci. Eng., C, 37 (2014) 264–270.

[15] R.N. Adams, Carbon-paste electrodes, Anal. Chem., 30 (1958) 1576, doi: 10.1021/ac60141a600.

[16] H. Beitollahi, I. Sheikhshoaie, Electrochemical behavior of carbon nanotube/Mn(III) salen doped carbon-paste electrode and its application for sensitive determination of N-acetylcysteine in the presence of folic acid, Int. J. Electrochem. Sci., 7 (2012) 7684–7698.

[17] A. Afkhami, T. Madrakian, A. Shirzadmehr, M. Tabatabaee, H. Bagheri, New Schiff base-carbon nanotube–nanosilica–ionic liquid as a high performance sensing material of a potentiometric sensor for nanomolar determination of cerium(III) ions, Sens. Actuators, B, 174 (2012) 237–244.

[18] A. Moutcine, C. Laghlimi, O. Ifguis, M.A. Smaini, S.E. El Qouatli, M. Hammi, A. Chtaini, A novel carbon-paste electrode modified by NP-Al_2O_3 for the electrochemical simultaneous detection of Pb(II) and Hg(II), Diamond Relat. Mater., 104 (2020) 107747, doi: 10.1016/j.diamond.2020.107747.

[19] A. Moutcine, C. Laghlimi, Y. Ziat, M.A. Smaini, S.E. El Qouatli, M. Hammi, A. Chtaini, Preparation, characterization and simultaneous electrochemical detection toward Cd(II) and Hg(II) of a phosphate/zinc oxide modified carbon-paste electrode, Inorg. Chem. Commun., (2020) 107911, doi: 10.1016/j.inoche.2020.107911.

[20] C. Laghlimi, M. Ennachet, H. Saâdane, M.A. Smaini, J. Elmastour, A. Chtaini, Electrochemical chelation of heavy metals by 2-benzimidazole, J. Powder Metall. Min., 7 (2018) 188, doi: 10.4172/2168-9806.1000188.

[21] C. Laghlimi, Y. Ziat, A. Moutcine, M. Hammi, Z. Zarhri, O. Ifguis, A. Chtaini, A new sensor based on graphite carbon paste modified by an organic molecule for efficient, Chem. Data Collect., 31 (2021) 100595, doi: 10.1016/j.cdc.2020.100595.

[22] C. Laghlimi, Y. Ziat, A. Moutcine, M. Hammi, Z. Zarhri, R. Maallah, O. Ifguis, A. Chtaini, Analysis of Pb(II), Cu(II) and Co(II) in drinking water by a new carbon-paste electrode modified with an organic molecule, Chem. Data Collect., 29 (2020) 100496, doi: 10.1016/j.cdc.2020.100496.

[23] C. Laghlimi, M.A. Smaini, R. Maallah, S. Touzara, S. El Qouatli, A. Chtaini, Organic sensor for the detection of ammonium, J. Biosens. Bioelectron., 8 (2017) 239, doi: 10.4172/2168-9806.1000188.

[24] M.A. Smaini, R. Maallah, S. Touzara, C. Laghlimi, S. El Qouatli, Electrochemical detection and removal of mercury(II) at DNA modified carbon-paste electrode, Biol. Syst. Open Access, 6 (2017) 2, doi: 10.4172/2329-6577.1000173.

[25] M.A. Smaini, I. Smaini, M. Ennachete, C. Laghlimi, H. Saâdane, A. Moutcine, A. Chtaini, Electrochemical determination of adenosine by natural phosphate modified carbon-paste electrode: analytical application in serum, Sens. Bio-Sens. Res., 23 (2019) 100272, doi: 10.1016/j.sbsr.2019.100272.

[26] P. Konieczka, J. Namieśnik, Quality Assurance and Quality Control in the Analytical Chemical Laboratory: A Practical Approach, CRC Press, Boca Raton, 2018. Available at: https://doi.org/10.1201/9781315295015

[27] W.G. Miller, J.H. Nichols, Chapter 5 – Quality Control, W. Clarke, M.A. Marzinke, Eds., Contemporary Practice in Clinical Chemistry, Academic Press, 2020, pp. 77–95. Available at: https://doi.org/10.1016/B978-0-12-815499-1.00005-3

[28] N.T. Constantine, J.D. Callahan, D.M. Watts, Retroviral Testing: Essentials for Quality Control and Laboratory Diagnosis, CRC Press, Boca Raton, 2020. Available at: https://doi.org/10.1201/9780429279867

[29] Q. Wang, Y. Li, Y. Liu, J. Ren, Y. Zhang, G. Qu, T. Wang, Effective removal of the heavy metal-organic complex Cu- EDTA from water by catalytic persulfate oxidation: performance and mechanisms, J. Cleaner Prod., 314 (2021) 128119, doi: 10.1016/j.jclepro.2021.128119.

[30] G.C. Barker, The influence of interactions between electrode processes on the structure of the equivalent electrical circuit for the electrode-solution interface, J. Electroanal. Chem. Interfacial Electrochem., 40 (1972) 45–62.

[31] M.L. Yola, N. Atar, M.S. Qureshi, Z. Üstündağ, A.O. Solak, Electrochemically grafted etodolac film on glassy carbon for Pb(II) determination, Sens. Actuators, B, 171 (2012) 1207–1215.

[32] V.K. Gupta, M.L. Yola, N. Atar, Z. Ustundağ, A.O. Solak, A novel sensitive Cu(II) and Cd(II) nanosensor platform: graphene oxide terminated p-aminophenyl modified glassy carbon surface, Electrochim. Acta, 112 (2013) 541–548.

[33] A.M. Beltagi, E.M. Ghoneim, M.M. Ghoneim, Simultaneous determination of cadmium(II), lead(II), copper(II) and mercury(II) by square-wave anodic stripping voltammetry at a montmorillonite-calcium modified carbon-paste electrode, Int. J. Environ. Anal. Chem., 91 (2011) 17, doi: 10.1080/03067310902962577.

[34] M.A. Kamyabi, A. Aghaei, Electromembrane extraction and anodic stripping voltammetric determination of mercury(II) using a glassy carbon electrode modified with gold nanoparticles, Microchim. Acta, 183 (2016) 2411, doi: 10.1007/s00604-016-1884-6.