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Carbon paste electrode modified with 5-Br-PADAP as a new electrochemical sensor for the detection of inorganic mercury(II)

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Abstract

A differential pulse voltammetry (DPV) method was developed for the sensitive and selective determination of mercury(II) with a 2-(5'-Bromo-2'-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) modified carbon paste electrode (CPE). The optimized experimental conditions, for determination of mercury(II) with cathodic differential pulse voltammetry at 5-Br-PADAP-CPE, include: supporting electrolyte: acetate buffer (0.1 $mol.L^{-1}$), pH: 4.7, amount of mixed 5-Br-PADAP in the CPE: 0.2% (w/w), open circuit accumulation time: 120 s. The monitored current was linear over the range of $3\ 10^{-8} – 1.8\ 10^{-7}$ and the detection limit is 10^{-8} $mol.L^{-1}$. The relative standard deviation for 10 successive determinations of Hg(II) was 1.6%. A study of interfering substances was also performed and the method was applied to the direct determination of mercury in real samples.

1. Introduction

Heavy metal contamination in soils and groundwater is a common problem encountered at many hazardous waste sites. Once released into the soil matrix and waters, most heavy metals are strongly retained and their adverse effects can last for a long time. Metal contaminants such as lead cadmium, copper, zinc, mercury, and also cyanide are among the most frequently observed. They are present at elevated concentration at many National Priority List sites. Heavy metals are toxic to people and pose a great risk for safe ground water supply. Sites located around gold mining ore are described as critical environments frequently subjected to heavy metal and cyanide contaminations. Degraded environment due to gold mining activities have recently increased. Contaminated soil and water with mercury due to both artisanal small scale mining and large-scale industrial mining, therefore have been in resident concern around the area [1].

Mercury is one of the most harmful pollutants and it has become widespread into the environment mainly as a result of anthropogenic activities. [2,3]. Mercury has no beneficial biological function, and its presence in living organisms is associated with cancer, birth defects, and other undesirable outcomes

[4,5]. One of the routes of incorporation of mercury into the human body is drinking water [6]. The acceptable limit of inorganic Hg(II) in drinking water has been set by the World Health Organization (WHO) as 30 nM [7]. According to the above health effects and environmental impacts, control of mercury is becoming increasingly important, especially in water sources.

The detection of inorganic Hg(II) can be achieved with various analytical methods, which include visible spectrophotometry or colorimetric assay [8], gas chromatography [9], atomic fluorescence spectrometry [10], atomic emission spectroscopy [11], inductively coupled plasma [12] X-ray fluorescence spectrometry [13] cold vapor atomic fluorescence spectrometry [14] high performance liquid chromatography [15], enzyme-linked immunosorbent (ELISA) [16], and electrochemiluminescent immunoassay [17]. Generally, these techniques are reliable and have good sensitivity. However, they may need extensive sample preparation or a speciation/separation step prior to analysis (which is complicated) and may face difficulties in the detection of trace or ultra-trace levels of Hg(II) owing to matrix interferences and insufficient sensitivity. In addition, they are all limited with respect to *in-situ* analysis and may require professional training of the user [18].

To overcome these limitations, attention has turned to voltammetry, in particular adsorptive cathodic stripping voltammetry, due to its ability to achieve high sensitivity and selectivity. Additionally, it is user-friendly, allows rapid analysis, is relatively inexpensive and highly suitable for in situ applications [19-21]. Selectivity of determination of metal ions by adsorptive stripping voltammetry was improved by their complexation or chelation with specific ligands [22]. Cathodic stripping voltammetry technique was successfully used for the determination of metal ions with different ligands at mercury, glassy carbon, carbon paste, carbon film and bismuth film electrodes [23]. The determination of Hg(II) has been performed by chemically modified carbon paste electrodes (MCPE) by organic compounds and nanomaterials [24-26]. Mercury has been preconcentrated by complexation with poly (Eriochrome Black T) [27], poly(EDTA-like) [28] or clay nanoparticle [29]. The detection limits obtained vary to 0.012 ppb to 20 ppb [19].

2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) is a ligand capable of forming complexes with several metal ions as Hg(II) [30,31]. It was successfully used as a complexing agent for cathodic stripping voltammetric determination of Mn(II) [32], Cu(II) [33], Fe(III) [34], V(V) [35,36], Bi(III) [37], Cr(III) [38], Co(II)[39] and Ti(IV)[40] at the mercury electrodes. However, 5-Br-PADAP ligand has never been used before as a complexing agent for voltammetric determination of mercury(II) ions using the carbon paste electrode (CPE).

This work aimed to describe a simple and precise differential pulse voltammetry (DPV) method for the determination of Hg(II) in water samples as 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol complex using a modified carbon paste electrode.

2. Methodology

2.1 Chemicals and reagents

Graphite powder (99.9995%) was purchased from Alfa Aesar. Mineral oil, ethanol and 2-(5'-Bromo-2'-pyridylazo)-5-diethylaminophenol (5-Br-PADAP, 97 %) were purchased from Sigma Aldrich. Stock solution of 5-Br-PADAP was prepared by dissolving the required amount in ethanol. Mercury(II) nitrate monohydrate ($Hg(NO_3)\cdot 2H_2O$) was purchased from J.T. Baker. Acetic acid (99.8%) and sodium nitrate used for preparation of acetate buffer come respectively from Merck and VWR. Other solutions tested as electrolytes, prepared with NaCl, $NaNO_3$ and sodium tetraborate ($Na_2B_4O_7$), come from Fisher Chemical. Nitric acid (HNO_3) was provided by Sigma Aldrich. Metal ions used in interference studies were purchased from Prolabo for Manganese(II) sulfate, from Fluka for Aluminium(III) nitrate nonahydrate, from Sigma Aldrich for Zinc(II) sulfate heptahydrate and for Copper(II) nitrate hydrate. The supporting electrolytes and other solutions were prepared with Milli-Q water. Tap water samples were collected from laboratory.

2.2 Apparatus

The electrochemical experiments (cyclic and DPV measurements) were carried out using a Palmsens potentiostat (Palm Instrument BV) running with the PStrace software. The conventionnal three-electrode system was used for the electrochemical experiments, which comprised a bare or modified carbon paste electrode as working electrode, an Ag/AgCl, 3 mol.L^{-1} KCl as reference electrode (Metrohm) and a platinum wire as the counter electrode (Radiometer Analytical).

2.3 Preparation of working electrode

The fabrication of Carbon Paste Electrode (CPE) and 5-Br-PADAP modified CPE (5-Br-PADAP-CPE) were as follows:

i. The CPE was prepared by mixing 1 g of graphite powder and 0.3 mL of mineral oil using a mortar and pestle until homogenous paste was obtained. The paste was then incorporated into the electrode cavity of the body of an electrode dedicated to carbon paste, and polished on smooth paper.
ii. The 5-Br-PADAP-CPE was prepared in the same manner by thoroughly mixing appropriated amounts of 1 g of graphite powder with 5-Br-PADAP and 0.3 mL of mineral oil until a uniformly wetted paste was obtained. After that, the paste was inserted into the cavity of the electrode. The electrode surface could be renewed by simple extrusion of a small amount of paste from the tip of the electrode. Otherwise, before each use the electrode surface, it was rubbed with a piece of paper until a smooth surface was observed.

2.4 Mesurements and procedure

i. When analysis with bare CPE, 40 mL of supporting electrolyte 0.1 mol.L^{-1} acetate buffer (pH 4.7) containing Hg(II) ions and ligand 5-Br-PADAP were introduced into the voltammetric cell. Solution was stirred for a selected time. At the end of accumulation time, stirring was stopped and a 30 s rest period was allowed for the solution to become quiescent. The voltammogramm was then recorded by scanning the potential in the cathodic direction using cyclic and differential pulse voltammetry.

ii. The same previous experiences were repeated when using 5-Br-PADAP-CPE, except the step of adding 5-Br-PADAP in supporting electrolyte. A new surface electrode was used before the commencement of each experiment. All the mesurements were carried out at room temperature. To avoid contamination, the voltammetric medium was changed after each experiment.

2.5 Differential-pulse parameters

Differential-pulse parameters (scan rate, pulse amplitude ΔE, scan increment a, duration θ) used to obtain intense and well-defined peak for mercury(II) determination at 5-Br-PADAP-CPE by differential pulse voltammetry, were as follow: scan rate 25 mV.s^{-1}, $\Delta E = 70$ mV; $a = 4$ mV, $\theta = 10$ ms.

3. Results and Discussion

3.1 *Mercury(II) and 5-Br-PADAP complex formation in aqueous solution*

5-Br-PADAP, a pyridylazo compound, is a well-known analytical chelating reagent [31]. It is endowed with two redox groups: an azo and a phenol group [41], as shown in Figure 1.

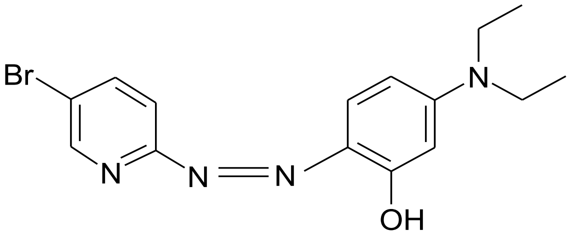

Figure 1. Structure of 5-Br-PADAP [42]

The molecular structure of 5-Br-PADAP can change as pH changes. It exists in different forms at different pH value [42]:

$$\mathbf{H_3L^{2+}} \overset{\text{pKa} = 0.63}{\rightleftharpoons} \mathbf{H_2L^{+}} \overset{\text{pKa} = 2.77}{\rightleftharpoons} \mathbf{HL} \overset{\text{pKa} = 11.2}{\rightleftharpoons} \mathbf{L^{-}}$$

Therefore, for optimal complexation of 5-Br-PADAP with mercury(II), a pH value above 2.8 must be chosen. The formation of the complex between 5-Br-PADAP and Hg(II) causes a change in color of the reagent phase from orange to purple.

Relatively strong complex was formed between Hg(II) and the ligand with a corresponding bathochromic shift. Figure 2 shows the structure of the complex between 5-Br-PADAP and Hg(II).

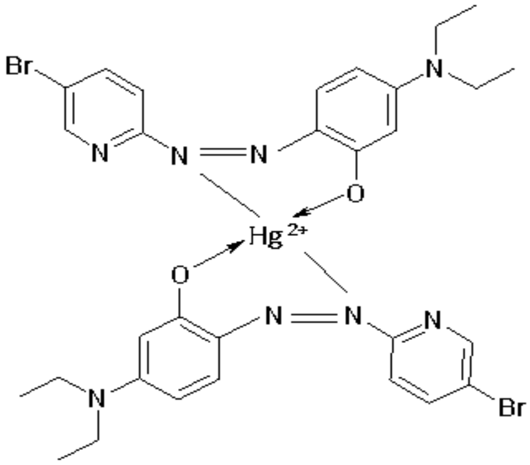

Figure 2. Structure of [(Hg^{2+})-(5-Br-PADAP$)_2$] complex [43].

3.2 *Electrochemical behavior Hg(II) ions and 5-Br-PADAP in aqueous solution*

Fisrt, cyclic voltammogramms of 5-Br-PADAP in the presence and in absence of Hg(II), in 0.1 mol L^{-1} acetate buffer (pH 4.7) recorded at bare carbon paste electrode, are shown in Figure 3. The reductions of the azo group are observed at -0.05 V and -0.38 V (Figure 3a). This is in good agreement with literature. Azo-ligand such as 5-Br-PADAP exhibits two reductions peaks when pH is above to 3.5 [41]. In oxidation a small redox wave near 0.15 V appeared after reduction. This wave belongs to the reduct products at the surface of electrode according to same authors. The peaks observed in the presence of the ligand alone are due to the reduction of the azo group. The reduction mechanism involves the formation of hydrazo derivatives followed by the cleavage of the N=N bond and the final formation of amines, according to references [41, 44-46]:

$$-\mathrm{N}=\mathrm{N}- \; +2\mathrm{H}^+ + 2\mathrm{e}^- \;\rightarrow\; -\mathrm{NH}-\mathrm{NH}-$$

$$-\mathrm{NH}-\mathrm{NH}- \; +2\mathrm{H}^+ + 2\mathrm{e}^- \;\rightarrow 2(-\mathrm{NH}_2)$$

With Hg(II) ions, the voltammogramm exhibits a large reduction peak, around -0.34 V, and no oxidation peak return (**Figure 3b**), except oxidation observed in case of 5-Br-PADAP only. In the presence of some metal ions, like Hg(II) ions in this study, the new peak that appears, at more cathodic potentials, is related to the reduction of the ligand involved in the complexation, allowing the detection of the metal. The potential shift is likely due to the involvement of the azo group in complexation, with a consequent stabilization of the nitrogen electrons in the ring, which makes it less available to reduction. Of the two possible reaction mechanisms, i.e., ligand reduction inside the complex or after complex dissociation, the first one seems to be most likely, since evidence of the presence of metal-hydrazo complexes was found [44-46].

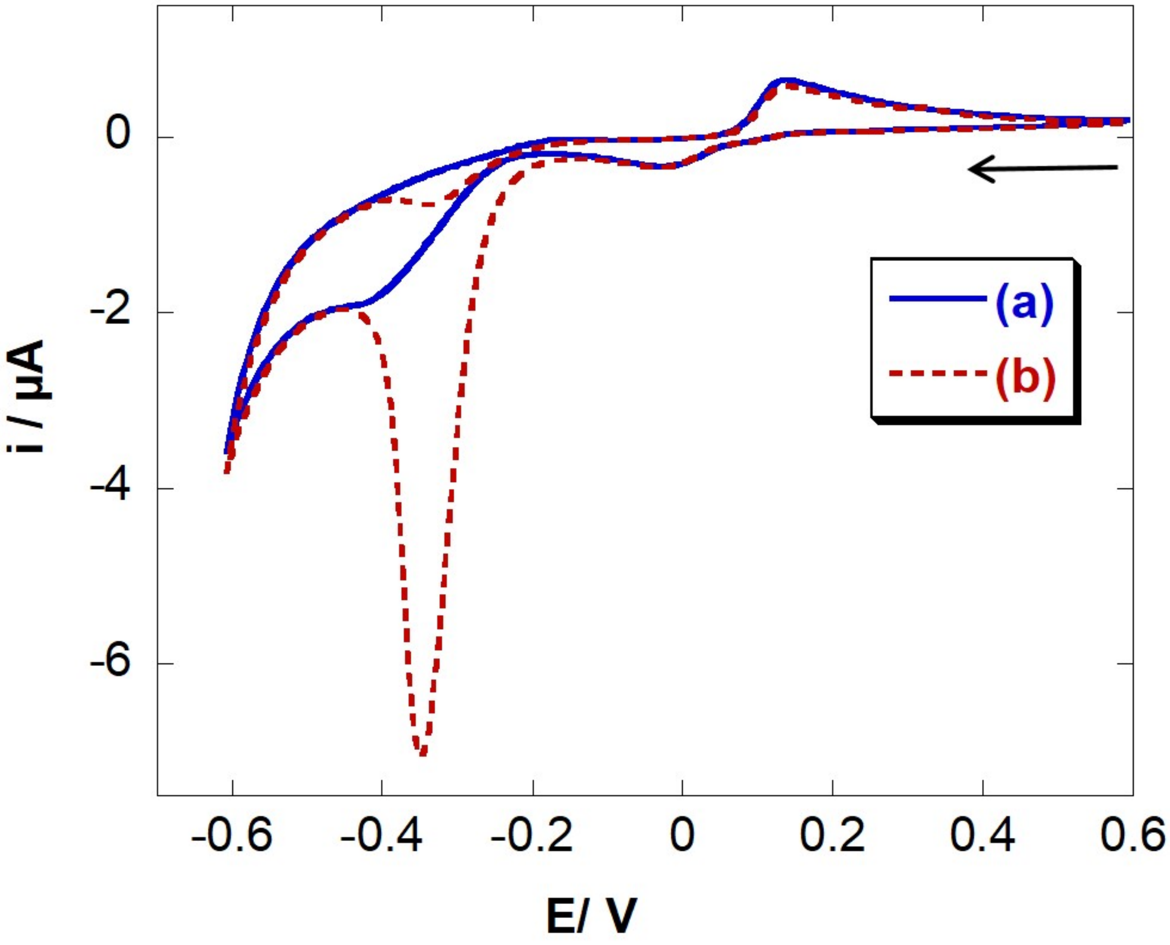

Figure 3. Cyclic voltammogramms obtained at bare CPE in 0.1 mol L^{-1} acetate buffer pH 4.7, scan rate 25mV.s^{-1}
(a) 2 10^{-5} M 5-Br-PADAP
(b) 2 10^{-5} M 5-Br-PADAP with 10^{-5} M of Hg(II)

3.3 Electrochemical behavior of Hg(II) ions at modified 5-Br-PADAP-carbon paste electrode

As shown in **Figure 4**, when using a 5-Br-PADAP-carbon paste electrode (1% modification), we have the same behavior as when the ligand is in solution. The potential of the reduction peak, in the presence of Hg(II) ions, is located at -0.34 V. Inserting ligand in carbon paste electrode is easier and working with this electrode is simple and permit easier on-line measurements **[47, 48]**. So, this modified carbon paste electrode was used for further measurements.

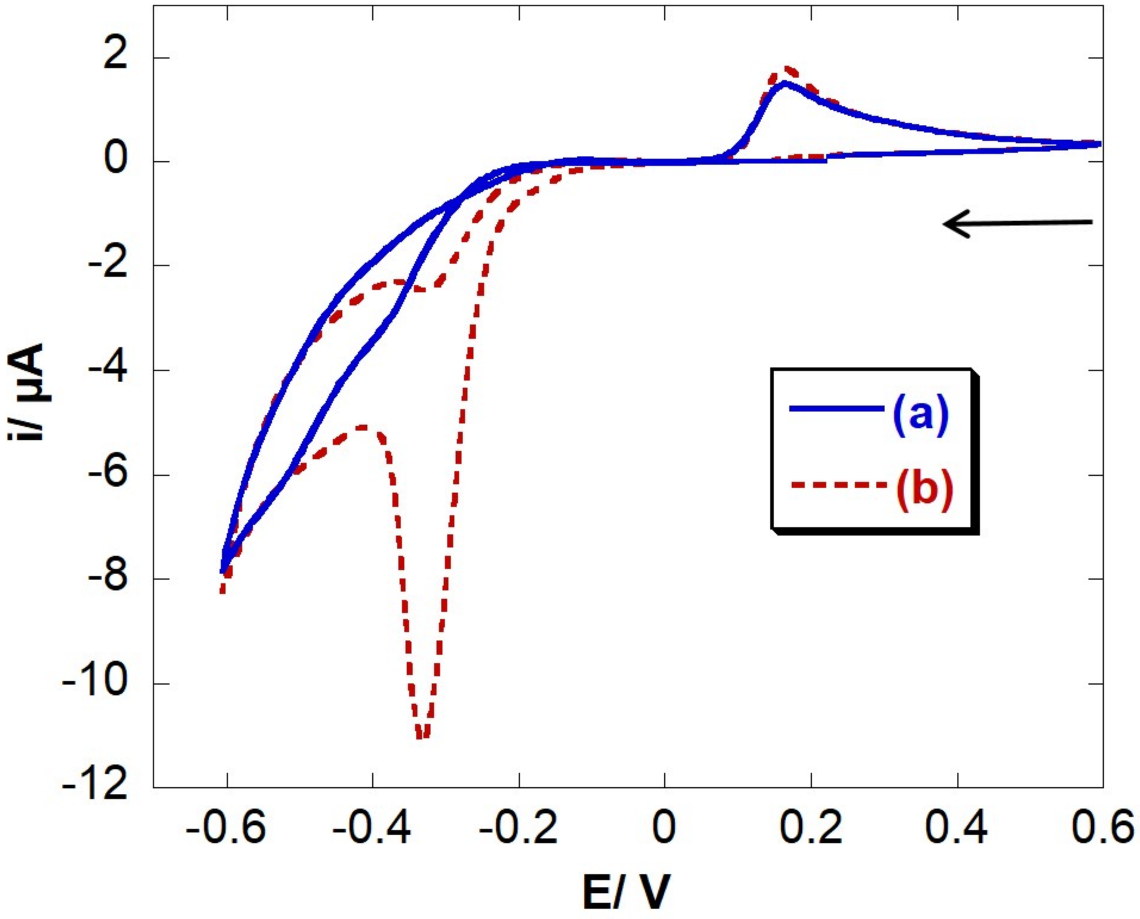

Figure 4. Cyclic voltammogramms obtained at 5-Br-PADAP-modified CPE (1%) in 0.1 mol.L^{-1} acetate buffer pH 4.7, scan rate 25mV.s^{-1}.
(a) 5-Br-PADAP-CPE (1%)
(b) 10^{-5} mol.L^{-1} of Hg(II) with 5-Br-PADAP-CPE (1%)

The effect of scan rate was studied in the range: 5 - 100 mV.s^{-1}. **Figure 5** shows the cyclic voltammogramms response recorded by immersing the 5-Br-PADAP-CPE in the presence of 10^{-5} mol.L^{-1} Hg(II). Percentage of mixed amount of 5-Br-PADAP was maintained at 1%. On raising the scan rate, the potential of the cathodic peak was shifted cathodically confirming the irreversible nature of the electrochemical reduction process of Hg-5-Br-PADAP complex. By contrast to surface electrochemical process where the current is linearly related to the potential scan rate, we found that the reduction peak current increased linearly with the square root of the potential scan rate between 5 and 100 mV.s^{-1} (**Inserted in Figure 5**) as for a process controlled by diffusion **[49, 50]**. It can be attributed to the free motion of the Hg(II) ions in the microenvironment of the modified electrode **[51]**.

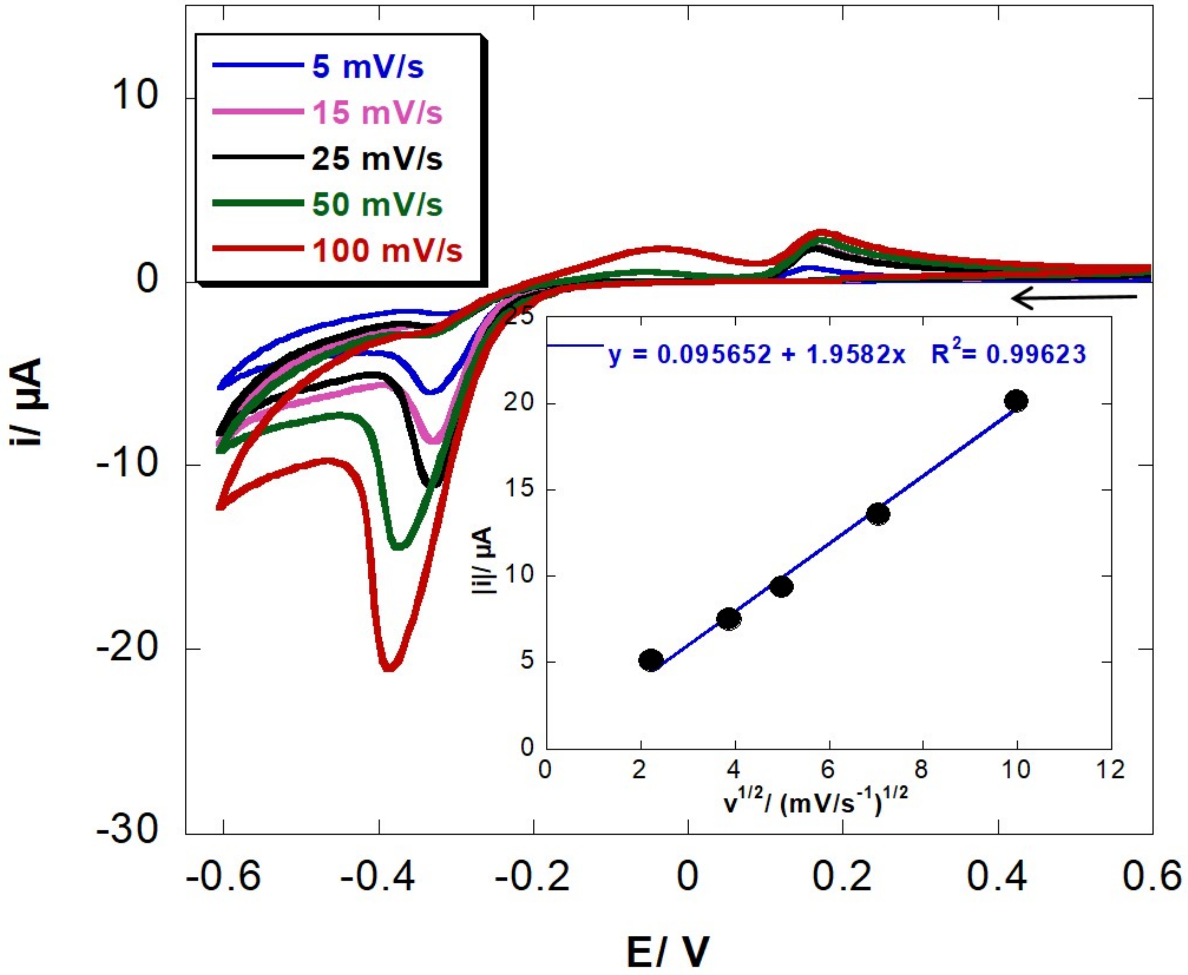

Figure 5. Cyclic voltammogramms obtained at 5-Br-PADAP-modified CPE (1%) at different scan rates: 100, 50, 25, 15, 5 mv/s. **Inserted**: relation between reduction peak and current square root of the scan rate

To confirm irreversible process of the reduction, the dependence of pH was investigated over pH range (pH 4–6) by recording differential pulse voltammogramms of Hg(II)-5-Br-PADAP complex in acetate buffer 0.1 mol.L^{-1}. The plot of the change of the cathodic peak potential vs pH was linear (**Figure 6**). On increasing the pH of the solution, the cathodic peak current was shifted to more negative potential confirming the irreversible nature of the electrochemical reduction process and the electrode reaction involves hydrogen ions. The observed dependence of the reduction peak of the complex, on the pH can be explained by a direct exchange of four electrons in two successive two-electrons steps with splitting of the N=N group to form –NH_2–NH_2 **[44-46]**.

3.4 Optimisation of analytical parameters

3.4.1 Supporting electrolyte

Various electrolytes have been tested: HNO_3 (0.1 mol.L^{-1}, pH 1), $NaNO_3$/HNO_3 (0.1 mol.L^{-1}, pH 4.7), Acetate buffer (0.1 mol.L^{-1}, pH 4 - 6), NaCl (0.1 mol.L^{-1}, pH 5.4), $NaNO_3$ (0,1 mol.L^{-1}, pH 6.2), Borate buffer (pH 8.4). Acetate buffer (0.1 mol.L^{-1}, pH 4.7) gave us better cathodic peak current. It was chosen as supporting electrolyte for further experiments.

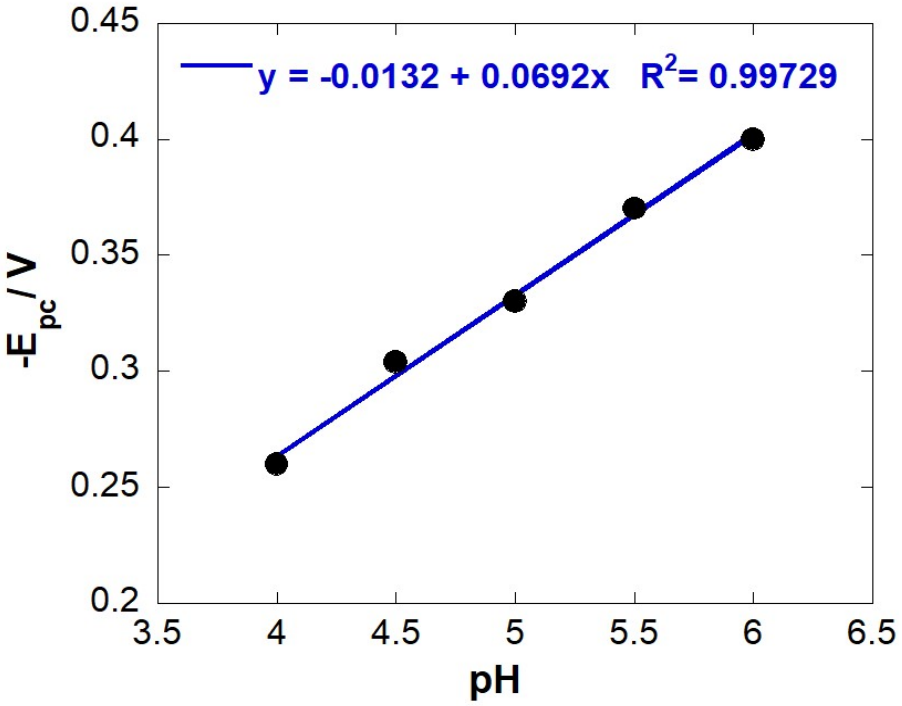

Figure 6. Relation between cathodic peak potential and the pH.

3.4.2 Effect of amount of mixed 5-Br-PADAP

To found which amount of 5-Br-PADAP will give us better an well-defined peak, the influence of the content percentage of the modifier in carbon paste mixture was studied by differential pulse cathodic voltammetry of 10^{-5} mol.L^{-1} of Hg(II) in 0.1 mol.L^{-1} acetate buffer (pH 4.7). Percent of 5-Br-PADAP were varied from 0% to 10 %. The voltammetric cathodic response, of the 5-Br-PADAP-carbon paste modified electrode for the different percent of 5-Br-PADAP in the carbon mixture (0%, 0.1%, 0.2%, 0.5%, 1%, 2%) is illustrated in **Figure 7**. Cathodic current reached maximum with 1% of 5-Br-PADAP in the paste, but with this composition the reduction of the free ligand take place and affect the peak current response. This reduction of free ligand increase when we increase amount of 5-Br-PADAP to 2 %. At 5% and 10% amounts of 5-Br-PADAP, peak currents are completely displaced because reduction of free ligand 5-Br-PADAP dominates reduction of complexed ligand. With 0.2% composition of 5-Br-PADAP we have better current peaks and therefore, a quantity of 0.2% of 5-Br-PADAP (w/w) in weight in the composition of the electrode has been chosen as the best for other experiences. We chose 0.2% also because it permits lower consumption of modifier 5-Br-PADAP despite the maximum peak current is 1 %.

3.4.3 Effect of open circuit-accumulation time

The effect of open circuit accumulation time on the response was studied ranging from 0 s to 240 s as illustrate in **Figure 8**. The peak currents of the complex increase with accumulation time from 0 to 120 s and then become constant. This phenomenon is explained by the surface saturation where the equilibrium between the complexed metal ions and the ions in solution take place. Thus, the accumulation time of 120 s was chosen for further experiments.

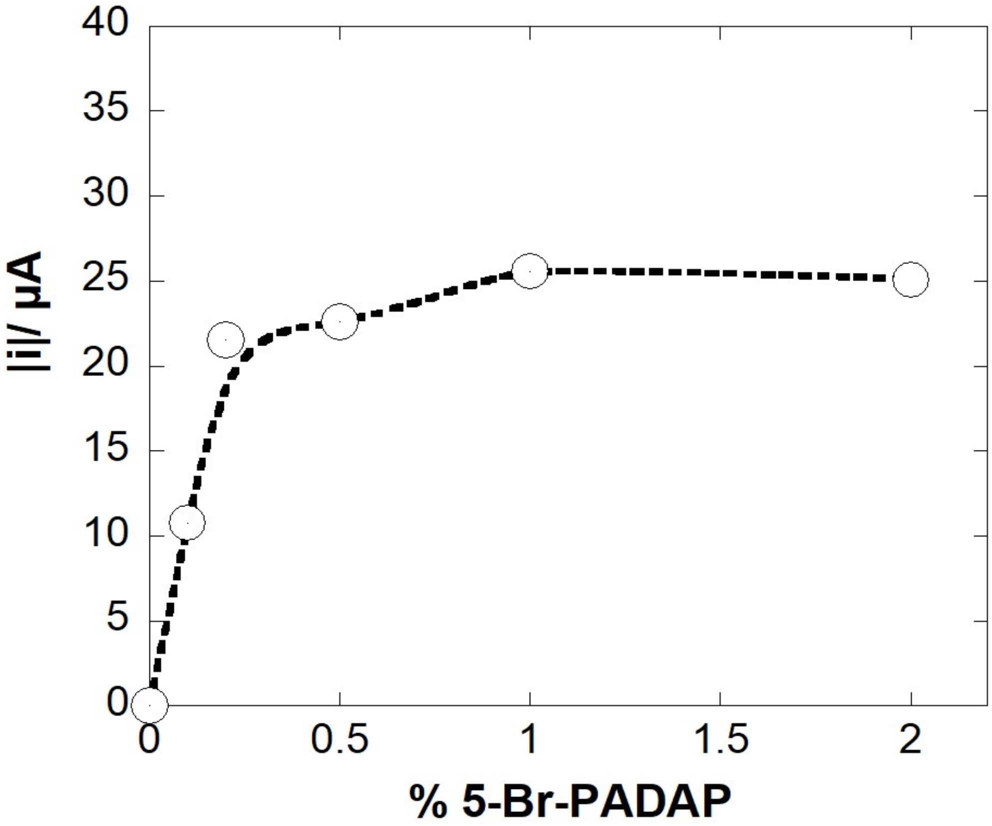

Figure 7. Influence of the content of 5-Br-PADAP in carbon paste mixture on cathodic peak currents (0.1 M acetate buffer (pH 4.7) containing 10^{-5} mol.L^{-1} Hg(II)).

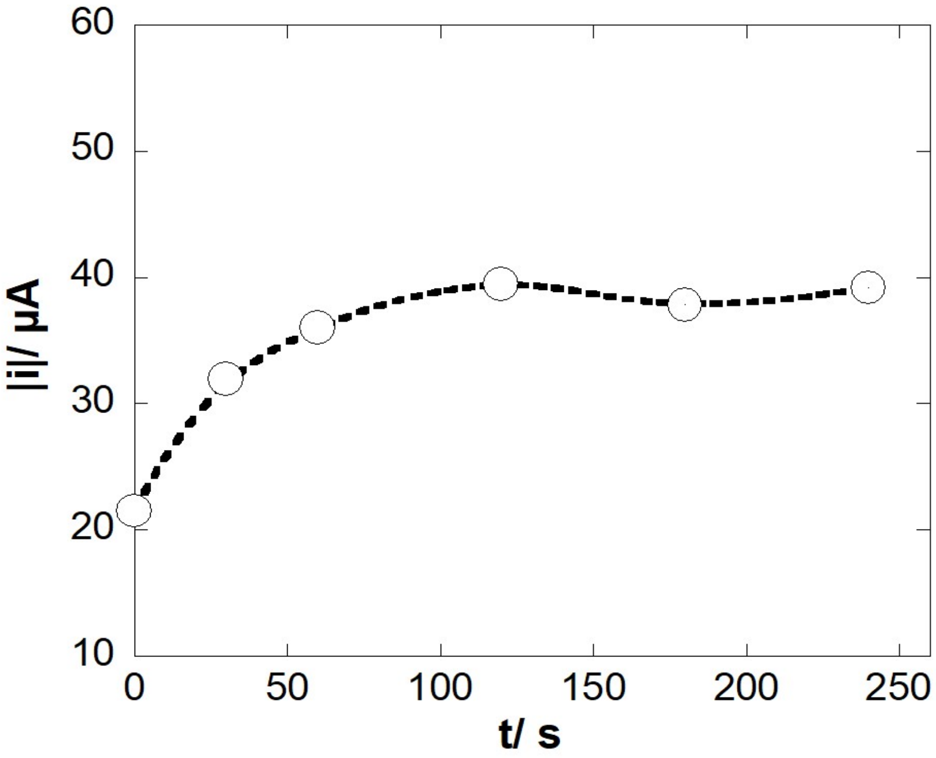

Figure 8. Effect of open-circuit accumulation time on the cathodic peak intensity of 10^{-5} mol.L^{-1} Hg(II) at 0.2% 5-Br-PADAP-CPE in 0.1 mol.L^{-1} acetate buffer solution (pH 4.7)

3.5 *Electrochemical determination of Hg(II) with 5-Br-PADAP modified carbon paste electrode*

Figure 9 presents the differential voltammetry curves and calibration curve, for different concentration of Hg(II) in the range 3 10^{-8} – 1.8 10^{-7} mol.L^{-1}. The cathodic peak current of Hg(II) (|ipc|) increases with increasing its concentration. A linear equation was obtained: y = -0,50048x + 0,83 with the correlation coefficients of R^2 = 0.9982. The relative standard deviation (%RSD) for ten repetitions analysis in 0.1 mol L^{-1} acetate buffer pH 4.7, containing 10^{-5} mol.L^{-1} of Hg(II) was 1.6%.

The limit of detection (LOD) was calculated based on statistical analysis. The formula utilized was LOD = kS_b/m, where LOD is the limit of detection, k is the signal-to-noise ratio (S/N=3), and S_b is the standard deviation of the blank [27, 52]. The LOD of Hg(II) at 5-Br-PADAP-CPE in 0.1 mol.L^{-1} Acetate buffer pH 4.7, is 10^{-8} mol.L^{-1}. This LOD is lower than the WHO standard for mercury(II) in natural waters (3 10^{-8} mol.L^{-1}) [7]. This result indicates so, that this sensor allows analysis of low concentrations of mercury in water.

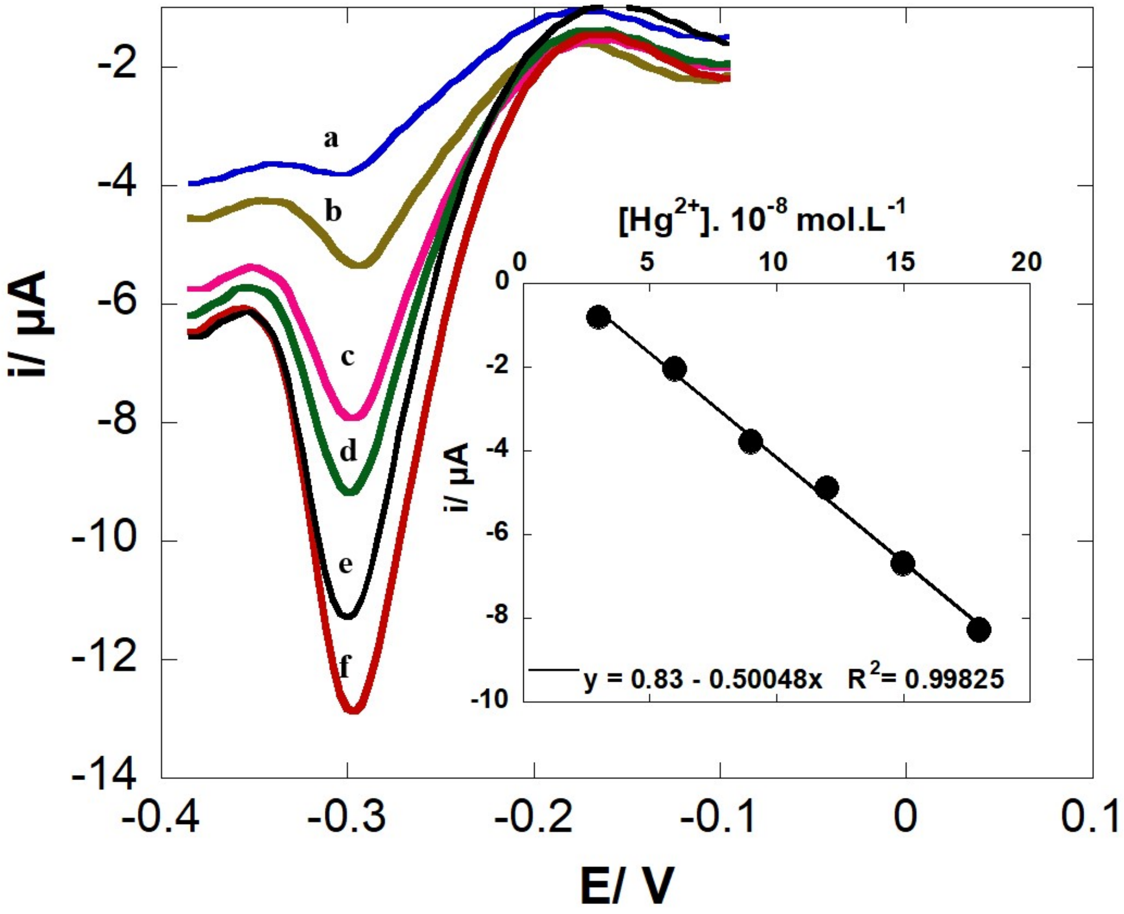

Figure 9. Differential voltammetry curves and calibration curve for different Hg(II) concentrations (**a**: 3 10^{-8} M, **b**: 6 10^{-8} mol.L^{-1}, **c**: 9 10^{-8} mol.L^{-1}, **d**: 1.2 10^{-7} mol.L^{-1}, **e**: 1.5 10^{-7} mol.L^{-1}, **f**: 1.8 10^{-7} mol.L^{-1}), in 0.1 mol.L^{-1} acetate buffer (pH 4.7), at 0.2% 5-Br-PADAP-CPE

The performance of our modified 5-Br-PADAP-CPE, in Mercury(II) determination, is evaluated and compared with other carbon paste modified electrodes as shown in **Table 1**. The results show that our electrode has a good reproducibility (in term of % RSD) and high sensitivity (LOD) for determination of Hg(II) ions as other previously electrodes reported in the **Table 1**.

Table 1. Comparison of 5-Br-PADAP with other carbon paste modified electrodes in Hg(II) determination

Electrode	Technique	Accumulation time	LOD (mol.L^{-1})	RSD (%)	Reference
Poly(Eriochrome Black T)/CPE	ASV*	2 min	2.2 10^{-10}	2.4	[27]
EDTA/CPE	SWV**	5 min	8.6 10^{-9}	3.1	[47]
Indigo Carmine/CPE	DPV	10 min	7.5 10^{-9}	/	[53]
Crown ether/CPE	CSV***	2 min	2 10^{-6}	11	[54]
Tetraphenylborate/CPE	ASV	10 s	6 10^{-9}	4	[55]
SBA-15/ CPE	ASV	3 min	4 10^{-7}	5	[56]
Sepiolite/FeS_2 /CPE	ASV	2 min	0.41 10^{-8}	7.1	[57]
5-Br-PADAP/CPE	DPV	2 min	10^{-8}	1.6	Present work

*Anodic Stripping Voltammetry, **Square wave voltammetry, *** Cathodic Stripping Voltammetry

3.6 Behavior of modified 5-Br-PADAP-CPE for Hg(II) analysis with other metallic ions

In environmental sample, Hg(II) ions coexist with many other ions. The major sources of interferences are likely to be from metal ions coming from gold mining process and capable of forming complexes with the used chelating agent 5-Br-PADAP, hence affecting response of the electrode via an overlapping peak or competing for avalaible ligand. Based on previous studies of an artisanal gold mining groundwater in the locality of Komabangou (Niger) [58], the metal ions identified to be most interfering are: Cu(II), Mn(II), Al(III) and Zn(II). The effect of these metal ions was tested at the optimal experimental conditions, with all concentration 1-fold and 10-fold that of Hg(II). The concentration of Hg(II) used was 5 10^{-7} mol.L^{-1}. Table 2 surveys the results obtained by studying the selected ions at concentrations 1-fold and 10-fold as large as that of Hg(II). Results show that these interfering ions reduced the electrode response to mercury by competing with Hg(II) ions for available ligand because they caused decrease of peak current.

To minimize effect of complex matrix, analysis of mercury content in real sample was performed by standard addition method instead of using calibration curve.

Table 2. Interference of selected metal ions with the determination of 5 10^{-7} mol.L^{-1} of Hg(II)

Metal ion	Concentration of the interferent	Change in peak current, %
Al(III)	1-fold	-9.1
	10-fold	-26.4
Mn(II)	1-fold	-55.2
	10-fold	-58
Zn(II)	1-fold	-16.5
	10-fold	-22.1
Cu(II)	1-fold	-26.4
	10-fold	-36.3

3.7 Real sample

In order to assess the analytical utility of the modified electrode, it was necessary to evaluate this electrode in a real sample. To do this, the developed sensor was tested in the tap water under optimized parameters, as a selective and sensitive working electrode for the determination of Hg(II) without any previous pre-treatment of the samples. Tap water samples were spiked with Hg(II) at different concentrations. The accuracy of the developed method was demonstrated by recovery studies. Good quantitative recoveries were observed, as illustrated in **Table 3**. These data indicate that in the spiked water samples the recovery is more than 95% what is satisfactory.

Table 3. Results of determination of Hg(II) in tap water with 5-Br-PADAP-CPE

Element	**Concentration spiked (mol.L^{-1})**	**Concentration found (mol.L^{-1})**	**Recovery (%)**
Hg(II)	5 10^{-7}	4.9 10^{-7} ± 0.28	98
	10^{-6}	1.07 10^{-6} ± 0.1	107

Conclusion

A novel an easy 5-Br-PADAP-CPE was developed in this work for sensitive determination of Hg(II) based on reduction. The results show that the developed sensor was easy to prepare, has good reproducibility (RSD 1.6%) and low LOD (10^{-8} mol.L^{-1} after 2 min accumulation) comparable with other modified CPEs and application of this sensor in real sample were satisfactory. In addition, utilization of portable potentiostat (like Palmsens used in this study) makes 5-Br-PADAP-CPE sensor suitable for on-site use.

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Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.

References

[1] N. Hidayati, T. Juhaeti, F. Syarif, "Mercury and Cyanide Contaminations in Gold Mine Environment and Possible Solution of Cleaning Up by Using Phytoextraction", *HAYATI Journal of Biosciences*, 16 (2009) 88-94. https://doi.org/10.4308/hjb.16.3.88

[2] R. Eisler, "Mercury hazards from gold mining to humans, plants, and animals", *Rev. Environ. Contam. Toxicol.* 181 (2004) 139-198. doi : 10.1007/0-387-21733-9_4.

[3] E. G. Pacyna, J. M. Pacyna, J. Fudala, E. Strzelecka-Jastrzab, S. Hlawiczka, D. Panasiuk, "Mercury emissions to the atmosphere from anthropogenic sources in Europe in 2000 and their scenarios until 2020", *Sci. Total Environ.* 370 (2006) 147-156. doi:10.1016/j.scitotenv.2006.06.023.

[4] A. Bhan, N. N. Sarkar, "Mercury in the environment: effect on health and reproduction", *Rev. Environ. Health*, 20 (2005) 39-56. doi: 10.1515/reveh.2005.20.1.39.

[5] M. Valko, H. Morris, M. T. D. Cronin, "Metals, toxicity and oxidative stress", *Curr. Med. Chem.* 12 (2005) 1161-11208. doi: 10.2174/0929867053764635.

[6] J. C. Clifton II., "Mercury exposure and public health", *Pediatr. Clin. North Am.* 54 (2007) 237.e1-237e45. https://doi.org/10.1016/j.pcl.2007.02.005

[7] World Health Organization, "Guidelines for Drinking-Water Quality, fourth ed. ", *World Health Organization*, 1 (2011) 389-390.

[8] J. Du, Z. Wang, J. Fan, X. Peng, "Gold Nanoparticle-Based Colorimetric Detection of Mercury Ion via Coordination Chemistry", *Sensors Actuators, B Chem.* 212 (2015) 481-486. https://doi.org/10.1016/j.snb.2015.01.110

[9] Y. Lin, Y. Yang, Y. Li, L. Yang, X. Hou, X. Feng, C. Zheng, "Ultrasensitive Speciation Analysis of Mercury in Rice by Headspace Solid Phase Microextraction Using Porous Carbons and Gas Chromatography-Dielectric Barrier Discharge Optical Emission Spectrometry" *Environmental Science and Technology,* 50 (2016) 2468-2476. DOI:10.1021/acs.est.5b04328

[10] L. Wu, Z. Long, L. Liu, Q. Zhou, Y. -I. Lee, C. Zheng, "Microwave-Enhanced Cold Vapor Generation for Speciation Analysis of Mercury by Atomic Fluorescence Spectrometry", *Talanta* 94 (2012) 146-151. DOI:10.1016/j.talanta.2012.03.009

[11] M. D. Ioannidou, G. A. Zachariadis, A. N. Anthemidis, J. A. Stratis, "Direct Determination of Toxic Trace Metals in Honey and Sugars Using Inductively Coupled Plasma Atomic Emission Spectrometry", *Talanta* 65 (2005) 92–97. doi: 10.1016/j.talanta.2004.05.018.

[12] Y. Fang, Y. Pan, P. Li, M. Xue, F. Pei, W. Yang, N. Ma, Q. Hu, "Simultaneous Determination of Arsenic and Mercury Species in Rice by Ion-Pairing Reversed Phase Chromatography with Inductively Coupled Plasma Mass Spectrometry", *Food Chem.* 213 (2016) 609-615. DOI:10.1016/j.foodchem.2016.07.003

[13] P. R. Aranda, L. Colombo, E. Perino, I. E. De Vito, J. Raba, "Solid-Phase Preconcentration and Determination of mercury(II) Using Activated Carbon in Drinking Water by X-Ray Fluorescence Spectrometry". *X-Ray Spectrom*., 42 (2013) 100-104. https://doi.org/10.1002/xrs.2440

[14] X. Li, Z. Wang, "Determination of Mercury by Intermittent Flow Electrochemical Cold Vapor Generation Coupled to Atomic Fluorescence Spectrometry", *Anal. Chim. Acta* 588 (2007) 179-183. DOI : 10.1016/j.aca.2007.02.003

[15] C. Harrington, "The Speciation of Mercury and Organomercury Compounds by Using High-Performance Liquid Chromatography", *TrAC Trends Anal. Chem.,* 19 (2000) 167-179. DOI:10.1016/S0165-9936(99)00190-9

[16] H. He, F. Wu, M. Xu, S. Yang, C. Sun, Y. Yang, D. E. Wylie, R. C. I. Blake, J. Zhang, Q. Chen, et al., "Development and Validation of a Competitive Indirect Enzyme-Linked Immunosorbent Assay for the Determination of Mercury in Aqueous Solution", *Anal. Methods,* 3 (2011) 1859-1864. https://doi.org/10.1039/C1AY05108C

[17] F. Cai, Q. Zhu, K. Zhao, A. Deng, J. Li, "Multiple Signal Amplified Electrochemiluminescent Immunoassay for Hg^{2+} Using Graphene-Coupled Quantum Dots and Gold Nanoparticles-Labeled Horseradish Peroxidase", *Environ. Sci. and Technol.*, 49 (2015) 5013-5020. https://doi.org/10.1021/acs.est.5b00690

[18] A. L. Suherman, E. E. Tanner, R. G. Compton, "Recent Developments in Inorganic Hg^{2+} Detection by Voltammetry", *Trends in Analytical Chemistry*, 94 (2017) 161-172. https://doi.org/10.1016/j.trac.2017.07.020

[19] C. Gao, X. J. Huang, "Voltammetric Determination of mercury(II)", *TrAC - Trends Anal. Chem.,* 51 (2013) 1-12. DOI:10.1016/j.trac.2013.05.010.

[20] M. Zaib, M. M. Athar, A. Saeed, U. Farooq, "Electrochemical Determination of Inorganic Mercury and Arsenic-A Review", *Biosensors and Bioelectronics,* 74 (2015) 895-908. DOI:10.1016/j.bios.2015.07.058

[21] D. Martín-Yerga, M. B. González-García, A. Costa-García, "Electrochemical Determination of Mercury: A Review", *Talanta* 116 (2013) 1091-1104. doi: 10.1016/j.talanta.2013.07.056.

[22] J. Wang, "Stripping Analysis: Principles, Instrumentation and Application", *VCH, Deerfield Beach*, (1985).

[23] E. M. Ghoneim, "Simultaneous determination of Mn(II), Cu(II) and Fe(III) as 2-(5'-bromo-2'-pyridylazo)-5-diethylaminophenol complexes by adsorptive cathodic stripping voltammetry at a carbon paste electrode", *Talanta,* 82 (2010), 646-652. doi: 10.1016/j.talanta.2010.05.025.

[24] A. Bahrami, A. B. Seidani, A. Abbaspour and M. Shamsipur, *Materials Science and Engineering C*, 48 (2015) 205.

[25] H. Khani, M. K. Rofouei, P. Arab, V. K. Guptac and Z. Vafaei, *Journal of Hazardous Materials*, 183 (2010) 402.

[26] W. Yantasee, Y. Lin, T. S. Zemanian and G. E. Fryxell, Voltammetric detection of lead(ii) and mercury(ii) using a carbon paste electrode modified with thiol self-assembled monolayer on mesoporous silica (SAMMS), *Analyst*, 128 (2003) 467. https://doi.org/10.1039/B300467H

[27] K. S. Guha, R. J. Mascarenhas, T. Thomas and O. J. D'Souza, Differential pulse anodic stripping voltammetric determination of Hg^{2+} at poly (Eriochrome Black T)-modified carbon paste electrode*, Ionics*, 20 (2014) 849-856. https://doi.org/10.1007/s11581-013-1040-9

[28] G. O. Buica, C. Bucher, J. C. Moutet, G. Royal, E. Saint-Aman and E. M. Ungureanu, Voltammetric Sensing of Mercury and Copper Cations at Poly(EDTA-like) Film Modified Electrode, *Electroanalysis*, 21 (2009) 77-86. https://doi.org/10.1002/elan.200804386

[29] I. K. Tonle, E. Ngameni and A. Walcarius, *Sensors and Actuators B*, 110 (2005) 195.

[30] W. Fu-sheng, Z. Yu-Rui, Y. Fang, "Spectrophotometric Determination of Mercury Using 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol", *Analytical Letters*, 13 (1980), 1533-1540, DOI: 10.1080/00032718008055731

[31] A. Z. Abu-Zuhri, "Pyridylazo coumpounds as analytical reagents-A review", *An-Naj. J. Res*., I (1987) 30-40. http://hdl.handle.net/20.500.11888/1910

[32] J. Wang, J. Lu, "Adsorptive stripping voltammetry of trace manganese in the presence of 2-(5'-bromo-2'-pyridylazo)-5-diethylaminophenol (5-Br-PADAP)", *Talanta*, 42 (1995) 331-335. DOI:10.1016/0039-9140(95)01396-S

[33] S. Tanaka, K. Sugawara, M. Taga, "Adsorption Voltammetry of the Copper(II) 2-(5-Bromo-2-Pyridylazo)-5-Diethylaminophenol Complex", *Talanta*, 37 (1990) 1001-1005. doi: 10.1016/0039-9140(90)80140-b

[34] J. Zhao, W. Jin, "A study on the adsorption voltammetry of the iron(III)-2-(5'-bromo-2'-pyridylazo)-5-diethylaminophenol system", *J. Electroanal. Chem.*, 267 (1989) 271-278. DOI:10.1016/0022-0728(88)85016-2

[35] J. Lu, W. Jin, S. Wang, "Adsorption voltammetry of the vanadium-2-(5′-bromo-2′-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) system", *Anal. Chim. Acta*, 238 (1990) 375-381. DOI:10.1016/s0003-2670(00)80561-9

[36] W. Jin, S. Shi, J. Wang, "Determination of ultra-trace vanadium by 1.5th and 2.5th order derivative adsorption voltammetry", *J. Electroanal. Chem.*, 291 (1990) 41-47. DOI:10.1016/0022-0728(90)87175-J

[37] J. Zhao, W. Jin, "A study on the adsorption voltammetry of the bismuth- 2-(5'-bromo-2'-pyridylazo)-5-diethylaminophenol system", *J. Electroanal. Chem.*, 256 (1988) 181-191. http://dx.doi.org/10.1016/0022-0728(88)85016-2

[38] J. Lu, W. Jin, S. Wang, T. Sun, "Determination of trace chromium(III) by linear sweep adsorption voltammetry", *J. Electroanal. Chem.*, 291 (1990) 49-57. DOI:10.1016/0022-0728(90)87176-K

[39] J. Wenrui, L. Xixia, "1.5th- and 2.5th-order derivative adsorption voltammetry of the cobalt(II)—2-(5′-bromo-2′-pyridylazo)-diethylaminophenol system", *Anal. Chim. Acta*, 236 (1990) 453-458. DOI:10.1016/S0003-2670(00)83349-8

[40] J. Zhou, R. Neeb, "Determination of titanium by adsorption-voltammetry with 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol (5-Br-PADAP)", *Fresenius J. Anal. Chem.*, 338 (1990) 905-907. DOI:10.1007/BF00322030

[41] T. Hattori, N. Tsurumi, R. Kato, M. Nakayama, "Adsorptive Voltammetry of 2-(5-Bromo-2-pyridyl)azo-5-[N-n-propyl-N-(3-sulfopropyl)amino]phenol on a Carbon Paste Electrode in the Presence of Organic Cations and Polycation", *Analytical Sciences*, 22 (2006) 1577-1580. doi: 10.2116/analsci.22.1577

[42] Z.-T. Jiang, R. Li, J.-B. Xi, B.-Q. Yi, "Determination of trace amount of manganese by β-cyclodextrin polymer solid phase spectrophotometry using 2-(5'-Bromo-2'-pyridylazo)-5-diethylaminophenol", *Analytica Chimica Acta,* 392 (1999) 247-253. DOI:10.1016/s0003-2670(99)00175-0

[43] N. A. Yusof, W. A.R. Wan Abdul Kadir, "Optical test strip for trace Hg(II) based on doped sol-gel film", *Spectrochimica Acta Part A*, 72 (2009) 32-35. doi: 10.1016/j.saa.2008.07.019.

[44] O. Abollino, M. Aceto, C. Sarzanini, E. Mentasti, "Behavior of Different Metal/Ligand Systems in Adsorptive Cathodic Stripping Voltammetry", *Electroanalysis*, 11 (1999) 870-878. https://doi.org/10.1002/(SICI)1521-4109(199908)11:12<870::AID-ELAN870>3.0.CO;2-L

[45] S. Pysarevska, L. Dubenska, I. Spánik, J. Kovalyshyn, S. Tvorynska, "Reactions of o,o′-Dihydroxy Azo Dyes with the Third Group M(III) Ions: A Spectroscopic and Electrochemical Study", *Journal of Chemistry*, (2013) 1-10. https://doi.org/10.1155/2013/853763

[46] Y. Karaman, "Investigation of electrochemical behavior of calmagite at a glassy carbon electrode", *Dyes and Pigments,* 106 (2014) 39-44. https://doi.org/10.1016/j.dyepig.2014.02.014

[47] A. Moutcine, A. Chtaini, "Electrochemical determination of trace mercury in water sample using EDTA-CPE modified electrode", *Sensing and Bio-Sensing research,* 17 (2018) 30-35. https://doi.org/10.1016/j.sbsr.2018.01.002

[48] B. Mostafiz, D. Hatamabadi, S. A. Bigdeli, K. Banan, H. Afsharara, F. Ghorbani-Bidkorbeh, P. Mousavi, C. M. Hussain, R. Keçili, "Molecularly imprinted polymer-carbon paste electrode (MIP-CPE)-based sensors for the sensitive detection of organic and inorganic environmental pollutants: A review", *Trends in Environmental Analytical Chemistry*, 32 (2021) 1-12. https://doi.org/10.1016/j.teac.2021.e00144

[49] D. Ilager, N. P. Shetti, K. R. Reddy, S. M. Tuwar, T. M. Aminabhavi, "Nanostructured graphitic carbon nitride (g-C3N4)-CTAB modified electrode for the highly sensitive detection of amino-triazole and linuron herbicides", *Environmental Research*, 204 (2022) 111856. https://doi.org/10.1016/j.envres.2021.111856

[50] F. Fazl, M. B. Gholivand, "High performance electrochemical method for simultaneous determination dopamine, serotonin, and tryptophan by ZrO_2–CuO co-doped CeO_2 modified carbon paste electrode", *Talanta*, 239 (2022) 122982.

https://doi.org/10.1016/j.talanta.2021.122982

[51] A. Ayouba Mahamane, B. Guel, P.-L. Fabre, "Electrochemical behaviour of iron(II) at a Nafion-1,10-phenanthroline-modified carbon paste electrode: assessing the correlation between preconcentration potential, surface morphology and impedance measurements", *Journal de la Société Ouest-Africaine de Chimie*, 39 (2015) 41-56.

[52] D. A. Skoog, D. M. West, F. J. Holler, S. R. Crouch "Fundamentals of analytical chemistry", Cengage, USA (2003).

[53] R. S. N'Dri, M. Coulibaly, A. N. Yao, D. Bemba, E. G. Zoro, "An electrochemical method for the determination of trac of Mercury (II) by formation of complexes with Indigo Carmine food dye and its analytical application", *Int. J. Electrochem. Sci.*, 11 (2016) 5342-5350. doi: 10.20964/2016.06.61

[54] J. Wang, M. Bonakdar "Preconcentration and voltammetric measurement of mercury with a crown ether modified carbon paste electrode", *Talanta*, 35 (1988) 277-280. https://doi.org/10.1016/0039-9140(88)80085-7

[55] I. Švancara, K. Vytrˇas "Voltammetric determination of mercury(II) at a carbon paste electrode in aqueous solutions containing tetraphenylborate ion", *Talanta,* 39 (1992) 391-396. https://doi.org/10.1016/0039-9140(92)80153-5

[56] I. Cesarino, G. Marino, J. do Rosario Matos, E.T. Gomes Cavalheiro, "Evaluation of a carbon paste electrode modified with organofunctionalised SBA-15 nanos-tructured silica in the simultaneous determination of divalent lead, copper and mercury ions", *Talanta*, 75 (2008) 15-21. https://doi.org/10.1016/j.talanta.2007.06.032

[57] M. S. Koshki, M. Baghayeri, M. Fayazi, "Application of sepiolite/FeS_2 nanocomposite for highly selective detection of mercury(II) based on stripping voltammetric analysis", *Food Measure,* 15 (2021) 5318–5325. https://doi.org/10.1007/s11694-021-01097-0

[58] A. Tankari Dan-Badjo, D. A. Tidjani, T. Idder, Y. Guero, N. Dan Lamso, A. Matsallabi, J. M. K. Ambouta, C. Feidt, T. Sterckeman, G. Echevarria, "Diagnostic de la contamination des eaux par les éléments traces métalliques dans la zone aurifère de Komabangou – Tillabéri, Niger", *Int. J. Biol. Chem. Sci.*, 8 (2014) 2849-2857. DOI: 10.4314/ijbcs.v8i6.41

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