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Development of an efficient electrochemical sensor for the determination of cyanide ions in aqueous media

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Abstract

The aim of this work is to develop an efficient electrochemical sensor based on a glassy carbon electrode coated with a thin film of mercury for the determination of cyanide ions in aqueous media. The sensor is characterised by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), differential pulse anodic stripping voltammetry (DPASV), to understand its behaviour and evaluate its performances. Cyclic voltammetry measurements indicate a "Nernst" type system with decreasing reversibility at pH 10. Impedance techniques indicate an easier charge transfer on the glassy carbon electrode modified with the mercury film compared to the bare glassy carbon electrode. The optimal parameters (Analytical and Differential pulse voltammetry) for cyanide determination are identified. The limits of detection (LOD) and quantification (LOQ) obtained are 0.013mg.L⁻¹ and 0.043mg.L⁻¹ respectively. In addition, the new sensor has good linearity, good repeatability with a calculated Relative Standard Deviation (RSD) equal to 1.88%. The studied sensor was successfully employed for the analysis of cyanide ions in well water samples using the standard addition method and the results obtained are satisfactory.

Keywords: Cyanide, electrochemical sensor, mercury thin film, cyclic voltammetry (CV), impedance measurements, differential pulse voltammetry (DPV)

Introduction

The expression "cyanides" is employed to designate compounds which contain in their structure the $-C \equiv N$ group¹. In the environment, cyanide compounds can exist in many forms, such as free cyanide (HCN and CN⁻), simple cyanides, complex cyanides or metallocyanides and organic cyanides (nitriles, acetonitrile, glucosides)²⁻⁵. The highly volatile hydrogen cyanide HCN and the cyanide anion, CN, are the most toxic forms of cyanides whose preponderance in water depends on pH^{5,6}. The presence of cyanide and its compounds in environmental matrices (air, water, soil and food) is attributable to natural or anthropogenic sources. The main sources of contamination of natural waters are found in effluents from gold and silver mining facilities, electroplating processes, leaching of mine tailings, coke plants, pharmaceutical industries as well as various chemical plants^{4,7}. The WHO standard of cyanides ions in drinking water is 70 µg.L^{-1 4}.

Cyanides are extremely toxic compounds, easily absorbed by living organisms which can cause very serious health problems with the contamination of water sources. Cyanide is used in artisanal gold mining with little or no control by the authorities and in industrial gold mining⁸. Accidents associated with the use of cyanide have had very serious environmental and health impacts through the pollution of water, soil and food.¹⁰. Because of the health effects and environmental consequences cited

previously, the measurement of cyanide in environmental samples demands particular attention. It is, necessary to monitor the quality of the water around the localities in the vicinity of gold mines. This topic has been the subject of research into different methods for cyanide analysis. Many classical methods titrimetry. UV-Visible spectrophotometry, (such as chromatography, colorimetry, and fluorimetry) have been used for the determination of cyanide ions^{4,9,11-15}. However, most of these methods can only be used in an analytical laboratory. They are expensive, time-consuming and they require specialized personnel. In addition, these methods require a pretreatment of samples and the use of additional chemicals.

To overcome these difficulties, electrochemical sensors have been proposed as simple and alternative methods to the existing traditional analytical methods for cyanide determination. Some electrochemical sensors based on electrochemical methods (such as amperometry, potentiometry, ion selective electrodes, polarography, voltammetric techniques and continuous flow analysis¹⁶⁻²⁰) are used because of the various characteristics obtained: low detection limit, good sensitivity, good selectivity, good stability, good reproducibility, good repeatability, simplicity, portability, low cost and fast response time and also the use of less chemical.

The objective of this study is to develop an efficient electrochemical sensor for the determination of cyanide ions.

Indeed, several electrochemical sensors with Hanging Mercury Drop Electrode (HMDE) were utilized for the cyanide analysis. ^{18,20,21}. However, in this work an efficient electrochemical sensor using a mercury film electrode is employed for the cyanide ions analysis in aqueous media.

Materials and methods

Reagents and chemicals: All chemicals used were part of analytical grade. A $0.1 \text{mol}.\text{L}^{-1}$ HClO₄ solution prepared with distilled water was used as the supporting electrolyte for the mercury film deposition. The mercury solution is prepared from HgCl₂10⁻²mol.L⁻¹ which is dissolved in the supporting electrolyte. The cyanide stock standard solution (1000mg.L⁻¹) was made up by the dissolution of 0.251g of potassium cyanide, KCN (Merck) in 100mL of potassium hydroxide, KOH 10⁻²mol.L⁻¹. The working standard solutions were prepared daily by diluting the stock standard solution with the same 10^{-2} mol.L⁻¹ KOH solution. The supporting electrolyte solution, borate buffer (KOH 0.2mol.L⁻¹ + H₃BO₃ 0.2mol.L⁻¹) was prepared by dissolving 11.2220g KOH and 12.3660g of boric acid (H₃BO₃) in distilled water and then adjusting the volume to 1000mL.

Apparatus: The electrochemical investigations were performed with the use of a Palm Sens 4 Potentiost at controlled by a laptop computer using PS Trace 5.7 software. All tests were made at room temperature in a three-electrode electrochemical cell. The electrochemical cell consists of a mercury film-coated glassy carbon working electrode, an Ag/AgCl. KCl 3mol.L⁻¹ reference electrode and a platinum auxiliary electrode.

Preparation of the working electrode: The working electrode was prepared by depositing a film of mercury on a glassy carbon electrode, polished on two abrasive papers (Alumina polishing pad and Diamond polishing pad). The mercury film was formed by cathodic deposition using a $0.1 \text{mol}.\text{L}^{-1}$ mercuric HgCl₂ 5.10⁻³mol.L⁻¹ and HClO₄ solution as the supporting electrolyte, by chronoamperometry at a potential of -0.2V for 180 s.

Analytical procedure: The analytical approach for the analysis of cyanide ions by differential pulse voltammetry (DPV) is carried out by immersing the three electrodes in an electrochemical cell filled with the measuring solution. The supporting electrolyte used is a borate buffer solution. When the electrodes are immersed, the solution is stirred for one minute and then the stirring is stopped. The detection by DPV is done without stirring and the scan is performed in anodic direction.

Results and discussion

Electrochemical behaviour of the mercury thin film electrode in the presence of cyanide ions: Cyclic voltammetry: Cyclic voltammetry was used to characterise the glassy carbon electrode/mercury thin film/cyanides ions system (GCE/Hg/CN⁻). The influence of the scan rate on the electrochemical behaviour of this system was studied at different scan rates from 2 to 100mV.s⁻¹. The cyclic voltammograms obtained (Figure-1) are characterised by the apparition of anodic and cathodic current peaks. The amplitude of the peaks increases with the scan rate.



Figure-1: Cyclic voltammograms of a 20mg.L⁻¹ solution of cyanide ions in borate buffer electrolyte, pH 10.

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The electrochemical data obtained from these cyclic voltametric curves are shown in Table-1. This table includes the values of the anodic ipa and cathodic ipc peak currents, the anodic Epa and cathodic Epc peak potentials, the ratio of the peak currents (ipa/ipc) and the potential difference between the anodic and cathodic peak potentials Δ Ep.

From Table-1, for all scan rates the value of the ipa/ipc ratio varies from 0.987 to 1.035, a value very close to 1 showing that the electrochemical reaction is a Nernst reaction, and the system is reversible. The average value of the potential difference between the anodic and cathodic peak potentials Δ Ep is equal to 93 mV. These were similar to the results reported by Moon et al²¹ who measured cyanide ions on a mercury drop electrode. This author showed that at pH 7 the ipa/ipc ratio is equal to 1.1 and the difference Δ Ep is equal to 60mV. This difference increases when the pH increases from 7 to 10, as shown in this study, and it reveals that the reversibility decreases when the pH $> 7^{21}$.

Furthermore, a linear relationship is obtained between the reduction (ipc) and oxidation (ipa) peak currents and the square root of the scan rate, in the interval from 2 to 100mV/s. This is a characteristic of a diffusion controlled process²².

This study of the GCE/Hg/CN⁻ system by cyclic voltammetry shows that both the cathodic and the anodic peak are suitable for the electrochemical quantification of cyanide ions in aqueous media.

Impedances measurements: Electrochemical impedance spectroscopy was used to characterise the GCE/CN⁻ and GCE/Hg/CN⁻ systems. Frequency was varied from 50mHz to 50kHz. The Nyquist plots show two parts: a semicircle representing the charge transfer resistance and a linear part corresponding to the diffusion limitation stage of the electrochemical process (Figure-3).

Table-1:	Electrochen	nical data fi	rom cyclic	voltammograms	as a func	tion of scan rate.
				0		

v (mV/s)	i_{pc} (μA)	E _{pc} (V)	$i_{pa}\left(\mu A ight)$	E _{pa} (V)	$\Delta E_{p}(V)$	E° (V)	i_{pa}/i_{pc}
2	2.785	-0.480	2.748	-0.380	0.100	-0.430	0.987
5	3.514	-0.480	3.638	-0.380	0.100	-0.430	1.035
10	5.189	-0.480	5.194	-0.390	0.090	-0.435	1.000
15	6.124	-0.490	6.149	-0.400	0.090	-0.445	1.004
25	7.899	-0.490	7.854	-0.410	0.080	-0.450	0.994
50	10.157	-0.500	10.196	-0.410	0.090	-0.455	1.004
100	14.257	-0.510	14.266	-0.410	0.100	-0.460	1.000







Figure-3: Impedance diagrams in Nyquist representation for a glassy carbon electrode in a solution containing 20mg.L⁻¹ of cyanide ions: (a) bare GCE. (b) GCE modified by the mercury thin film.

The diameter of the semicircle is therefore equal to the chargetransfer resistance (R_{ct}). The charge transfer resistance falls from 14k Ω for the GCE/CN⁻ system to 2k Ω for the GCE/Hg/CN⁻ system (Table-2). This diminution could mean that the charge transfer is faster for the GCE/Hg/CN⁻ system^{22,23}.

Table-2: Electrochemical impedance results.

System	$R_{ct}\left(k\Omega\right)$
GCE/CN⁻	14
GCE/Hg/CN ⁻	2

Differential pulse voltammetry (DPV): As the current measurement is differential in nature, the curve obtained is in the form of a peak. The ionic cyanide depolarises the mercury (Hg) film electrode to give $Hg(CN)_2$ at high pH values (12 to 13) as follows²¹:

$$Hg + 2CN^{-} \leftrightarrow Hg(CN)_2 + 2e^{-}$$
 (1)

When the cyanide concentration and pH are lower (pH < 12), the reaction involved is given by²¹:

$$2Hg + 2CN^{-} \leftrightarrow Hg_{2}(CN)_{2} + 2e^{-}$$
(2)

The current, produced by the reaction of the mercury anode and the cyanide ion (anodic polarisation), is an anodic curve, the height (ip) being proportional to the cyanide concentration (ip = kC). In the case of this technique, the cyanide peak is observed at a characteristic potential around -0.4 V.

Optimisation of analytical parameters and differential pulse parameters: The optimised analytical parameters are: mercury deposition potential and time, mercury solution concentration, nature and pH of the supporting electrolyte, solution stirring speed. Then, the optimised DPV parameters are: potential scan rate, pulse amplitude and equilibrium time.

Optimisation of the deposition potential of the mercury film: The influence of the mercury film deposition potential was studied for different potentials between -0.3 and 0.1 V. The deposition by chronoamperometry was performed at values: $[Hg^{2+}] = 5.10^{-3}$ mol.L⁻¹, deposition time =180s. The DPV measurements (Figure-4) were carried out at cyanide ion concentration $[CN^{-}] = 0.5$ mg.L⁻¹. From -0.3 to -0.2V the peak height increases.

From -0.2V there is a slight plateau up to 0.05V. Then, up to 0.1V this height decreases. Although there is a relative fluctuation around the potential -0.2V, this value is the potential around which the highest peak is recorded. This potential of -0.2 V has been selected as the optimal deposition potential (Ed) for the further work.

Optimisation of the mercury film deposition time: The effect of deposition time on the growth of the mercury film on the glassy carbon electrode surface was studied over the range of 30-300s. The DPV measurements (Figure-5) were carried out at cyanide ion concentration $[CN^-] = 0.5 \text{mg}.\text{L}^{-1}$. An increase in peak intensity is observed from 30 to 60s. From 60s a plateau is established before decreasing slightly from 180s to 300s. The time of 180s was selected as the best deposition time (td) for the further work.



Figure-4: Influence of the deposition potential on the voltammetric peak current (Deposition supporting electrolyte HClO₄ 0.1 mol.L⁻¹, measurement supporting electrolyte borate buffer pH 10, stirring speed 500 rpm, $[Hg^{2+}] = 5.10^{-3}mol.L^{-1}$, time = 180 s, $[CN^{-1}] = 0.5mg.L^{-1}$).



Figure-5: Influence of the deposition time on the voltammetric peak current (Deposition supporting electrolyte HClO₄ 0.1 mol.L⁻¹, measurement supporting electrolyte borate buffer pH 10, stirring speed 500rpm, $[Hg^{2+}] = 5.10^{-3}mol.L^{-1}$, Ed = -0.2V, $[CN^{-}] = 0.5$ mg.L⁻¹).

Optimisation of mercury concentration: The effect of the mercury ion content in the deposition medium on the intensity of the anodic redissolution peak was studied in the concentration range of 5.10^{-4} to 5.10^{-3} mol.L⁻¹. The results obtained show that the intensity of the cyanide ion peak of concentration 0.5mg.L⁻¹ in the reaction medium decreases when the concentration of Hg²⁺ increases from 5.10^{-4} to 4.10^{-3} mol.L⁻¹ in the deposition medium. This decrease can be explained by the fact that as the concentration of Hg²⁺ ions increases in the

deposition solution, the competition for the formation of $Hg(OH)_2$ and $Hg_2(OH)_2$ compounds increases at the surface of the working electrode²¹. The binding of these substances to the surface of the electrode prevents any future reaction. In addition, at this concentration range the peaks are less resolved. After 4.10⁻³mol.L⁻¹ the peak intensity starts to increase to 5.10⁻³ mol.L⁻¹ which gives a better resolved peak and good sensitivity (Figure-6). Therefore, the concentration 5.10⁻³mol.L⁻¹ was chosen for further work.

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Optimisation of the supporting electrolyte solutions: The effect of the medium has a very important role on the sensitivity of the technique. The influence of the supporting electrolyte on the detection of cyanide ions of concentration $[CN^{-}] = 0.5 \text{mg.L}^{-1}$ using the mercury film electrode was studied in several media including borate buffer (KOH + H₃BO₃, pH = 10), potassium hydroxide (KOH 5.10⁻²mol.L⁻¹), sodium hydroxide (NaOH 5.10⁻²mol.L⁻¹), potassium nitrate (KNO₃, 0.1mol.L⁻¹) and potassium

chloride (KCl 0.1mol.L⁻¹). The results of this study showed that the best response in terms of CN⁻ current intensity was obtained in the borate buffer medium (Figure-7). The borate buffer provides a low background current compared to other supporting electrolytes tested²⁰. Therefore, the borate buffer medium was chosen as the best supporting electrolyte for future work.



Figure-6: Influence of the mercury concentration on the height of the voltammetric peak (Deposition supporting electrolyte HClO₄ 0.1mol.L⁻¹, measurement supporting electrolyte borate buffer pH 10, stirring speed 500rpm, Ed = -0.2V, td = 180s, [CN⁻] = 0.5 mg.L⁻¹).



Figure-7: Influence of the supporting electrolyte on the voltammetric peak height (Deposition supporting electrolyte HClO₄ 0.1 mol.L⁻¹, $[Hg^{2+}] = 5.10^{-3}$ mol.L⁻¹, stirring speed 500 rpm, Ed = -0.2V, td = 180 s, $[CN^{-}] = 0.5$ mg.L⁻¹)

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Optimisation of the pH of the supporting electrolyte: The effect of the pH of the supporting electrolyte on the detection of cyanide ions by the mercury thin film electrode deposited on the glassy carbon electrode was studied. The pH below 7 was avoided to ensure that the loss of cyanide as volatile HCN was minimised. The pH studied in this work was varied between 8 and 12. The obtained results indicate the following: as the pH increases towards 10, the intensity of the cyanide peak increases and consequently the sensitivity of the analysis, and then decreases after pH 10 (Figure-8). When the pH is higher than 10, the mercury hydroxide peak $Hg(OH)_2$ and $Hg_2(OH)_2$ can interfere with the cyanide peak^{21,25}. Therefore, pH 10 was chosen for further work.

Optimisation of the stirring speed of the deposition solution: The mechanical stirring of the solution is an important parameter in electro analytical methods²⁶. This is a very significant parameter in mercury deposition. The influence of the solution stirring speed was studied between 100 and 1000 revolutions per minute (rpm). The DPV measurement (Figure-9) was carried out at cyanide ion concentration $[CN^-] = 0.5 \text{mg.L}^{-1}$. The results obtained show that the intensity of the cyanide peak increases slightly with the stirring speed from 100 to 500rpm. From 500 to 700rpm the peak height increases sharply. From 700 to 800rpm, a plateau is reached. From 800rpm the peak height decreases until 1000rpm. For high stirring speeds, the creation of air bubbles in the solution is observed, which is disturbing for the reproducibility of measurements. Thus, for the rest of the work, the speed of 500rpm, which gives a good homogenisation of the solution and without suspension of air bubbles, was adopted.



Figure-8: Influence of the pH of the supporting electrolyte on the height of the voltammetric peak (Deposition supporting electrolyte HClO₄ 0.1mol.L⁻¹, measurement supporting electrolyte borate buffer, [Hg²⁺] = 5.10^{-3} mol.L⁻¹, stirring speed 500rpm, Ed = -0.2V, td = 180 s, [CN⁻] = 0.5mg.L⁻¹).



Figure-9: Influence of the stirring speed on the height of the voltammetric peak (Deposition supporting electrolyte HClO₄ 0.1 mol.L⁻¹, measurement supporting electrolyte borate buffer pH 10, $[Hg^{2+}] = 5.10^{-3}$ mol.L⁻¹, Ed = -0.2V, td = 180 s, $[CN^{-}] = 0.5$ mg.L⁻¹).

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Influence of dissolved oxygen: The cyanide solution was bubbled with nitrogen gas for periods of 5 to 10 minutes to remove dissolved oxygen and to study its influence on the measurement. The bubbling was carried out for a constant cyanide ion concentration of 0.5mg.L⁻¹. Peaks with almost similar heights were obtained without and with bubbling, so this work was continued without bubbling.

Optimisation of Differential-pulse parameters: DPV parameters (scan rate, pulse amplitude ΔE , equilibration time) were optimised to obtain intense and well-defined peak for CN⁻ determination on thin film mercury by differential pulse voltammetry. The results were as follow: scan rate 0.005V/s, $\Delta E = 80$ mV, equilibration time 5s.

Evaluation of the performances of the sensor: Analytical performance: After the optimisation studies of the analytical parameters and the DPV parameters, the optimal conditions selected are applied for the elaboration of the calibration curve. Table-3 shows the parameter values to be filled in on the PS Trace software of the DPV method for the determination of cyanide ions.

Table-3: Parameters for differential pulse voltammetry (DPV).

Parameter	Value
Equilibration time	5 s
Initial Potential (E begin)	-0.55 V
Final Potential (E end)	-0.25 V
Scan Increment (E step)	0.004 V
Amplitude of impulsions (E pulse)	0.08 V
Time of impulsions (t pulse)	0.1 s
Scan rate	0.005 V/s

Calibration is performed using different cyanide concentration standards ranging from 0 to 1mg.L⁻¹. The i = f(E) curves obtained are shown in Figure-11. Figure-10 (a) shows that as the cyanide concentration increases, the current intensity increases. Indeed, the potentials of the peaks move towards more negative potentials with an increasing concentration of cyanide ion. A representation of the average of the current intensities of the three peaks measured as a function of the different concentrations gives the calibration curve i = f(C) showed in Figure-10(b). These results show a satisfactory correlation (correlation coefficient $R^2 = 0.9991$) in the concentration range studied and show that the sensor thus developed gives a satisfactory response with respect to cyanide ions.

The limit of detection (LOD) and limit of quantification (LOO), respectively, were determined by the equations: LOD = 3s and LOQ = 10s. "s" is the standard deviation of ten replicates of a 0.06mg.L⁻¹ cyanide solution²⁷⁻²⁹. The calculated LOD is 0.013 mg.L⁻¹ (5 10⁻⁷mol.L⁻¹) and the LOQ is 0.043mg.L⁻¹ (6.6 10⁻⁷ mol.L⁻¹). We also calculated the conformity ratio (R) of the procedure expressed by the equation: $R = \overline{X}/LOD$, where \overline{X} is the arithmetic mean of a series of measurements²⁸. The conformity ratio R obtained is 5. This number in the range of 4 to 10 indicates that the concentration employed is appropriate for the estimation of the Limit of Detection and the Limit of Quantification. The repeatability between 10 measurements was evaluated for a constant cyanide ion concentration equal to 0.5mg,L⁻¹. The standard deviation found between the measurements is 0.0426. Finally, the relative standard deviation (RSD) was used to evaluate the repeatability and is calculated as the ratio between the standard deviation ''s'' and the mean \overline{X} according to the following equation $RSD = 100 \text{ s}/\overline{X}^{30}$. The value is 1.88%. The analytical performances of this method (Table-4) are good; therefore, the method is reliable for cyanides analysis in aqueous media.

Parameter	Value
LOD	0.013 mg.L ⁻¹
LOQ	0.043 mg.L ⁻¹
Conformity Ratio (R)	5
RSD	1.88 %

Table-4: Analytical performances of the GCE/Hg sensor.

Study of interferences: The contribution of the interfering ions to the intensity of the cyanide peak was studied in a test solution containing 0.5 mg.L⁻¹ cyanide ions. According to the literature¹ the most important interfering ions are: Cl⁻, $SO_4^{2^-}$, NO_3^{-} and $CO_3^{2^-}$. These ions are tested at concentrations equal to 1-fold the concentration of CN⁻ and 10-fold the concentration of CN⁻ (Table-5). The presence of these test ions does not prevent the determination of cyanide ions in solution, but a decrease in current is observed for some ions. The ions that interfere most significantly when their concentration is high are: $SO_4^{2^-}$, NO_3^{-} and $CO_3^{2^-}$. Given these results, the response is not remarkably disturbed.

Comparison of the sensor to other sensors in the literature: The performances of this sensor were compared with others reported in the literature (Table-6). According to the RSD and LOD values, the GCE/Hg, with simple procedure, low testing cost, shows good analytical performances compared to other sensors in the literature. As a result, the GCE/Hg could be considered as a good choice for CN⁻ determination in aqueous media.



Figure-10: Calibration (a) curves and (b) plot by DPV of CN⁻ from 0 to 1mg.L⁻¹ (Deposition supporting electrolyte HClO₄ 0.1 mol.L⁻¹, measurement supporting electrolyte borate buffer, $[Hg^{2+}] = 5.10^{-3}$ mol.L⁻¹, stirring speed 500rpm, Ed = -0.2V, td = 180s, [CN⁻] = 0.5mg.L⁻¹, scan rate = 0.005V/ s, equilibration time = 5 s).

Analytical application: The developed electrochemical sensor was applied to the determination of cyanide in well water samples. For the determination of cyanide using the standard addition technique which minimises the matrix effect. First an evaluation was made with distilled water to get a good understanding of the spiking technique. The analyses in well water and distilled water were carried out in the same way at

cyanide ion concentrations (C) of: 0.1mg.L^{-1} , 0.25mg.L^{-1} , 0.5mg.L^{-1} and 0.75mg.L^{-1} . The results obtained by the proposed method are summarised in Table-7, and indicate that the recovery rates obtained are very satisfactory as these rates vary from 96.2 to 108.73%. Given these results, the sensor appears to be reliable for the determination of CN⁻ ions in aqueous media.

Table-5: Interference of some ions with the determination of CN⁻.

Ions	Concentration of interferent	Change in peak current (%)
Cl-	1-fold [CN ⁻]	-3.96 %
	10-fold [CN ⁻]	+1.44 %
NO ₃ -	1-fold [CN ⁻]	-6.27 %
	10-fold [CN ⁻]	-20.45 %
CO3 ²⁻	1-fold [CN ⁻]	-19.65 %
	10-fold [CN ⁻]	-19.29 %
SO 4 ²⁻	1-fold [CN ⁻]	-27 %
	10-fold [CN ⁻]	-26.2 %

Table-6: Comparison of GCE/Hg sensor with other sensors of the literature.

Electrode	Method	LOD	RSD	Reference
HMDE	Differential Pulse Polarography	0.001 mg.L ⁻¹	2.62 %	20
HMDE	Differential Pulse Cathodic Stripping Voltammetry	3×10 ⁻⁷ mol.L ⁻¹ (0.0078 mg.L ⁻¹)	-	21
HMDE	Differential Pulse Polarography	10µg.L ⁻¹ (0.01 mg.L ⁻¹)	1-3 %	25
HMDE	DPV	$82.854 \mu g.L^{-1} (0.082854 mg.L^{-1})$	3.55 %	31
Silver disc	DPV	0.35µmol.L ⁻¹ (0.009 mg.L ⁻¹)	2.1 %	22
rotated electrode	Square Wave Voltammetry	1.2µmol.L ⁻¹ (0.03 mg.L ⁻¹)	0.8 %	52
GCE/Hg	DPV	0.013 mg.L ⁻¹	1.88 %	This work

Table-7: Results of CN⁻analysis in distilled water and well water with the GCE/Hg sensor.

Medium	Concentration of CN ⁻ spiked (mg.L ⁻¹)	Concentration of CN ⁻ found (mg.L ⁻¹)	Recovery (%)
	0.1	0.1087	108.73
Distilled water	0.25	0.2577	103.09
	0.5	0.5042	100.85
	0.75	0.77	102.67
Well water	0.1	0.1086	108.67
	0.25	0.2646	105.86
	0.5	0.4810	96.20
	0.75	0.742	98.93

Conclusion

This paper presents a new electrochemical sensor for the efficient determination of cyanide ions in aqueous media employing a glassy carbon electrode coated with a mercury film. Cyclic voltammetry revealed a system with decreasing reversibility at pH 10 and a diffusion-controlled process. Electrochemical impedance spectroscopy showed the suitability of the mercury electrode for cyanides ions analysis. The developed sensor has a good linear range and a low detection limit. In addition, the new sensor has been applied to the analysis of cyanide ions in well water samples and the results obtained are satisfactory.

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