

Short Communication

An Electrochemical Method for the Determination of Trace Mercury (II) by Formation of Complexes With Indigo Carmine Food Dye and Its Analytical Application

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The interaction between mercury and indigo carmine (IC) was studied using differential pulse voltammetry (DPV) technique. In aqueous medium, a decrease of oxidation current of IC was observed due to the formation of a complex of IC with Hg (II). The reaction of complexation was monitored and some important parameters such as metal concentration, pH, temperature and time of reaction were investigated and optimized. Under the optimum conditions, the linear range of the calibration curve, obtained by representing the IC oxidation current as function of the Hg (II) concentration (pH 10), was from 25 nM (5 ppb) to 200 nM (40 ppb) Hg (II) and the detection limit was 7.5 nM (1.5 ppb). The results show that this new method enable simple, a sensitive and rapid determination of mercury.

Keywords: Differential pulse voltammetry; carbon paste electrode; mercury; indigo carmine

1. INTRODUCTION

Mercury (Hg) is considered as one of the most toxic metals found in environment and having no known essential biological function [1]. It has now been recognized as a priority pollutant because of its accumulation in environment and its toxicity to organisms. Some mercury compounds can accumulate in living organisms and damage their central nervous system [2].

Usually, the analytical methods for the determination of mercury are the spectrometry techniques such as X-ray fluorescence spectrometry [3], inductively coupled plasma mass

spectrometry (ICP-MS) [4], atomic fluorescence spectrometry [5], cold vapor atomic absorption spectrometry [6], and high- inductively coupled plasma performance liquid chromatography (HPLC-ICP-MS) [7]. These techniques have a good sensitivity for the quantification of mercury but they are based on expensive and sophisticated instruments and require a transportation of samples. The portable nature of electrochemical technique and its excellent sensitivity, its low cost, its easy operation with high selectivity and good accuracy make them attractive for field monitoring of trace metals [8].

The use of chemically modified electrodes (CMEs) have received an increasing attention for the determination of metal ions [9-11]. The complexation reactions or ions exchange with organic or inorganic reagents have been reported [12–15]. The determination of Hg (II) has been performed by chemically modified carbon paste electrodes (MCPE) by organic compounds and nanomaterials [16-18]. Mercury has been preconcentrated by complexation with poly (Eriochrome Black T) [19], poly (EDTA-like) [20] or clay nanoparticle [21]. The detection limits obtained vary to 0.012 ppb to 20 ppb [22].

Indigo carmine is a water soluble aromatic heterocyclic compound, used as redox indicator [23] and as a dye in food and cosmetic industries [24]. The reaction between mercury and IC has been used for spectrophotometric determination of metals content of variety of samples [25,26]. Zanoni et al. [25] first used the complexation between IC and metals for analytical purposes. They used spectrophotometric technique for the determination of Cu (II) in pharmaceutical compounds [25]. Recently, the spectrophotometric determination of mercury has been performed using IC – Hg (II) complex [26].

The voltammetric behavior of indigo carmine has been also studied on different electrodes [27-29]. Our group has previously reported the IC voltammetric response on graphite electrode. This study has showed two well separated, quasi-reversible peak pairs ($\Delta E_p > 0.057/2$); the more positive oxidation peak has been used for copper detection by DPV [30].

In this work, an electrochemical method for mercury determination, based on Hg (II) reaction with IC and using DPV measurements performed at carbon paste electrode, was proposed. The experimental parameters affecting the Hg (II) - IC complex formation (pH, reaction time and temperature) were optimized. Due to the electro-inactivity of Hg (II) - IC complex, the decrease of the IC oxidation current measured in alkaline medium (pH 10) was used to draw a calibration curve allowing the determination of Hg (II) concentrations. Then, the determination of mercury in some samples using its reaction with IC is also investigated.

2. EXPERIMENTAL

2.1 Apparatus

Differential pulse voltammetric measurements were performed using a computer-controlled potentiostat (PalmSens, Ecochemie, Netherlands) and PSTrace software. A conventional three electrodes cell (10 mL) consisting of a carbon paste electrode (CPE) as working electrode, a Ag/AgCl, KCl sat as reference electrode and a Pt wire as counter electrode, was used. The solutions pH

was measured using a digital pH meter (Hanna Instruments, USA). Each individual experiment was performed at least three times and the results were averaged.

2.2 Reagents

Indigo carmine (3, 3 dioxo-2, 2 bis-indolyden-5, 5 - disulfonic acid disodium salt) was purchased from Sigma Aldrich (St. Louis, MO, USA). ICP-standard of mercury from Merck, Germany (1,000 mg.dm⁻³) was used as stock. All used chemicals were of analytical grade. Aqueous solutions were prepared with distilled water.

2.3 Procedure

2.3.1 Carbone paste electrode

The carbon paste electrode CPE was prepared by mixing 1 g of graphite powder “Sigma-Aldrich” (particle diameter $\phi = 0.1$ mm) and 300 μ L of paraffin oil using mortar and pestle until homogenous paste was obtained. The paste was then incorporated into the electrode cavity and polished on smooth paper. A stainless still wire provided the electrical contacts. The electrode surface could be renewed by simple extrusion of a small amount of paste from the tip of the electrode. Before each use of CPE, it was rubbed with a piece of paper until a smooth surface was observed.

2.3.2 Mercury (II) determination by DPV method

The electrode was immersed in aqueous solution containing IC in basic medium and appropriate mercury was added to a 10 mL cell. The resulting solution containing mercury was kept some time in chosen temperature. Quantitative measurements are performed by differential pulse voltammetry. The current response of IC was measured as I_1 . When mercury ions are added to IC solution, they form an electro-inactive complex with IC. Unreacted IC was then measured as described in the first step. The percentage of decrease in the IC signal due to the addition of Hg (II) ions can be expressed as: $\% I = \frac{I_1 - I_2}{I_1} * 100$

2.3.3 Real samples

Tap water was collected in the laboratory and well water from Azito close to Abidjan (Ivory Coast). All samples of tap water were analyzed without any pre-treatment. The determination of mercury in real samples as described in paragraph 2.3.2. Because of complexity of matrix, the mercury content was determined by the multiple standard addition method.

3. RESULTS AND DISCUSSION

3.1 Mercury – Indigo carmine complex formation

To determine the formation of IC - Hg (II) complex, we reacted 100 $\mu\text{mol.L}^{-1}$ of IC with different concentrations of aqueous Hg (II). Figure 1 shows the percentage decrease in IC signal as a function of the Hg (II) concentration using DPV method in basic media. It can be seen also from Fig. 1, mercury ions added to the solution (using the procedure described in paragraph 2.3.2) form an electro-inactive complex species with IC, which leads a decrease of IC current.

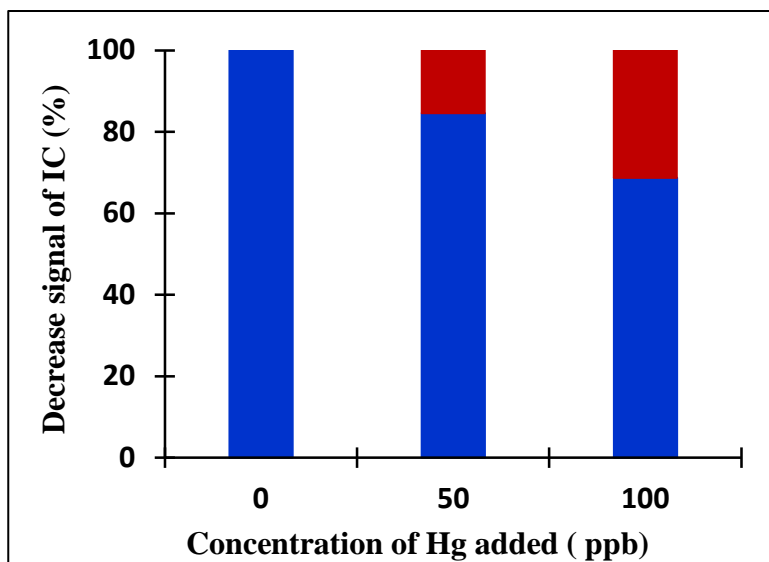


Figure 1. The percentage decrease in Indigo carmine signal as a function of the mercury concentration added using DPV method. Electrolyte 0.1 M carbonate buffer, scan rate 0.03 V/s; pulse amplitude, 100 mV. Brown bars represent Hg-IC complex and blue bars represent IC.

3.2. Optimum conditions for complex formation

When Hg (II) ions are added to an alkaline solution of IC, the Hg- IC or $(\text{Hg})_2\text{IC}$ complex is formed [26]. The main parameters influencing the complex formation (temperature, reaction time and pH) were investigated. The influence of the solution pH on the Hg - IC complex formation was investigated by measuring of the decrease of oxidation peak current induced by Hg (II) addition at different pH values (results not shown). The electrochemical behavior of IC is strongly affected by the pH of solution [30]. We have chosen pH 10 as working pH, considering that in spectrophotometric study, they showed at this range of pH, IC indigo carmine forms a stable complex with different ions as well as Hg^{2+} [25, 26]. In addition, the decrease of indigo carmine current was still significant at this pH and the buffering capacity of the carbonate solution is maximum.

3.2.1. Effect of temperature

The effect of the temperature on the formation of Hg- IC complex was studied by keeping the mixture Hg and IC solution for 15 min under different temperature. Figure 2 shows that the rate of reaction decreases with increasing the temperature. The percentage of decrease recorded at 10°C was above 45% but this percentage becomes less than 40 % up to 35°C. A great influence of temperature on rate of formation of Cu- IC was observed by Zazoni et al. [25]. In order to study at room temperature, it was decided that 25°C were an appropriate temperature.

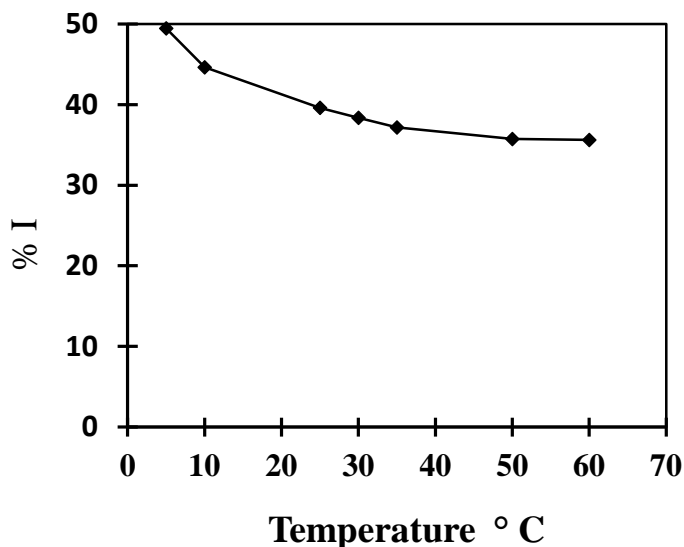


Figure 2. Effect of the temperature of the reaction on the formation of Hg- IC complex, IC 1mM, 0.5 μM (100 ppb) mercury ion. Scan rate 0.03 V/s; pulse amplitude, 100 mV.

3.2.2. Incubation time

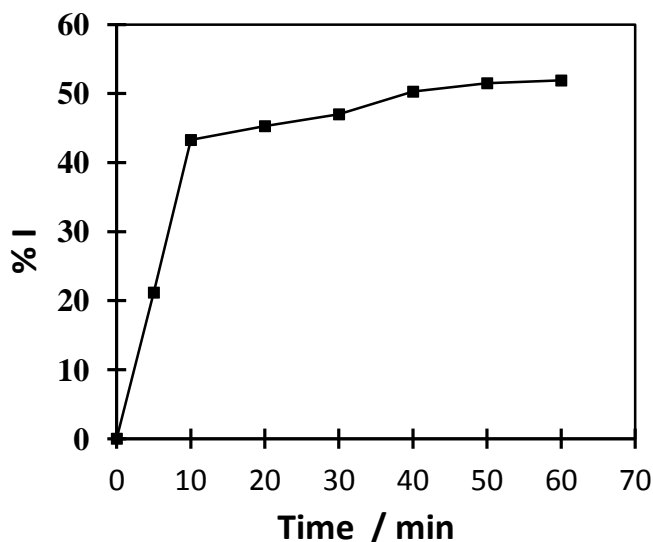


Figure 3. Effect of the time of reaction on the formation of IC –Hg complex; IC 1mM, mercury ion 0.5 μM (100 ppb). Temperature 25°C. Scan rate 0.03 V/s; pulse amplitude, 100 mV.

To estimate the time required for the reaction to be completed, Hg (II) ions were incubated with IC in alkaline medium (pH 10) for various periods of time (5 -120 min). The experimental results show that a maximum degree of conversion of IC to Hg-IC complex is attained between 10 to 20 min. Considering that response time is an important analytical feature, 10 min was considered as the reaction time.

3.2.3. Calibration and detection limit

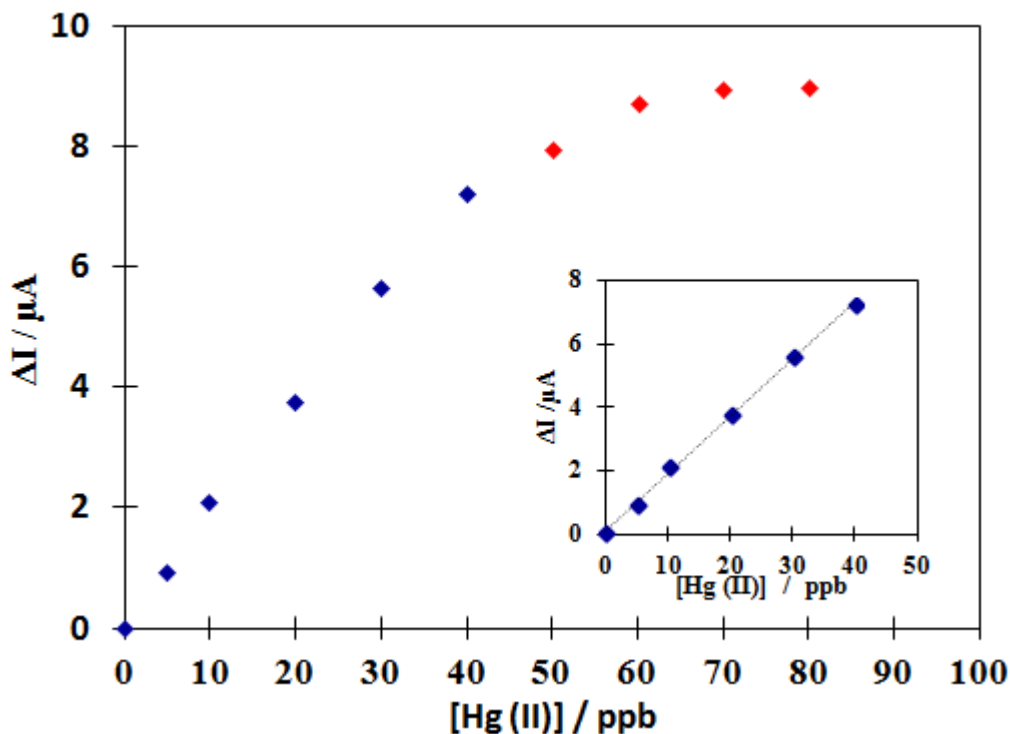


Figure 4. Calibration plot for mercury ions: 1mM indigo carmine; 0.1M carbonate buffer, pH 10. Experimental conditions: reaction time 10 min; Temperature 25°C; scan rate 0.03 V/s; pulse amplitude, 100 mV

Under the optimal experimental conditions, (temperature =25°C, time for reaction =10 min and pH 10), the variation of the percentage decrease in the IC signal as a function of concentration of mercury ions added to the solution was studied. The concentration of Hg used in this study were within relevant ranges ($2 \cdot 10^{-8}$ M to $5 \cdot 10^{-7}$ M). The linear domain is from $2 \cdot 10^{-8}$ M (5 ppb) to $2 \cdot 10^{-7}$ M (40 ppb) Hg(II), corresponds to the following regression equation: $y = 0.1805x + 0.0998$ with $R^2 = 0.998$. After 40 ppb the molar ratio of $[IC] / [Hg^{2+}]$ could influence the degree of conversion to the complex Hg -IC. However, taking into account the low concentration of mercury in environment [31], the range between 5 ppb to 40 ppb is quite good for the detection of mercury in real sample. The limit of detection (LOD) was estimated at 7.5 nM for a signal-to-noise ratio of 3.

3.3. Interference

To assess the selectivity of IC toward Hg (II), the same experiment was carried out in the presence of different metal ions: Zn^{2+} , Cu^{2+} , Pb^{2+} , Fe^{2+} under the optimized conditions given above. It was found that these ions have no significant effect on the selectivity and sensitivity of the analysis for the same concentration of mercury. However, because of the low concentration of mercury in environment, excess quantities of Zn (II) Cu (II), Fe (II) and Pb (II) relative to the mercury content were studied. Table 1 shows the ion concentration it takes to get 10% decrease in the oxidation current of indigo carmine. From these results it can be concluded that it is necessary to use the masking agent to determine mercury in presence of Zn (II) and Cu (II) as 5% decrease is enough to represent a significant interference.

Table 1. Concentration of ions causing 10% reduction in the oxidation current of 1 mM indigo carmine

Ions	Hg ²⁺	Cu ²⁺	Zn ²⁺	Fe ²⁺	Pb ²⁺
Concentration (μmol / L)	0.015	0.21	0.57	12.3	8.2

3.4. Application: Analysis of real samples

Table 2. Determination of Hg (II) in tap water

Sample N°	Spiked (ppb)	Found (ppb)	Recovery %
1	10	9,15	91,5
2	25	24,13	98,2
3	30	30,58	101,93

In order to evaluate the performance of this method, it was used for the determination of Hg (II) in potable tap water and well water samples.

The tap water samples were spiked with Hg (II) at different concentrations. Table 2 presents the results obtained from analysis of three samples. These data indicate that in the spiked water samples the recovery is more than 90% what is satisfactory.

The method was also applied to the well water samples analysis; Because of complexity of matrix, the multiple standard addition method was employed and each data of measurement was the average of at least three distinct analysis. The standard additions of 30 ppb of Hg (II) were injected to the samples. Without pre-treatment, the results obtained show a low recoveries (51%). As trace metals dissolved in natural waters may exist as free ions and in complexes forms, therefore mercury can be unavailable to form complexes with indigo carmine. After the filtration, the well water samples were acidified at pH 2.0 and diluted with buffer, the pH was also adjusted to pH 10 before analysis. The results are given in Table 3.

Table 3. Determination of Hg²⁺ in well water

	Sample non treated	Sample treated
Detected value after 30 ppb spike	15,3	24,13
Recovery (%)	51	80,43
RSD (%)	5	7

The results presented in table 3 show a low rate of recovery after the analysis of the real water samples. This result suggest that our method is not sufficiently selective to allow the determination of mercury for the real samples. However, it could be a useful pathway for the routine assessment of mercury in environmental samples after pretreatment.

4. CONCLUSION

DPV measurements performed at carbon paste electrode were successfully used for mercury determination in water samples, exploiting the Hg (II) reaction with IC in alkaline medium (pH 10). The results suggest that this method is simple with a relatively short analysis time and a low cost. In addition, utilization a portable potentiostat (Palmsens) makes this method applicable for field use.

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