**Research Article**

# New Method for Determination of Mercury in Contaminated Water by using Nano Composite Carbon Paste Electrode

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## Abstract

In this research, we constructed chemical sensor for determining mercury in contaminated water because we needed fast, simple, low-cost, and accurate determination of mercury in different environmental systems. Although several methods have been developed for determination of mercury ion in contaminated water, there is no a cheap, simple, accurate and rapid method to measure this ion. Aim of this study is to develop a new method to measure the mercury based on using nanosilica, multi-walled carbon nanotube (MWCNT) and 1,13-Bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix 5) as an ionophore for modification of a CPE. The optimum composition of modified CPE was determined as 63.6% of graphite powder, 25% of paraffin oil, 4% of multi-walled carbon nanotube (MWCNT), 0.4% nanosilica and 7% of ionophore. This optimum composition was shown high selectivity, with appropriate Nernestian slope ($29.5 \pm 0.4$mV/decade), linear range (from $1.0\times10^{-2}$ to $1.0\times10^{-8}$M), with a detection limit of ($2.0\times10^{-9}$M), The response of the sensor is independent of pH in the range of $3.1 - 8.4$, and The interference of different ionic species with the response of the electrode shows a good selectivity of the proposed sensor The proposed sensor is successfully applied in determination of mercury ions in some contaminated water samples. The results of this study to introduce a cheap accurate and simple method for determination of mercury ion in contaminated water.

**Keywords:** Multi-walled carbon nanotubes; Kryptofix 5; Sensor; Carbon paste ion selective; Potentiometry

## Introduction

Mercury is generally found at very low concentration in the environment. Mercuric ion can be absorbed readily by humans and other organisms. It may cause kidney toxicity, neurological damage, paralysis, chromosome breakage, and birth defects [1]. Due to its serious hazardous effect on human health and toxicity in the environment, it is important to control its levels in natural and potable water. Thus, it is very necessary to monitor the mercury levels in our environment in the past decades, numerous methods have been developed to determine heavy metals, including spectrophotometry, inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), atomic absorption spectrometry (AAS), electro thermal atomic absorption spectrometry (ETAAS) [2-8]. However, the majority of the above techniques require complex devices, training special skills and time consuming operations, which result in high costs. Electrochemical methods such as potentiometric is one of the most favorable approaches for the determination of heavy metal ions, due to its high sensitivity, ability for portability, low cost and time saving. Also they are able to preconcentrate the analytes on the electrode surface and have ability to analyze element speciation with no or minimum sample change [9-14]. Carbon paste electrodes (CPEs) have gained much attraction as ion selective electrodes of potentiometric mostly due to their benefits over membrane

electrodes such as fixed response, renewability, low ohmic resistance and no necessity for internal solution [15-18]. Graphite powder usually becomes dispersed in a non-conductive mineral oil, as a binder, to make carbon paste [19]. Newly, CPEs have been chemically modifying to boost the sensitiveness, selectivity, detection limit and other aspects of these electrodes. For example, some matters such as functionalized nanoparticles and appropriate ligands, have been applied within the electrode structure [20-23]. In this area multi-walled carbon nanotube (MWCNT), have attractive physicochemical properties that make them favorable for using as electrode modifiers, like ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, ordered structure with high aspect ratio, high surface area and metallic or semi-metallic behavior [24-25]. Also, the ability of electron transfer between the electrodes and the electro active species offers great potential for creating electrochemical sensors. These aspects make CNTs unique materials for diverse electrochemical applications [26-28]. In this work, the application of Kryptofix5 as an ionophore shown in Figure 1 have been discussed for the detection of Hg(II) ions in drinking water samples. The sensor responds to Hg(II) ions. The recognition of small molecules in binding with heavy metals has gained importance in the field of research. The Kryptofix5 has two donating nitrogen atoms and five oxygen atoms, low molecular weight and flexible structure were expected to act as a suitable ionophore in the preparation of carbon paste sensors for mercury ions of proper size and charge. Structure
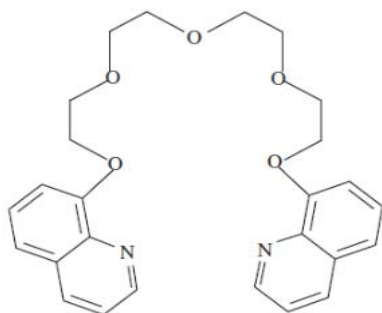
**Figure 1:** Structure of 1,13-Bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix 5).

of 1,13-Bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (Kryptofix5) (Figure 1). The main aim of this study is to develop a new method for determination of mercury ion in contaminated water based on using multi-walled carbon nanotube (MWCNT) and Kryptofix 5 as an ionophore for modification of a CPE.

## Experimental Parts

### Apparatus

The cell used for the measurements included the $Hg^{2+}$ carbon paste electrode as the working electrode and an Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode both of which were connected to a mili-voltmeter. The cell assembly constructed for the conduction of the electromotive force (Emf) measurements is as follows; Carbon paste electrode | sample solution (Contaminated Water) | Ag/AgCl–KCl (satd.).

### Reagents and materials

The ionophore Kryptofix 5 was purchased from Sigma-Aldrich. The graphite powder with a 1–2 μm particle size purchased from Merck. High purity paraffin oil obtained Aldrich. The multi-walled carbon nanotubes (MWCNTs) with 10–40 nm diameters, 1–25 μm length and with 95% purity were purchased from Research Institute of the Petroleum Industry (Iran). Nitrate and chloride salts of all the used cations (all from Merck Co.) were of the highest available purity and were used without any further purification. Doubly distilled water was used during the experiments.

### Carbon paste electrode preparation

For the purpose of preparing the carbon paste electrode the following proceeding was carried out respectively: First, different amounts of the paste ingredients such as ionophore (Kryptofix 5), binder (paraffin oil), graphite powder as an inert matrix, NS and MWCNTs as modifier entirely were pooled. Next, the resulting mixture was stirred to get homogenization paste about 30-40 min. Then, the final paste was transferred to the tip of a tube while a copper wire was put into the opposite side of the tube to electrical contact. It should be noted, in order to avoid possible air gaps which mostly lead to boost the electrode resistance, it is necessary to pack up the paste carefully and thoroughly into the tube tip. Last, to replace the new smoothed surface CPE by the old one, the external layer of the carbon paste was polished with soft paper. In the final stage, the electrode was conditioned for 48h by soaking it in a $1.0 \times 10^{-3}$ mol $L^{-1}$ $Hg(NO_3)_2$ solution. Unassayed Contaminated Water samples were analyzed for Mercury Ions.

## Results and Discussion

### Optimization of the CPEs

The ionophore used as the main ingredient of any ion-selective sensors is known to strongly influence the selectivity of such devices [29-33]. (Kryptofix 5) (Figure 1) was used in constructing a set of CPEs with a variety of compositions some of which were modified using the MWCNT, and nanosilica having the results of solutions studies in hand. The CP electrodes were then tested as sensing devices for $Hg^{2+}$ ion selective sensors and the results are illustrated in Table 1. The results show that the absence of the ionophore (Kryptofix 5) (compositions 1-3) in the composition of the carbon paste electrode leads to rather constant responses that are probably caused by the inherent (and probably unselective extraction of the cation into the sensing CPE surface). It was also observed that changing the amounts of the graphite powder as the filler and the nanosilica from 73.6-73.3 and 0.4-0.7 respectively, does not change the potential response of the sensor. It is noteworthy that graphite powder being a hydrophobic, high surface area compound improves the extraction of the ions into the surface of the CPE and also the mechanical resistant of the electrode.

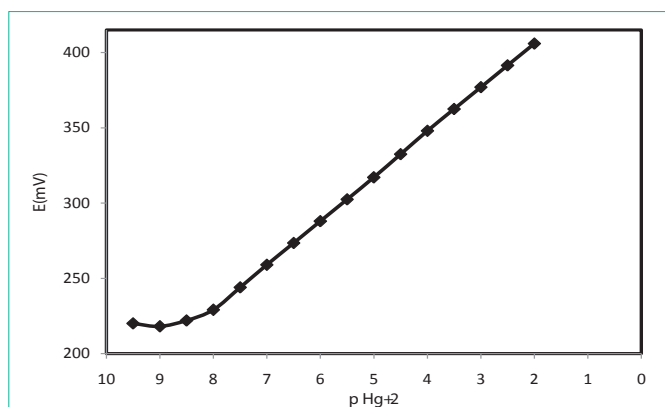The introduction of (Kryptofix 5) however leads to a meaningful

**Table 1**: The optimization of the carbon paste ingredients.

| Electrode No. | Composition of Carbon Paste (wt.%) | | | | | Slope (mV/decade) | Dynamic linear range (M) |
|---|---|---|---|---|---|---|---|
| | Binder (Paraffin oil) | Kryptofi5 | Graphite Powder | MWCNTs | Nano-Silica | | |
| 1 | 25 | 0 | 74.6 | 0 | 0.4 | 3.1±0.2 | $5.0 \times 10^{-4}$-$1.0 \times 10^{-10}$-2 |
| 2 | 25 | 0 | 74.5 | 0 | 0.5 | 2.5±0.3 | $4.0 \times 10^{-4}$-$1.0 \times 10^{-2}$ |
| 3 | 25 | 0 | 74.3 | 0 | 0.7 | 2.0±0.4 | $1.0 \times 10^{-4}$-$1.0 \times 10^{-2}$ |
| 4 | 25 | 4 | 70.6 | 0 | 0.4 | 18.7±0.5 | $1.0 \times 10^{-7}$-$1.0 \times 10^{-2}$ |
| 5 | 25 | 6 | 68.6 | 0 | 0.4 | 24.9±0.1 | $1.0 \times 10^{-8}$-$1.0 \times 10^{-10}$-2 |
| 6 | 25 | 7 | 67.6 | 0 | 0.4 | 28.9±0.3 | $1.0 \times 10^{-8}$ - $1.0 \times 10^{-2}$ |
| 7 | 25 | 8 | 66.6 | 0 | 0.4 | 33.4±0.5 | $1.0 \times 10^{-8}$-$1.0 \times 10^{-2}$ |
| 8 | 25 | 7 | 65.6 | 2 | 0.4 | 27.6±0.5 | $1.0 \times 10^{-8}$-$1.0 \times 10^{-2}$ |
| 9 | 25 | 7 | 64.6 | 3 | 0.4 | 32.5±0.2 | $1.0 \times 10^{-8}$-$1.0 \times 10^{-10}$-2 |
| 10 | 25 | 7 | 63.6 | 4 | 0.4 | 29.5 ± 0.4 | $1.0 \times 10^{-8}$-$1.0 \times 10^{-2}$ |
| 11 | 30 | 7 | 58.6 | 4 | 0.4 | 34.5 ± 0.4 | $1.0 \times 10^{-6}$-$1.0 \times 10^{-2}$ |

**Figure 2:** Calibration curves of the Kryptofix 5-based Hg²⁺ sensor.

increase in the potential response of the CP electrode which is, based on the previous observations, due to the enhanced and as was later observed, selective extraction of Hg²⁺ ion into the sensing surface of the electrode. This was a further support to the initial assumptions made about the selective tendency of (Kryptofix 5) towards Hg²⁺ ions. This trend further continued by increasing the amount of (Kryptofix 5) in the composition of CPE to 6 (no. 5) and 7 (no. 6) percents increasing the potential response to $24.9\pm0.1$ mV decade$^{-1}$ and $28.9\pm0.3$ respectively. Further increase in the amount of the amount of the ionophore to 8% wt. (no. 7), however, did not lead to any considerable changes in the response of the electrode. It was hence decided that 7% wt. is the optimum amount of the ionophore in the CPE. The electrode compositions were further modified by adding %2, %3 and %4 wt. of MWCNT to the composition (Nos. 8-10) which led to improvements in the potential response of the sensor from the sub Nernstian value of $27.6\pm0.5$ mV decade$^{-1}$ to the Nernstian values of $32.5\pm0.2$ mV decade$^{-1}$ and $29.5\pm0.4$ mV decade$^{-1}$ due to improving the conductivity of the composition.

## Calibration curve

The potential response of the Hg²⁺-CP electrode based on Kryptofix 5, Figure 2, which is known in terms of calibration curve displays the widish working linear range from $1.0\times10^{-9}$ to $1.0\times10^{-2}$ mol L$^{-1}$ for optimized Kryptofix 5-based mercury (II) carbon paste electrode, while according to Nernstian equation the slope of linear part of calibration curve is $29.5\pm0.4$ mV per decade with detection limit of $2.0\times10^{-9}$ mol L$^{-1}$ of mercury ions concentration which
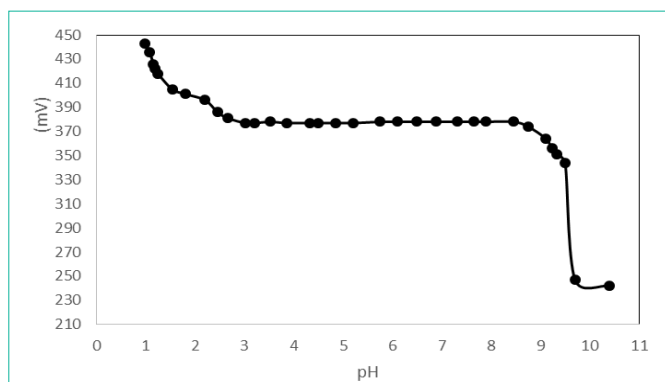
pursuant to the IUPAC recommendations is calculated by crossing of two extrapolated segments of the calibration curve [34-46]. The standard deviation for ten replicate measurements was ±0.4mV.

## The effect of pH

The influence of pH on the potential of the electrodes was investigated by measuring the Electro Motive Force (EMF) of the cell $1.0\times10^{-3}$ M of mercury (II) solutions. The pH values of the cell were adjusted by the addition of very small volumes of (0.01-0.1 mM) Hydrochloric acid or sodium hydroxide. The results are shown in Figure 3 it is evident that the electrode does not respond to pH changes in the range (3.1-8.4). Under more acidic conditions, the ligand may be protonated thereby losing its capacity to complex with the metal ions. The drift in potential at pH 8.5 is attributed to formation of mercury (II) hydroxide [47].

## Response time

Response time of the electrochemical sensors is evaluated through measuring the average time required to achieve potential values within ±0.1mV of the steady state potential of the electrode after its immersion in a series of solutions of the target ions, each having a ten-fold difference in concentration. Experimental parameters including stirring or the flow rate, the concentration and composition of each test solution, any previous application or preconditioning of the electrode, and the testing temperature can all affect the experimental response time of a sensor [48-54]. The response time of the proposed modified CPE was found to be less than 7s Figure 4.

## Selectivity of the Hg²⁺-CPE

One of the most important characteristics of the CPEs is its relative response towards the primary ion over other ions present in the solution, which is usually expressed in terms of potentiometric selectivity coefficients. In this work, the matched potential method was used for the evaluation of the selectivity of the sensor. The matched potential method selectivity coefficient, $K^{MPM}$, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K^{MPM} = a_A/a_B$. The resulting values are listed in Table 2. For all tested ions, the selectivity coefficients are in the order of $1.0\times10^{-3}$ or smaller, indicating they would not radically disturb the function of the developed Hg²⁺-CPE.

## Titration with EDTA

The proposed Hg²⁺-CPE was successfully applied as an indicator electrode in the titration of 25mL of contaminated water samples
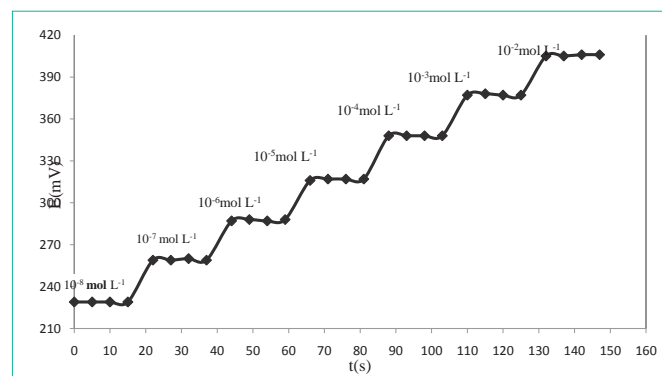


**Figure 3:** pH effect of the test solution ($1.0\times10^{-3}$ mol L$^{-1}$ of Hg²⁺) of the Hg²⁺ sensor based on Kryptofi 5.



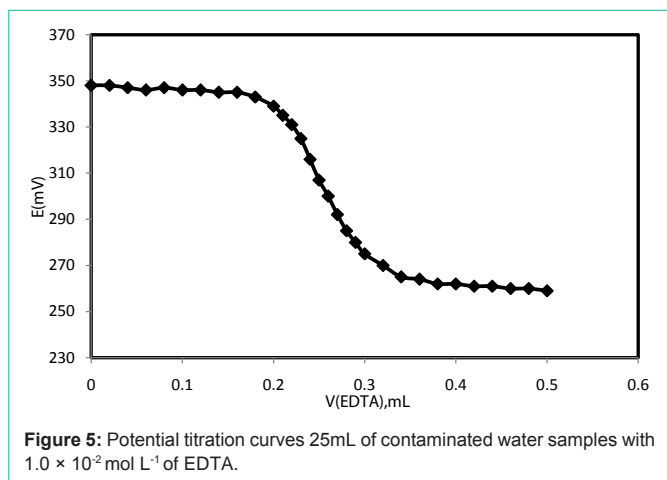**Figure 4:** Dynamic response time of Hg²⁺ sensor based on Kryptofi 5.

**Figure 5:** Potential titration curves 25mL of contaminated water samples with $1.0 \times 10^{-2}$ mol $L^{-1}$ of EDTA.

**Table 2:** Selectivity coefficients ($K_{Hg^{2+}}^{MPM}$) of proposed $Hg^{2+}$ -CPE.

| Interfering Ion | $K_{Hg,B}^{MPM}$ | Interfering Ion | $K_{Hg,B}^{MPM}$ |
|---|---|---|---|
| $Pr^{+3}$ | $8.0\times10^{-4}$ | $Yb^{+3}$ | $4.0\times10^{-4}$ |
| $La^{+3}$ | $8.0\times10^{-4}$ | $Mg^{+2}$ | $8.0\times10^{-4}$ |
| $Tm^{+3}$ | $4.0\times1^{0-4}$ | $Pb^{+2}$ | $8.0\times10^{-4}$ |
| $Nd^{+3}$ | $9.0\times10^{-4}$ | $Na^{+}$ | $4.0\times10^{-4}$ |
| $Eu^{+3}$ | $6.0\times10^{-4}$ | $K^{+}$ | $6.0\times10^{-4}$ |
| $Ho^{+3}$ | $\times9.0 10^{-4}$ | $Co^{+2}$ | $9.0\times10^{-4}$ |
| $Gd^{+3}$ | $4.0\times10^{-4}$ | $Cd^{+2}$ | $1.0\times10^{-3}$ |
| $Sm^{+3}$ | $8.0\times10^{-4}$ | $Ca^{+2}$ | $8.0\times10^{-4}$ |
| $Er^{+3}$ | $6.0\times10^{-4}$ | $Fe^{+3}$ | $2.0\times10^{-3}$ |
| $Tb^{+3}$ | $8.0\times10^{-4}$ | $Cr^{+3}$ | $1.7\times10^{-4}$ |
| $Dy^{+3}$ | $4.0\times10^{-4}$ | $Lu^{+3}$ | $6.0\times10^{-4}$ |

with a standard EDTA solution ($1.0\times10^{-2}$mol $L^{-1}$) and the resulting titration curve is shown in Figure 5. As can be seen from Figure 5, the endpoint of the titration is sharp and the sensor can monitor the amount of Mercury ions with good accuracy from the resulting titration curve.

# Conclusions

The proposed $Hg^{2+}$ selective electrode based on1, 1,13-Bis(8-quinolyl) 1,4,7,10,13-pentaoxatridecane (Kryptofix 5) as the electro active compound might be a useful analytical tool for the determinations of Hg(II) ions in the range from $1.0\times10^{-8}$ to $1.0\times10^{-2}$ M, and therefore an alternative to spectrophotometric methods. The proposed electrode was applied as indicator electrode and successfully used to determine mercury (II) in tap water samples with satisfactory results.

# Acknowledgement

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