

## Chemical Sensor for Determination of Mercury in Contaminated Water

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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. The constructed membrane composed of (Poly Vinyl Chloride) PVC as a matrix material, 1,5-diphenylthiocarbazon (dithizone) as electro active compound, and di-n-butyl phthalate (DBPH) as a plasticizer. The optimum membrane composition 30% PVC, 65% DBPH, 5% dithizone exhibited the better Nernstian response. The results showed that probe is high stability along the pH range from (3.5 to 8). The electrode displays a linear log  $[Hg^{2+}]$  versus Electromotive Force (EMF) response over a wide concentration range of ( $5 \times 10^{-6}$  to  $1 \times 10^{-2}$  M) with Nernstian slope of  $29.7 \pm 0.5$  mV decade<sup>-1</sup> and limit of detection  $3 \times 10^{-6}$  M. The proposed sensor shows relatively high selectivity for mercury ion in different matrix solution, other ions had negligible interference effect on the reading.

**Keywords:** Ion selective electrodes; Polymeric membranes; Determination of mercury

## 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 [1,2]. 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. The common methods for the purpose that are being adopted are complexometry and spectrophotometry [3], Cold Vapor Atomic Absorption Spectrometry (CV-AAS) [4] inductively coupled plasma Atomic emission spectrophotometry (ICP-AES) [5] and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [6,7], X-Ray fluorescence [8] and Voltammetry [9]. But the potentiometric technique has advantages such as high selectivity, sensitivity, good precision, simplicity and low cost. There is a considerable attention has been given for drug analysis using Ion-Selective Electrodes (ISEs) [10,11].

A number of ISEs based on conventional polymeric membrane, and coated wire electrodes utilizing various neutral ionophores were made for determination of mercury ion [12-15].

The aim of this paper was therefore to evaluate a simple method for inorganic mercury determination in aqueous solution by PVC-membrane electrode based on 1,5-diphenylthiocarbazon (dithizone) (Figure 1).

## Experimental

## Reagents and materials

All the reagents were of analytical grade and were used as received. Solvent mediator (plasticizer) di-n-butyl phthalate (DBPH) was

obtained from Merck (Germany). High molecular weight (PolyVinyl Chloride) (PVC) was obtained from Sigma-Aldrich (USA). AR grade tetrahydrofuran (THF), 1,5-diphenylthiocarbazon (dithizone), hydrochloric acid and sodium hydroxide were obtained from Fluka (Germany). Stock solutions (0.1 M) of  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Hg^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$  were prepared by direct dissolution of proper amounts of metal salts in doubly distilled water.

## Apparatus

Electrochemical measurements were made pH/ION/ Cond 750 Ion analyzer WTW at 25°C in conjunction with a ceramic junction calomel electrode. The electrochemical cell assembly used for this study was as follows: Ag/AgCl | Internal solution (0.1 M) of  $Hg^{2+}$  | PVC membrane | Sample solution | Hg/Hg<sub>2</sub>Cl<sub>2</sub>, KCl (saturated). A pH meter WTW, inoLab<sup>®</sup> pH 720/7200 was used to check the pH of the solutions.

## Construction of mercury (II) membrane electrode

Membranes were prepared by the Moody-Thomas method [16].  $Hg^{2+}$ -selective membrane was prepared by dissolving 25 mg of dithizone as ionophore, 150mg PVC and 325 mg of DBPH in 5 mL THF. The solution was poured into glass Petri dishes (5 cm diameter), and was allowed to evaporate overnight at room temperature. The thickness of the obtained membrane was about 0.3 mm. Membranes (10 mm diameter) were cut out and glued to the polished end of PVC tubes by means of a PVC-THF solution. The electrode bodies consisted of a glass tube, to which the PVC tube was attached at one end and filled with an internal solution (0.1 M of  $Hg^{2+}$ ). The membrane was conditioned by immersing in a 0.1 M  $Hg^{2+}$  solution for 3 hours before measurements.

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## Direct potentiometric determination of mercury (II)

The electrode was calibrated by transferring 20 mL aliquots of  $1 \times 10^{-4}$

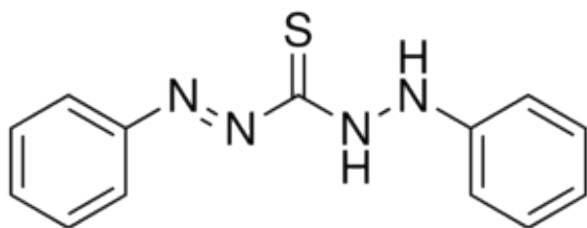


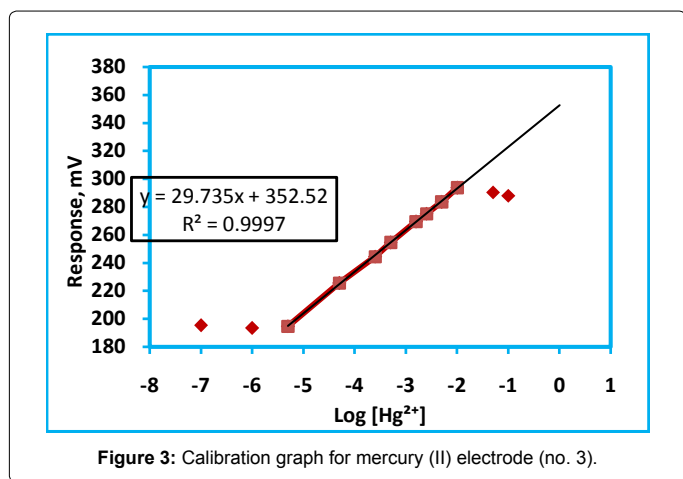
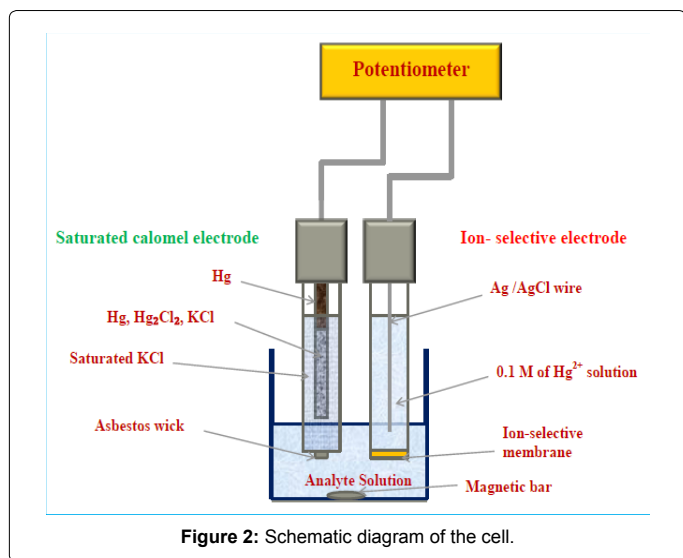
Figure 1: Chemical structure of dithizone.

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Received August 30, 2013; Accepted September 18, 2013; Published September 25, 2013

Citation: Hassan AK (2013) Chemical Sensor for Determination of Mercury in Contaminated Water. Mod Chem appl 1: 111. doi:10.4172/2329-6798.1000111

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$7 \cdot 10^{-1}$  M aqueous solutions of mercury (II) to 50 mL beakers, followed by immersing the Ion-selective membrane electrode, together with a calomel reference electrode in the solution. The potential readings were recorded after stabilization to  $\pm 0.5$  mV, and the EMF was plotted as a function of the logarithm of the mercury (II) concentrations. The calibration graph was used for subsequent determinations of unknown mercury (II) concentrations. A typical calibration plot for electrodes No. 3 is shown in Figure 3.

### Selectivity of the electrode

The selectivity coefficients over interfering species were evaluated by the separate solution method [17-20] at  $1 \times 10^{-3}$  M concentration of mercury (II) solution and interfering.

## Results and Discussion

### Optimization of the electrodes

**Composition of the membranes:** Five membranes of the different compositions were investigated with the DBPH as plastizer given in (Table 1). For each composition, the amount of polymer (Poly Vinyl Chloride) (PVC) was kept constant (30% w/w) and varying the percentage (w/w) of dithizone as ionophore and plasticizer [21]. The results reveal that the composition having the 5% dithizone leads to exhibit a better slope ( $29.7 \pm 0.5$  mV decade<sup>-1</sup>); correlation coefficient

(0.9997) and wide concentration range ( $5 \times 10^{-6}$  to  $1 \times 10^{-2}$  M). In all subsequent studies electrodes made of the membrane composition No.3 (PVC, 30%; plasticizer, 65%; ionophore, 5%) were used (Table 1).

### The effect of pH

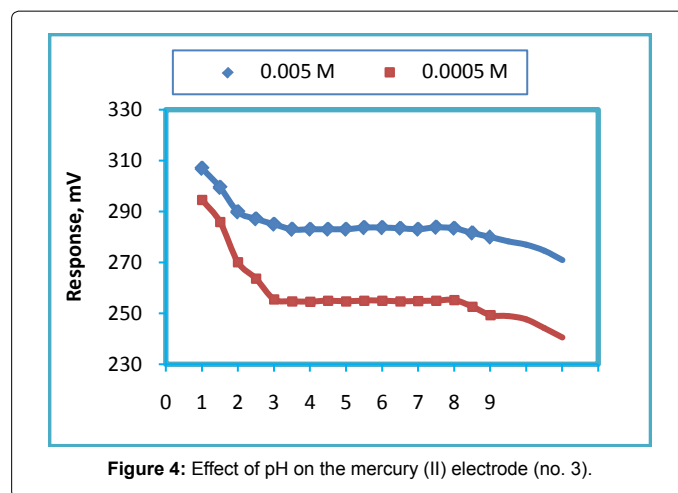
The influence of pH on the potential of the electrodes was investigated by measuring the Electro Motive Force (EMF) of the cell at  $5 \times 10^{-4}$  and  $5 \times 10^{-3}$  M of mercury (II) solutions. The pH values of the cell were adjusted by the addition of very small volumes of (0.01-0.1 M) Hydrochloric acid or sodium hydroxide. The results are shown in Figure 4 it is evident that the electrode does not respond to pH changes in the range (3.5-8.0). 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 [22] (Figure 4).

### Construction of the calibration graphs

The electrodes were calibrated by transferring 20 mL aliquots of ( $1 \times 10^{-7}$  to  $1 \times 10^{-1}$  M) aqueous solutions of mercury (II) to 50 mL beakers, followed by immersing the mercury-selective electrode in conjunction with a calomel reference electrode in the solution. The potential readings were recorded after stabilization to  $\pm 0.5$  mV and the EMF was plotted as a function of the logarithm of the mercury (II) concentration. The calibration graph was used for subsequent determination of unknown mercury (II) concentrations. A typical calibration plot for electrodes No.3 is shown in Figure 3.

### Response time and life span

Long-term stability of electrode potential is an important parameter in practical applications of ion-selective electrodes. Large potential drift is a major drawback. A purpose of this work was to shade some light on stability of prepared electrode. Potential stability of mercury ISE



No.	Composition % (w/w)			Slope (mV/decade)	Correlation coefficient
	PVC, %	DBPH, %	Dithizone, %		
1	30	69	1	27.3	0.986
2	30	67	3	28.6	0.989
3*	30	65	5	29.7	0.999
4	30	63	7	27.2	0.991
5	30	60	10	23.8	0.980

\*Optimum composition

**Table 1:** Composition of different membranes and slopes of the corresponding calibration graphs.

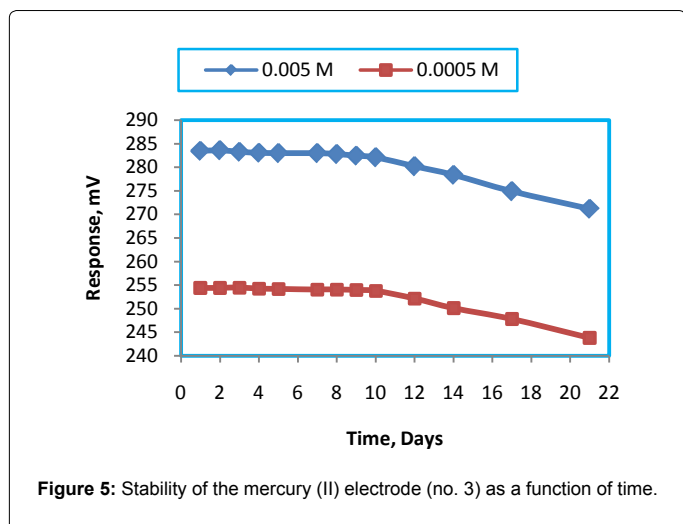


Figure 5: Stability of the mercury (II) electrode (no. 3) as a function of time.

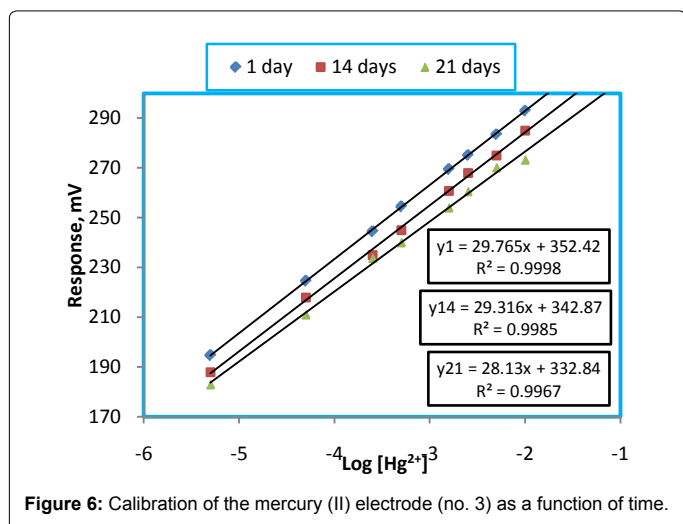


Figure 6: Calibration of the mercury (II) electrode (no. 3) as a function of time.

Parameter	
Slope (mV decade <sup>-1</sup> )	29.7 ± 0.5
Linear concentration range (M)	5 × 10 <sup>-6</sup> - 1 × 10 <sup>-2</sup>
Intercept (mV)	352.5
Correlation coefficient, r	0.9997
Lower detection limit (M)	3.0 × 10 <sup>-6</sup>
Response time for 1 × 10 <sup>-3</sup> (M) solution (sec)	20 ± 1
Working pH range	3.5 - 8.0
Life time (day)	14

Table 2: Summary of the response characteristic of the mercury sensor

electrodes was monitored over 21 days by measuring their potentials in 5 × 10<sup>-3</sup> and 5 × 10<sup>-4</sup> M standard mercury (II) solutions each day as show in Figure 5. The slope of each electrode in mV per decade was calculated and compared with the original slope obtained when this electrode was calibrated at the first time in the 1 × 10<sup>-6</sup> to 1 × 10<sup>-2</sup> M mercury (II) solutions. Electrode was considered no longer suitable for measurements when the slope differences exceeded 1.0 mV per decade Figure 5.

In Figure 5, the potentials of electrode were shown to be significantly stable up to 10 days. A drift of <5 mV per decade was observed after 14 days. It indicate that, electrode remains fully operational and the Ag/AgCl internal reference remains free from water transport for at least 14 days. It was observed that the investigated electrode (no. 3) exhibited

good stability in terms of slope in the linear domain of concentration and the electrode can be used continuously for about 14 days without considerable decrease in its slope value as show in Figure 6. A decrease in electrode stability after 14 days might be attributed to leaching the ionophore (dithizone) from the membrane. A 15-30 s response times were recorded for prepared electrode in the 1 × 10<sup>-2</sup> to 1 × 10<sup>-5</sup> M mercury (II) solutions. After 14 days, a decrease in electrodes stability is associated with increase in response times up to 1-2 min. (Table 2) showed summary of the response characteristic of the mercury sensor (Table 2).

### Selectivity of the electrode

The selectivity coefficients are the most important characteristics of the membrane sensor, informing about the ability of the electrode in discriminating the primary ion against other ions of the same charge signs. Selectivity coefficients were determined by the separate solution method [17-20] in which the following equation was applied:

$$\log K_{Hg^{2+}, j^{z+}}^{pot} = (E_2 - E_1) / S + \log [Hg^{2+}] - \log [j^{z+}]^{1/z} \quad (1)$$

E<sub>1</sub> is the electrode potential in a 1.0 × 10<sup>-3</sup> M Hg<sup>2+</sup> solution.

E<sub>2</sub> is the potential of the electrode in a 1.0 × 10<sup>-3</sup> M solution of the interferent ion (j<sup>z+</sup>).

S is the slope of the calibration plot.

The influence of some inorganic cations on the electrode response was investigated. This method is considered to be the simplest way to evaluate the degree of interference that might be taking place and is used to perform measurements in aqueous samples. The selectivity coefficients obtained by this method. Table 3 showed that the proposed electrode was highly selective toward Hg<sup>2+</sup> ion. The inorganic cations did not interfere due to the differences in their mobility's and permeability's as compared with Hg<sup>2+</sup> ion. As can be seen from Table 3, most ions have negligible interference; the ions Pb<sup>2+</sup> show intermediate effect, which is common interfering ion on Hg (II) ion-selective electrode as they have comparable size and characteristics to those of mercury ions [22] (Table 3).

### Analytical applications

The proposed sensor was found to work well under laboratory conditions. It is clear that the amount of Hg<sup>2+</sup> ions can be accurately determined using the proposed sensor. To assess the applicability of the proposed sensor to real samples, Hg<sup>2+</sup> was measured in treated tap water. Each sample was analyzed in triplicate, using this sensor by the direct method. The results in (Table 4) show an average recovery of 97% with Relative Standard Deviation (RSD) of 2% and indicate the utility of the proposed electrode (Table 4).

Foreign ion	K <sub>Hg<sup>2+</sup>, j<sup>z+</sup></sub> <sup>pot</sup>
Na <sup>+</sup>	1.2 × 10 <sup>-3</sup>
K <sup>+</sup>	1.9 × 10 <sup>-3</sup>
Mg <sup>2+</sup>	4.0 × 10 <sup>-3</sup>
Ca <sup>2+</sup>	5.9 × 10 <sup>-3</sup>
Zn <sup>2+</sup>	5.1 × 10 <sup>-3</sup>
Cu <sup>2+</sup>	4.9 × 10 <sup>-3</sup>
Cr <sup>3+</sup>	2.7 × 10 <sup>-3</sup>
Fe <sup>3+</sup>	4.9 × 10 <sup>-3</sup>
Pb <sup>2+</sup>	6.5 × 10 <sup>-2</sup>
Hg <sup>2+</sup>	3.1 × 10 <sup>-2</sup>

Table 3: Selectivity coefficient values for mercury (II) electrode (no. 3).

Hg <sup>2+</sup> added, (M)	Hg <sup>2+</sup> Found*, (M)	RE, %	Rec., %	RSD, %
5.0×10 <sup>-5</sup>	4.83×10 <sup>-5</sup>	-3.4	96.6	1.8
1.0×10 <sup>-4</sup>	0.97×10 <sup>-4</sup>	-3.0	97.0	2.3
5.0×10 <sup>-3</sup>	4.88×10 <sup>-3</sup>	-2.4	97.6	1.9

\*Average of three determinations

**Table 4:** Recovery of mercury ions from tap water

## Conclusion

The proposed Hg<sup>2+</sup> selective electrode based on 1,5-diphenylthiocarbazon (dithizon) as the electro active compound might be a useful analytical tool for the determinations of Hg(II) ions in the range from 5×10<sup>-6</sup> to 1×10<sup>-2</sup> 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.

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**Citation:** Hassan AK (2013) Chemical Sensor for Determination of Mercury in Contaminated Water. Mod Chem appl 1: 111. doi:10.4172/2329-6798.1000111

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