



## Potentiometric Determination of Mercury Ions by Ion Imprinted Polymer Coated Multiwall Carbon Nanotube: High Selective Sensor for Determination of Trace Amounts of Mercury Ions in Biological Samples

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### ABSTRACT

A Hg(II) ion imprinted polymer was synthesized and coated on multiwall carbon nanotube. This material was used for modification of a carbon paste electrode. The electrode was used for determination of trace amounts of mercury (II) ions in aqueous media. The electrode composition was graphite powder 66%, paraffin 24% and IIP@MWCNTs 11% (W/W). The linear range for mercury (II) was  $8.0 \times 10^{-8}$  to  $3.5 \times 10^{-3}$  mol L<sup>-1</sup> and the limit of detection was obtained  $6.3 \times 10^{-8}$  mol L<sup>-1</sup>. The response time and lifetime of the electrode were improved by coating of IIP on MWCNTs surface. The Method validation was performed by analyzing of some standard reference materials.

**Key words:** Carbon paste electrode, Mercury, Modified MWCNTs, Potentiometry, Ion imprinted polymer.

### INTRODUCTION

Mercury is one of the most toxic elements which has intensive impact on ecosystem health even at low concentrations<sup>1</sup>. This element is released into the environment from both anthropogenic and natural sources. By population growth and urbanization, more and more mercury have been released all over the world till mercury pollution becomes a worldwide environmental

problem nowadays<sup>2</sup>. The allowed mercury level set by World Health Organization (WHO) for drinking water is 1 µg L<sup>-1</sup><sup>3</sup>. As a result of high toxicity even at low concentrations, developing a more accurate, precise and selective method for mercury determination is necessary. In this concern, lots of techniques such as cold vapor generation-atomic fluorescence spectrometry<sup>4,5</sup>, atomic absorption spectrometry in quartz furnace or graphite-furnace<sup>6-8</sup>, atomic fluorescence spectrometry<sup>9</sup>,

inductively coupled plasma atomic emission spectrometry<sup>10,11</sup>, voltammetry<sup>12</sup> and potentiometry<sup>13-15</sup> have been developed for determination of mercury concentration in different media. Among these methods, potentiometric methods using ion sensors are common due to their accuracy, high rate, low cost and also being non-destructive<sup>16</sup>. Potentiometric carbon paste electrodes (CPEs), in comparison to polymeric membrane electrodes, possess very attractive properties such as ease of preparation, renewable surface, stability of their response, low Ohmic resistance and no need of internal solution<sup>17,18</sup>. In order to increase the methods sensitivity and decrease the limit of detection value, a chemical modifier is needed to be introduced to carbon paste electrode<sup>19</sup>. Owing to interesting properties such as high electrical conductivity, high mechanical and thermal stability and high surface area, the usage of carbon nanotubes (CNT) as a chemical modifier in carbon paste electrodes has been increased recently<sup>20,21</sup>. However, in order to be selective, the CNT needs to be modified with an appropriate ligand<sup>22</sup>. The traditional simple modifiers suffer from lack of selectivity. By adverting ion imprinted polymers (IIP) for the first time in 1931, they have become so popular for their high selectivity due to construct tailor-made binding sites for a given target ion<sup>23</sup>.

In this work, multiwalled carbon nanotube have been modified with a novel Hg(II) imprinted polymer and used as a high selective sensor for fast determination of Hg(II) ions in environmental samples. The accuracy of this method was confirmed using some standard reference materials with certified amount of Hg(II) ions.

## EXPERIMENTAL

### Reagents and Solutions

All reagents were analytical grade and used without further purification. Ethylene glycol dimethacrylate (EGDMA) was obtained from Fluka (Buchs, Switzerland). 2,2'-Azobisisobutyronitrile (AIBN) was obtained from Acros Organics (New Jersey, USA). Paraffin oil and mercury nitrate were purchased from Fluka. Multi-walled carbon nanotubes (MWCNTs), industrial grade, 85% purity, 10–40 nm in diameters, 1–25  $\mu\text{m}$  in length, were purchased from Neutrino Company (Tehran, Iran).

All other chemicals were purchased from Merck Company and used without further purification. All solutions were made using deionized water, provided from a Milli-Q (Millipore, Bedford, MA, USA) purification system. A Ground water (ERM-CA615) and a Trace metal (RTC-QCI-049) standard reference materials were obtained from Chemistry Reference Laboratory Equipment (Turkey).

### Instrumentation

The glass cell, consisted of an R684 model Analion Ag/AgCl double junction reference electrode was used as a reference electrode. A Corning ion analyzer 250pH/mV meter was used for the potential measurements. The pH meter was a digital WTW Metrohm 827 Ion analyzer (Switzerland) equipped with a combined glass-calomel electrode. All measurements were made at  $25 \pm 1$  °C. Thermal gravimetric and differential thermal analysis (TG/DTA) was carried out on a Bahr STA-503 instrument under air atmosphere. IR spectra were recorded by BOMEM/MB series Spectrometer. The Elemental analysis was performed with a Thermo Finnigan Flash-2000 microanalyzer (Italy). Morphology and size of the particles was observed on a Vega-TeScan scanning electron microscope with gold coating.

### Preparation of Hg(II) Ion Imprinted Polymer Coated MWCNT

#### Preparation of MWCNT Vinyl Functionalized MWCNT

Vinyl functionalized MWCNT was prepared according to the earlier method<sup>24</sup>. In this approach, 1.0 g of COOH-MWCNT was suspended in 50 mL of dried  $\text{CH}_2\text{Cl}_2$ , afterward 5.0 mL of oxalyl chloride was added to the solution and the mixture was stirred for 24 h. Then the solvent was removed under reduced pressure and the residue was suspended in 50 mL THF and triethylamine mixture (1:3 V:V) and 5 mL 3-Aminopropyltriethoxy silane was added subsequently. After 2 h the particles were centrifuged, and placed in HCl solution (pH=4). The product was named  $\text{SiO}_2$ @MWCNT. To prepare vinyl functionalized MWCNT, 1.0 g of  $\text{SiO}_2$ @MWCNT was suspended in 50 mL of toluene, afterward 1.0 g of 3-vinyletriethoxy silane was added to the solution and the mixture was stirred for 24 h. The solid phase was separated from the solvent and washed 3 times with 50 mL of ethanol. The vinyl functionalization of

MWCNT was confirmed by IR spectroscopy and elemental analysis. Elemental analysis shows 0.48 mmol g<sup>-1</sup> vinyl coated on this sorbent (C=1.72 %, H=0.23%)

#### Preparation of Mercury(II) Complex

The ligand N-(pyridin-2-ylmethyl)ethenamine (V-Pic) has been synthesized by reaction of 1 mmol of 2-Picolylamine with the same molar amount of vinyl chloride in 50 mL of triethylamine and methanol (1:1, v:v). The mercury complex (Hg(V-Pic)<sub>2</sub>·2NO<sub>3</sub>) has been synthesized by reaction of 0.5 mmol mercury nitrate salt with N-(pyridin-2-ylmethyl) ethenamine.

#### Preparation of Mercury(II) Ion Imprinted Polymer Coated on MWCNT

In order to synthesis Hg(II) ion imprinted polymer coated on MWCNT, In a typical polymerization, in a two-necked glass reactor equipped with a condenser, a mechanical stirrer, and a gas inlet to maintain a nitrogen atmosphere, 1 mmol of mercury complex and 1 g of vinyl functionalized MWCNT, were dispersed in 100 mL of methanol. Then the mixture was heated to 60 °C. Afterward 0.1 g of AIBN and 1.0 mL EGDMA were added to the mixture. After 48 h, the composite was separated by a centrifuge and the template was removed by a solution containing 1 mol L<sup>-1</sup> solution of HClO<sub>4</sub>. The removal of the template was followed by ICP-OES. The ICP-OES data showed that the removal was completed after 8 times. In order to confirm the removal of Hg(II) ions, the amount of Hg(II) ions was determined by ICP-OES after treatment with piranha solution (H<sub>2</sub>SO<sub>4</sub>+H<sub>2</sub>O<sub>2</sub>). Piranha solution release mercury(II) ions in solution as it can dissolves organic parts of any composite. The formation of this IIP was confirmed by IR, TG/DTA analysis and also SEM photograph. A schematic diagram of this IIP is shown in Fig. 1.

#### Preparation of Modified Carbon Paste Electrode

Modified carbon paste was prepared by graphite powder 66%, paraffin 23% and IIP@MWCNTs 11% (W/W) following hand mixing in a mortar and pestle. The paste was then packed into the end of a glass tube (ca. 3.0 mm i.d. and 10 cm long). Electrical contact was made by inserting a copper wire into the glass tube at the back of the mixture. When necessary, a new surface was

obtained by pushing an excess of paste out of the tube and polishing it on a weighing paper.

#### Electrode Conditioning

Before all electrode measurements the electrode surfaces were conditioned by 1.0×10<sup>-4</sup> mol L<sup>-1</sup> Hg(NO<sub>3</sub>)<sub>2</sub> and 1.0×10<sup>-3</sup> mol L<sup>-1</sup> NaNO<sub>3</sub> for 48 hours. The pH of the solution was adjusted to 2.5. The electrodes were rinsed by deionized water before potentiometric measurements.

#### Emf Measurements

The electrochemical cell can be represented as follows:  
Ag, AgCl (s), KCl (3 mol L<sup>-1</sup>) || analyte solution | carbon paste electrode  
All measurements were done versus Ag, AgCl(s) reference electrode.

#### Sample Preparation

RTC-QCI-049 (Trace metal) standard reference material was analyzed without any pretreatment. Water samples were obtained from tap water (Tehran, Iran), distilled water, sea water (Caspian Sea, Sari, Iran) and sewage water (Karaj industrial zone, Iran). Water samples were collected in cleaned polyethylene bottles and were filtered through a 0.45 μm pore size nylon filter (Millipore) immediately after sampling.

The fish species were collected from commercial market landed at some local fishing port in Tehran-Iran in fall 2011. The samples placed in clean plastic bags and stored on ice in an ice chest. They were then transported to the laboratory, identified and kept in a freezer at -20 °C prior to preparation for chemical analysis. The samples were washed with distilled water and dried in tissue paper after defrosting in the laboratory. A portion of the edible muscle tissue was removed from the dorsal part of each fish, homogenized and stored in clean-capped glass vials and kept in -20 °C until analysis. The samples were digested with HCl (37%) and 2 mL of HNO<sub>3</sub> (65%) in a microwave digestion system. Digestions were carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W and then vented for 8 min. Afterward, the residues of digestion were diluted with deionized water.<sup>25</sup>.

## RESULTS AND DISCUSSION

**Characterization of Hg(II) Ion Imprinted Polymer Coated MWCNT**

Formation of ion imprinted polymer on the surface of MWCNT was confirmed by IR

spectroscopy, thermal analysis and SEM micrograph. Modification of nano-size MWCNT surface with vinyl groups was carried out through the earlier method using carboxyl MWCNT according to the sol-gel method<sup>24</sup>. The reaction of vinyl functionalized MWCNT as a monomer with

**Table 1: Optimization of the electrode composition**

Electrode No.	Graphite powder (%)	Paraffin (%)	IIP polymer	Unmodified MWCNTs (%)	IIP-MWCNTs (%)	Slope (mV)	Linear range (mol L <sup>-1</sup> )	R <sup>2</sup>
1	75	25	0	0	0	8.2±3.1	-	-
2	73	24	3	0	0	13.7±2.4	8.5×10 <sup>-6</sup> to 5.0×10 <sup>-2</sup>	0.903
3	72	23	5	0	0	16.3±2.0	4.0×10 <sup>-6</sup> to 5.0×10 <sup>-2</sup>	0.921
4	71	22	7	0	0	17.2±1.8	2.0×10 <sup>-6</sup> to 5.0×10 <sup>-2</sup>	0.933
5	70	21	9	0	0	18.1±1.6	1.0×10 <sup>-6</sup> to 5.0×10 <sup>-2</sup>	0.943
6	68	21	11	0	0	16.8±1.9	3.0×10 <sup>-6</sup> to 5.0×10 <sup>-2</sup>	0.928
7	73	24	0	3	0	10.4±2.8	-	-
8	72	23	0	5	0	13.2±2.5	8.0×10 <sup>-6</sup> to 5.0×10 <sup>-2</sup>	0.901
9	70	23	0	7	0	15.3±2.1	5.0×10 <sup>-6</sup> to 5.0×10 <sup>-2</sup>	0.919
10	68	23	0	9	0	17.1±1.9	1.5×10 <sup>-6</sup> to 5.0×10 <sup>-2</sup>	0.929
11	67	22	0	11	0	16.8±2.0	3.0×10 <sup>-6</sup> to 5.0×10 <sup>-2</sup>	0.925
12	63	23	9	5	0	20.2±1.6	6.5×10 <sup>-7</sup> to 1.5×10 <sup>-3</sup>	0.955
13	61	23	9	7	0	24.9±1.4	2.1×10 <sup>-7</sup> to 3.5×10 <sup>-3</sup>	0.975
14	59	23	9	9	0	28.9±1.1	7.0×10 <sup>-8</sup> to 4.0×10 <sup>-3</sup>	0.989
15	58	22	9	11	0	27.2±1.3	1.0×10 <sup>-7</sup> to 3.5×10 <sup>-3</sup>	0.980
16	72	23	0	0	5	24.1±1.5	2.5×10 <sup>-7</sup> to 3.5×10 <sup>-3</sup>	0.970
17	70	23	0	0	7	26.6±1.4	1.0×10 <sup>-7</sup> to 3.5×10 <sup>-3</sup>	0.980
18	68	23	0	0	9	27.9±1.2	1.0×10 <sup>-7</sup> to 3.5×10 <sup>-3</sup>	0.982
19	66	23	0	0	11	28.2±1.2	8.0×10 <sup>-8</sup> to 3.5×10 <sup>-3</sup>	0.988
20	64	23	0	0	13	27.8±1.3	1.3×10 <sup>-7</sup> to 3.5×10 <sup>-3</sup>	0.980

**Table 2 Performance characteristics modified carbon paste electrodes number 14 and 19 at different test solution temperatures**

Electrode No.	Temperature (°C)	Slope (mV)	Linear range (mol L <sup>-1</sup> )
14	25	28.9	7.0×10 <sup>-8</sup> to 4.0×10 <sup>-3</sup>
	35	29.3	1.0×10 <sup>-8</sup> to 4.0×10 <sup>-3</sup>
	45	30.5	2.5×10 <sup>-7</sup> to 4.0×10 <sup>-3</sup>
	55	33.9	4.0×10 <sup>-7</sup> to 4.0×10 <sup>-3</sup>
	65	31.7	3.0×10 <sup>-7</sup> to 4.0×10 <sup>-3</sup>
19	25	28.2	8.0×10 <sup>-8</sup> to 3.5×10 <sup>-3</sup>
	35	28.5	9.0×10 <sup>-8</sup> to 3.5×10 <sup>-3</sup>
	45	28.9	9.0×10 <sup>-8</sup> to 3.5×10 <sup>-3</sup>
	55	29.1	9.0×10 <sup>-8</sup> to 3.5×10 <sup>-3</sup>
	65	30.0	3.0×10 <sup>-7</sup> to 3.5×10 <sup>-3</sup>

**Table 3: Selectivity coefficient for interfering cations**

Interfering ions (X)	$k_{Hg,X}^{MPH}$
Na <sup>+</sup>	2.1×10 <sup>-4</sup>
K <sup>+</sup>	7.3×10 <sup>-4</sup>
Cs <sup>+</sup>	3.5×10 <sup>-3</sup>
Ca <sup>2+</sup>	3.2×10 <sup>-4</sup>
Mg <sup>2+</sup>	5.1×10 <sup>-4</sup>
Cd <sup>2+</sup>	4.1×10 <sup>-3</sup>
Ni <sup>2+</sup>	2.7×10 <sup>-3</sup>
Cu <sup>2+</sup>	3.5×10 <sup>-3</sup>
Cr <sup>3+</sup>	5.1×10 <sup>-3</sup>
Fe <sup>3+</sup>	2.4×10 <sup>-3</sup>
Ag <sup>+</sup>	1.3×10 <sup>-3</sup>
Zn <sup>2+</sup>	6.3×10 <sup>-3</sup>

mercury complex as another monomer in presence of AIBN and EGDMA as an initiator and crosslinker cause formation of this composite. A schematic diagram of this synthesized composite is shown in Fig. 1. The thermal analysis of this composite shows that its stable up to 220 °C as there is no meaningful reduction in TG curve cure up to this temperature (Fig. 2). Finally the SEM micrograph of polymer coated nano-tubes is represented in Figure 3.

#### Effect of Electrode Composition

The sensitivity and selectivity depend significantly on the carbon paste composition and the nature of the modifier and the conductivity of the electrode. Thus, the influence of the different integrates of the electrode composition was studied and the optimum amounts were investigated. The

**Table 4: The lifetime of the electrode no. 19 and electrode no. 14. The results are based on triplicate measurements**

Week	Electrode no. 19		Electrode no. 14	
	Slope (mV)	Linear range (mol L <sup>-1</sup> )	Slope (mV)	Linear range (mol L <sup>-1</sup> )
1st	28.2	8.0×10 <sup>-8</sup> to 3.5×10 <sup>-3</sup>	28.9	7.0×10 <sup>-8</sup> to 4.0×10 <sup>-3</sup>
2nd	28.1	8.5×10 <sup>-8</sup> to 3.5×10 <sup>-3</sup>	28.1	9.5×10 <sup>-8</sup> to 4.0×10 <sup>-3</sup>
3th	28.1	8.5×10 <sup>-8</sup> to 3.5×10 <sup>-3</sup>	27.1	1.5×10 <sup>-7</sup> to 4.0×10 <sup>-3</sup>
4th	28.0	8.5×10 <sup>-8</sup> to 3.5×10 <sup>-3</sup>	26.5	3.5×10 <sup>-7</sup> to 4.0×10 <sup>-3</sup>
5th	27.8	9.5×10 <sup>-8</sup> to 3.5×10 <sup>-3</sup>	25.2	5.5×10 <sup>-7</sup> to 4.0×10 <sup>-3</sup>
6th	27.8	9.5×10 <sup>-8</sup> to 3.5×10 <sup>-3</sup>	16.2	-
7th	27.5	9.5×10 <sup>-8</sup> to 3.5×10 <sup>-3</sup>	-	-
8th	27.0	1.0×10 <sup>-7</sup> to 3.5×10 <sup>-3</sup>	-	-
9th	26.8	1.0×10 <sup>-7</sup> to 3.5×10 <sup>-3</sup>	-	-
10th	26.5	1.5×10 <sup>-7</sup> to 3.5×10 <sup>-3</sup>	-	-
11th	26.3	2.5×10 <sup>-7</sup> to 3.5×10 <sup>-3</sup>	-	-
12th	26.1	4.5×10 <sup>-7</sup> to 3.5×10 <sup>-3</sup>	-	-
13th	18.3	-	-	-

**Table 5: Recovery of determination of mercury ions in aqueous samples**

Sample	Unit	Concentration		Added	Found
		Certified	Found		
RTC-QCI-049(Trace metal)	µg L <sup>-1</sup>	40.8	40.1	-	-
Tap water	µg L <sup>-1</sup>	-	ND	25.0	24.6
Distilled water	µg L <sup>-1</sup>	-	ND	25.0	24.6
Sea water	µg L <sup>-1</sup>	-	ND	25.0	24.3
Sewage water	µg L <sup>-1</sup>	-	81.4	25.0	106.4

data of some of the electrode compositions are presented in Table 1. In the first study no modifier was used and only graphite powder and Paraffin were thoroughly mixed and the responses were studied. In the electrode numbers of 2-6 the influence of amount of IIP polymer in the electrode composition was studied. In the electrode numbers of 7-11; different amounts of unmodified MWCNTs were added and the electrode performance was improved. In the electrode numbers of 12-15, the influence of presence both of IIP polymer and unmodified MWCNTs were studied and in the electrode number 14, a Nerstian slope of 28.9 mV was observed. The electrode composition in this electrode was graphite powder 59%, paraffin 23%, IIP polymer 9% and unmodified MWCNTs 9% (W/W). The electrode response was liner in the concentration of  $7.0 \times 10^{-8}$  to  $4.0 \times 10^{-3}$  mol L<sup>-1</sup>. In the electrode numbers of 16-20, IIP-MWCNTs were added to the electrodes as modifier. In electrode number of 19, with the composition of graphite powder 66%, paraffin 23%, and IIP modified MWCNTs 11% (W/W); a Nerstian slope of 28.2 mV was observed in the range of  $8.0 \times 10^{-8}$  to  $3.5 \times 10^{-3}$  mol L<sup>-1</sup>. This electrode was chosen and used in all of the following studies. In addition the performance of the electrode was compared to electrode number 14.

#### Calibration Curve

The measuring range of an ion selective electrode includes the linear part of the calibration graph as shown in Fig. 4. Measurements can be performed in this lower range. According to another definition, the measuring range of an ion selective electrode is defined as the activity range between the upper liner response and detection limits<sup>26,27</sup>.

**Table 6 Recovery of determination of mercury ions in fish samples**

Sample	Unit	Concentration	
		Certified	Found
SRM 1946	µg Kg <sup>-1</sup>	433	435.4
SRM 1947	µg Kg <sup>-1</sup>	254	251.5
Blue Shark	µg Kg <sup>-1</sup>	-	153.3
Sardine	µg Kg <sup>-1</sup>	-	79.5
Anchovy	µg Kg <sup>-1</sup>	-	69.3

The applicable measuring range of the modified sensor as shown in Fig. 4 is between  $8.0 \times 10^{-8}$  to  $3.5 \times 10^{-3}$  mol L<sup>-1</sup>. By extrapolating the linear parts of the ion selective calibration curve, the detection limit of an ion selective electrode can be calculated<sup>28-30</sup>. The detection limit of the electrode was  $6.3 \times 10^{-8}$  mol L<sup>-1</sup> by the extrapolating of the two segment of the calibration curve in Fig. 4.

#### Effect of pH

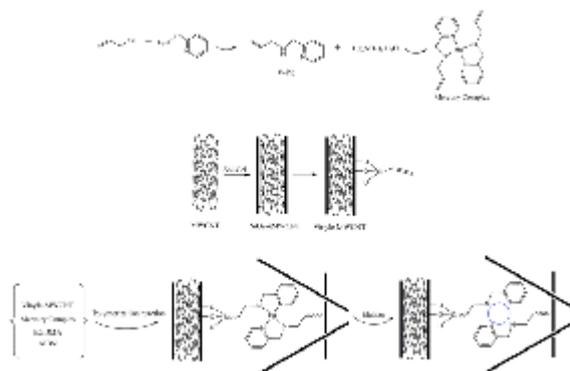
The effect of pH on the response of the modified electrode was examined with a sample solution of  $1.0 \times 10^{-5}$  M. The pH was adjusted by adding small volumes of (0.1-1.0 mol L<sup>-1</sup>) of HNO<sub>3</sub> or NaOH to the test solutions and the variation of potential was followed. As can be seen from Fig. 5, the potential readings of the electrodes are nearly fixed in pH 3.0 and 4.0. The pH of 3.5 was chosen as the optimum pH for all studies. Nevertheless, at pH values lower than 3.0, the increase in potential is attributed to the influence of hydrogen ions. On the other hand, at pH values higher than 4.0 the hydroxylation of mercury ions causes a decrease in its concentration and hence decreases the electrode potential. The effect of pH on electrode number 14 was similar to the above results which should be related interaction of IIP and mercury.

#### Effect of Temperature

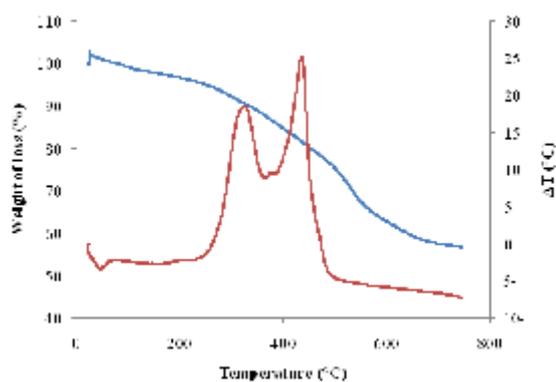
To study the thermal stability of the electrodes, calibration graphs were constructed for the electrodes number of 14 and 19 at different test solution temperatures covering the range 25-65°C. The slope and usable concentration range of the electrode at different test solution temperature are given in Table 2. The results indicate that the slopes of the calibration graphs still in the Nernstian range in spite of the increase of the temperature of the test solutions up to 55°C and the linear concentration ranges of the electrodes are almost unchanged with increasing the temperature of the test solution for electrode number 19. But for electrode number 14, the limitation was observed in temperatures over 35°C. This difference should be related to the thermal stability of IIP-MWCNTs in electrode 19 compared to free IIP in electrode 14.

#### Response Time

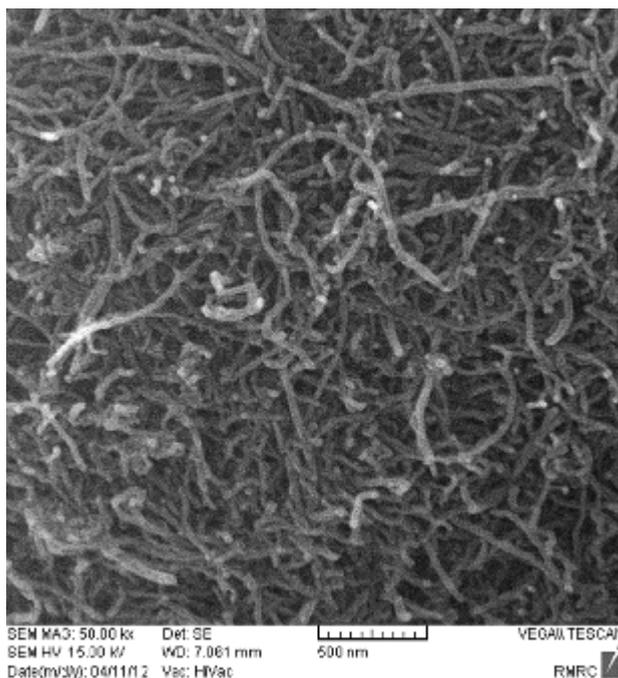
The average static response time was defined as the required time for the sensors to reach



**Fig. 1:** A schematic diagram for synthesis and coating of IIP on MWCNT



**Fig. 2:** TG-DTA diagram of IIP coated on MWCNT



**Fig. 3:** SEM micrograph of IIP coated on MWCNT

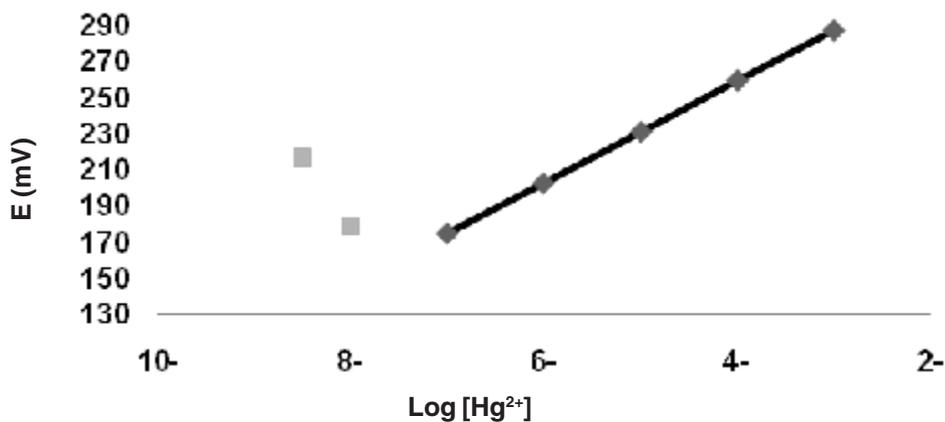


Fig. 4: The calibration curve for Hg(II) ion

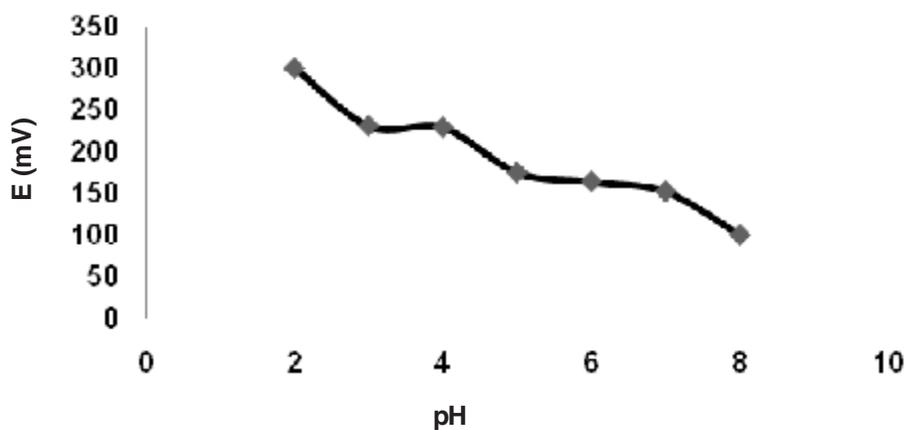


Fig. 5: Influence of pH on electrode response to Hg(II)

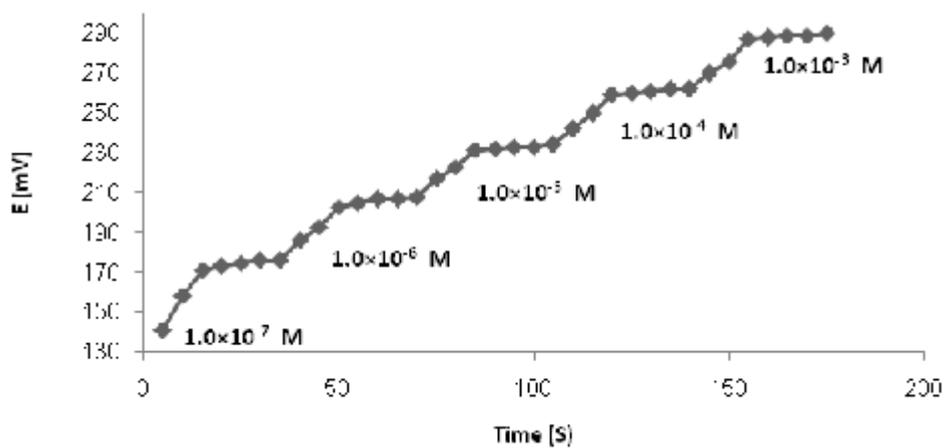


Fig. 6: Potential-time plot for the response of electrode to Hg(II)

a potential of 90% of the final equilibrium values, after successive immersions in a series of solutions, each having a 10-fold concentration difference<sup>31,32</sup>.

The electrode number 19 generates stable and reproducible potentials at relatively short response times. Fig. 6 represents potential-time plot. The average time required for the electrodes, each having a tenfold difference in concentrations, was 15 seconds for concentrations  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>. The fast response time is most probably due to the fast exchange kinetics of the complexation-decomplexation of mercury at the test solution in the IIP-MWCNTs. In contrast, the response time of electrode number 14 was determined to be 45 seconds. This should be related to lower exchange kinetics in this electrode.

#### Influence of Interference Ions

Selectivity is the most important character as it determines the extent of utility of any sensor in real sample measurements. It gives the response of ion-selective sensor for the primary ion in the presence of other ions in solution. Matched potential method (MPM) is the recommended method for studying Influence of interferences ions in ion selective electrodes by IUPAC<sup>33-36</sup>. This method has an advantage of removing limitation imposed by Nickolesky-Eisenman equation. These limitations include non-Nernstian behavior of the interfering ion and the problem of inequality of charges of primary and interfering ions. In this method, selectivity coefficient  $k_{Hg,x}^{MPM}$ , is given by:

$$k_{Hg,x}^{MPM} = \frac{\Delta a_{p^{Hg^{2+}}}}{a_x} = \frac{a_{p^{Hg^{2+}}}^f - a_{p^{Hg^{2+}}}}{a_x}$$

The selectivity coefficient is determined by measuring the change in potential upon increasing the concentration by a definite amount of the primary ion activity (pHg<sup>2+</sup>) from an initial value of  $a_{p^{Hg^{2+}}}$  to  $a_{p^{Hg^{2+}}}^f$  and  $a_x$  represents the activity of the interfering ion added to the same reference solution

of activity which brings about the same change in potential. The activity of Hg<sup>2+</sup> as reference solution was taken as  $5.0 \times 10^{-7}$  M in this study. The values are listed in Table 3. The electrode shows a good selectivity to mercury ion. In another study, the values were evaluated for electrode 14. The results were similar to electrode number 19. It shows that the selectivity of the electrode is only related to selectivity of IIP to mercury ion and modification of IIP on MWCNTs has no effect on IIP selectivity.

#### Lifetime

The lifetime of an electrode is the period of time that the electrode shows no changes in the efficiency of the measurements. To study this factor, the electrode was calibrated periodically with standard mercury solutions. Then the electrode was conditioned and calibrated in the next week. As the results in Table 4 show, the lifetime of the electrode was evaluated to be twelve weeks. The lifetime of the electrode no. 14 was evaluated to be five weeks. The long lifetime period of electrode no. 19 may be due to stability of IIP on the surface of MWCNTs.

#### Method Validation

Three standard reference materials, some aqueous real samples and fish samples were used for method validation. They were analysed by presented procedure at the optimum conditions and the results are collected in Table 5 and Table 6. As it can be seen, the results have good compatibility with certified ones, so this method could be a sensitive and confidence method for determination of Hg(II) ions.

#### CONCLUSION

A carbon paste electrode was developed for determination of mercury ions in aqueous media. The electrode was modified by IIP and high selectivity to mercury ion was observed. By adding MWCNTs, the electrode performance was improved. At last by coating IIP on the surface of MWCNTs, the lifetime and response time were improved. Method validation was done by analysis of a standard reference material.

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