

## Determination of Mercury (II) Ions by Modified Carbon Paste Electrode Based on Functionalized Nanoporous MCM-48 and Multi-Walled Carbon Nanotubes (MWCNTs)

Forouzan Aboufazeli, Hamid Reza Lotfi Zadeh Zhad, Vahid Amani, Ezatollah Najafi, Omid Sadeghi and Najmeh Tavassoli\*

Department of Chemistry, Islamic Azad University Shahr-e-Rey Branch, P. O. Box 18735-334, Tehran, Iran

Received: January 16, 2012, Accepted: July 03, 2012, Available online: August 06, 2012

**Abstract:** A carbon paste electrode for determination of mercury (II) ions in real samples was prepared. The main objective of the present study was to evaluate the concentration of mercury ions in different soil, water, plant, and animal muscle samples by utilizing modified carbon paste electrode. Functionalized nanoporous MCM-48 and multi-walled carbon nanotubes material were used in order to increase the efficiency and selectivity of the electrode for mercury ions determination. The electrode composition material was optimized as graphite powder 57%, Paraffin 22%, modified MCM-48 16% and MWCNTs 5% (W/W). The linear range of the electrode was calculated  $5.0 \times 10^{-8}$  to  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>, and a detection limit was obtained  $1.5 \times 10^{-8}$  mol L<sup>-1</sup>. The potential slope was achieved  $29.7 \pm 1.0$  mV, and lifetime for the electrode was investigated about 5 months. The proposed method was applied to a number of natural samples and the amount of mercury was determined.

**Keywords:** Mercury (II), Modified Carbon Paste, Functionalized MCM-48, MWCNTs, Potentiometry

### 1. INTRODUCTION

Mercury (II) is considered as a chemical pollutant, which its toxicity can be dangerous even if at low concentration. The growing awareness of environmental mercury pollution beside the agriculture, industrial and clinical importance of mercury-containing compounds, has paid for more accurate, precise and selective methods for the determination of mercury in a wide variety of materials. Several methods have been used for measurement and/or Extraction of mercury including Spectrophotometry [1], cold vapor atomic absorption spectrometry [2], X-ray fluorescence [3], furnace atomic absorption spectrometry [4], flame atomic absorption spectrometry [5], inductively coupled plasma [6], fluorimetry [7], voltammetry [8], and potentiometry [9]. Recently, investigators have demonstrated a new variation of electrochemical trace-metal analysis in which analyte preconcentration was carried out at chemically modified electrodes (CMEs), with surfaces specifically designed for target solute [10-11]. In this approach, the preconcentration is achieved by a purely nonelectrochemical deposition step, following which quantitation of the accumulated analyte at the surface can be carried out by usual electrochemical measurement. By doing so, two analytical advantages

in addition to the inherent sensitivity enhancement in the preconcentration are achieved. First, the electroanalytical quantitation might be extended to analytes that cannot be reductively deposited or which require excessively negative deposition potentials. Second, the selectivity of the chemical step used for the preconcentration might improve the overall selectivity of the entire analysis [12]. Although considerable attention has been given to the preparation of CMCPs, their applications in analytical chemistry have been mainly based on selective preconcentration followed by voltammetric determination, [13] and just a few of studies according to these electrodes have been carried out by simple potentiometric measurements [14]. The carbon paste electrodes are easy to construct, and have increased portability, robustness and economy. Besides, they present a stable electrochemical response that can be renewed by removing an outer layer of the paste and resmoothing the electrode surface. They have lower ohmic resistance than ion-selective electrodes based on polymeric membranes [15].

This work is to introduce a very simple and inexpensive (potentiometric) method in determination of Mercury (II) in a wide concentration range in the presence of variety of metal ions. The proposed method was applied to a number of natural samples and its accuracy and precision was also measured.

\*To whom correspondence should be addressed: Email: h2o.group.chem@gmail.com  
Phone: +98.2177447630

## 2. EXPERIMENTAL

### 2.1. Apparatus

For the potential measurements a Corning model 125 pH/ mV meter was used. All measurements were made at  $25 \pm 1^\circ\text{C}$ . The pH meter was a digital WTW Metrohm 827 Ion analyzer (Switzerland) equipped with a combined glass- calomel electrode.

### 2.2. Chemicals and reagents

All reagents were analytical grade and were used without further purification. Mercury nitrate salt and paraffin oil were purchased from Merck (Darmstadt, Germany). The multi-walled carbon nanotubes (MWCNTs) purchased from Research Institute of the Petroleum Industry (Iran). The graphite powder with a particle size smaller than  $50\ \mu\text{m}$ , 2-Amino-5-bromopyridine, 3-Chloropropyl trimethoxy silane, Tetraethyl orthosilicate (TEOS), triethylamine, Cetyltrimethylammonium Bromide (CTAB) and toluene were purchased from Merck. All of the required solutions were prepared using deionized water, provided from a Milli-Q (Millipore, Bedford, MA, USA) purification system.

### 2.3. Preparation of MCM-48 and functionalization with 2-Amino-5-bromopyridine

MCM-48 mesoporous silica was prepared according to the previous reported procedure [16]. In a typical reaction 1g MCM-48 was suspended in 50 mL of toluene; then 5.0 mL of 3-Chloropropyl trimethoxy silane was added to the mixture and refluxed for 24 hours. The white solid was removed from the solvent by filtration and washed with ethanol. Afterwards, the white solid was suspended in 50 mL of triethylamine and toluene (1:1) then 1g of 2-Amino-5-bromopyridine was added and refluxed for 24 hours. The yield white solid was removed from the mixture by filtration. The particles were washed by toluene and ethanol for several times and then dried at room temperature. Functionalization by 2-Amino-5-bromopyridine was confirmed by XRD, IR spectroscopy and elemental analysis.

### 2.4. Preparation of modified carbon paste electrode

The carbon paste electrode was prepared by thoroughly mixing graphite powder 57%, Paraffin 22%, modified MCM-48 16% and MWCNTs 5% (W/W). The body of the electrode was made from a 1mL polypropylene syringe. The carbon paste was packed into the end of the syringe. A copper wire was inserted into the opposite end to establish electrical contact. The external electrode surface was smoothed with a soft paper.

### 2.5. Conditioning the carbon paste electrode

The carbon paste electrode surface was renewed before the measurements. For this reason, the electrode was placed in a solution containing  $1.0 \times 10^{-4}\ \text{mol L}^{-1}\ \text{Hg}(\text{NO}_3)_2$  and  $0.1\ \text{mol L}^{-1}\ \text{NaNO}_3$  solution for 24 hours. The pH was adjusted to 5.5 by  $0.01\ \text{mol L}^{-1}$  acetate buffer. Then the electrode was washed with de-ionized water.

### 2.6. Emf measurements

All potential measurements were done versus Ag, AgCl(s) reference electrode. The electrochemical cell of the proposed electrode can be seen as follow:

Ag, AgCl (S), KCl ( $3\ \text{mol L}^{-1}$ ) || test solution | modified carbon

paste electrode

In all solutions the pH was adjusted to 5.5 by acetate buffer  $0.01\ \text{mol L}^{-1}$  (The pH was optimized in section 'Influences of pH').

### 2.7. Sample preparation

Tap water (Tehran, Iran), river water (Karooon River, Ahwaz, Iran), and Persian Gulf water (Bandar Imam, Khuzestan, Iran) were used as water samples. They were collected in cleaned polyethylene bottles and were filtered through a  $0.45\ \mu\text{m}$  pore size nylon filter (Millipore) right away after sampling. A layer of soil with the depth of 5 cm was collected in each sampling process with the distance of 5, 10, 15, 20 and 25 km from Tehran Petrochemical Company. All samples were collected over a period of 12 weeks during the spring of the year of 2011 and each time five samples were gathered.

Two samples, 2781 (Domestic sludge) and NIST SRM 1646 (Estuarine Sediment) were used as Standard material samples with certified mercury content. Reference materials and soil samples were digested with 6 mL of HCl (37%) and 2 mL of  $\text{HNO}_3$  (65%) in a microwave digestion system. Digestion was 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 venting for 8 min. The residue from digestion was then diluted with deionized water, as well as, a blank digestion.

One Standard material, NRCCDORM, with the certified amount of Hg was analysed to determine the concentration of Hg ions in dogfish muscle. The standard material sample was digested with concentrated  $\text{HNO}_3$  and then was transferred into a 100 mL Teflon beaker and 10 mL nitric acid was added. Afterward, the sample was heated at  $280^\circ\text{C}$  on a hot plate for 2 h. Then two milliliters of  $\text{HNO}_3$  1M was added to the residue and the solution was evaporated again and continued until it was digested. After cooling, 10 mL of  $\text{HNO}_3$  1M was added and diluted and filtered through membrane filter (with  $0.45\ \mu\text{m}$  pores).

To validate the present method for plant samples, one certified reference material (NIST SRM 1515 (apple leaves)) was used and digested. 10 g of standard material was grounded and dried out at  $80^\circ\text{C}$  and triturated in a porcelain mortar. After sieving fractionated to a particular size and then sizes less than  $20\ \mu\text{m}$  were dissolve in 10 mL of  $3\ \text{mol L}^{-1}\ \text{HNO}_3$  solution and diluted with distill water up to final volume of 100 mL.

Finally, the proposed method was applied to determination of mercury ions from the samples.

## 3. RESULTS AND DISCUSSION

Considering mercury as soft metal cation (soft acid), it is expected that it may interact with soft basis. The pyridine lone pairs are contributed in the ring resonance; and also the amine group provides a longer resonance possible, which makes pyridine as a soft basis; the bromide on the ring as electron withdrawer even makes it a softer basis. Therefore, the interaction between soft acid and basis makes the electrode act more selectively to mercury.

### 3.1. Characterization of the materials

In order to investigate the morphology and size of MWCNTs, the transmission electron microscopy (TEM) was applied to record MWCNTs micrograph. As it can be seen in Fig. 1, MWCNTs has approximately 10 nm diameters.

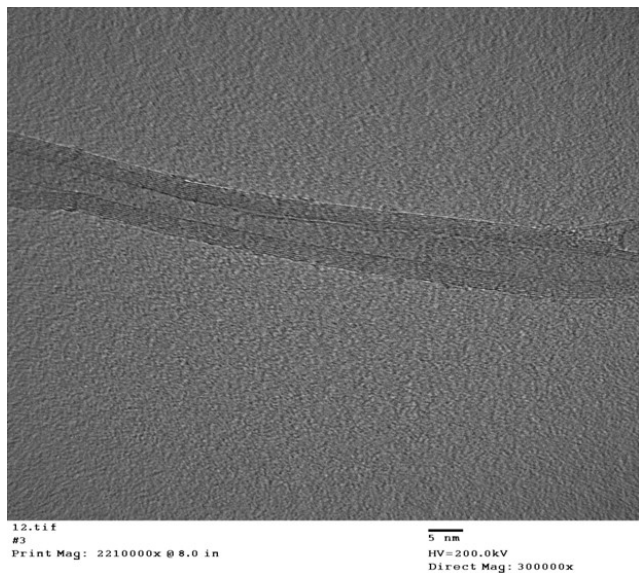


Figure 1. TEM micrograph of MWCNTs

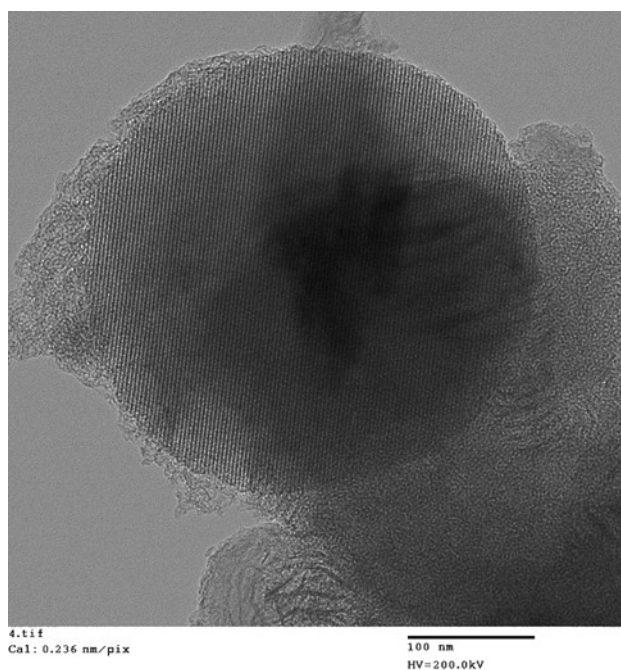


Figure 2. TEM micrographs of nanoporous MCM-48

The formation of modified MCM-48 has been confirmed by IR spectroscopy, elemental analysis, TEM micrograph and XRD pattern. According to the IR spectra, the 2-Amino-5-bromopyridine is grafted on the surface of MCM-48 nanopores. IR spectroscopy are given as follows: IR (KBr, cm<sup>-1</sup>): 3300 (NH), 2905 (CH, aliphatic), 2930 (CH, aliphatic), 1561 (C=N). The amount of grafted ligand was calculated using elemental analysis. The elemental analysis of sample shows that concentration of 2-Amino-5-bromopyridine is 1.3 mmol per gram of mesoporous silica. In order to confirm that the nano-pores of MCM-48 remained unchanged after functionaliza-

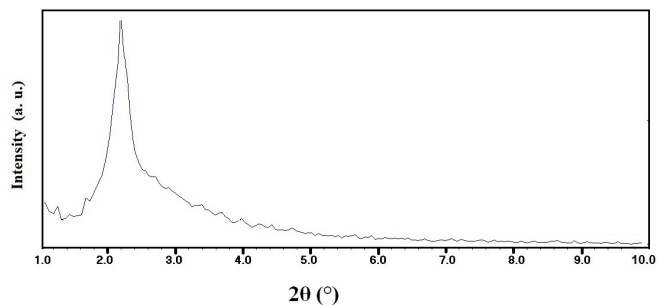


Figure 3. A schematic model for synthesis of functionalized MCM-48

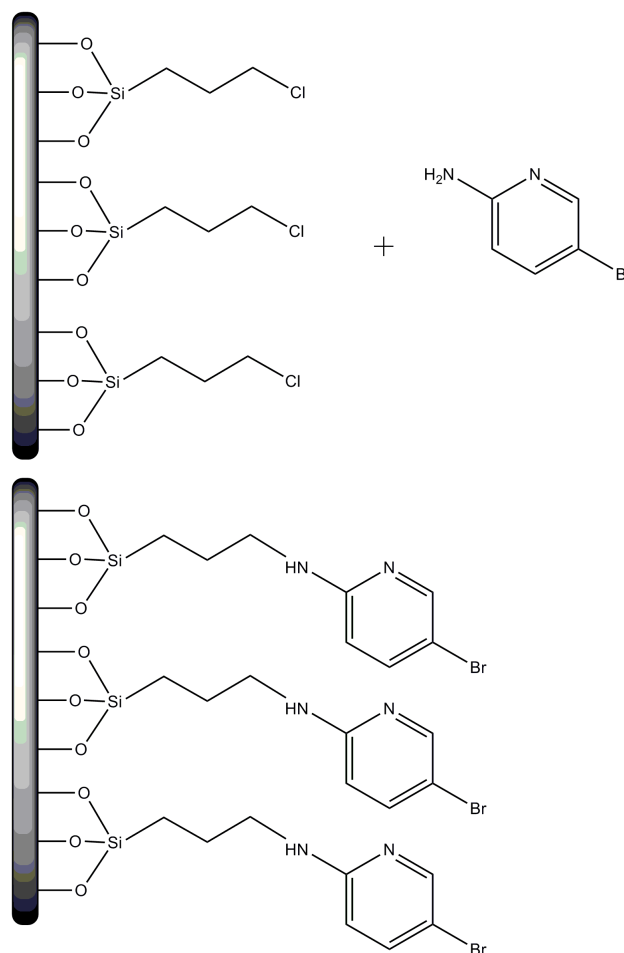


Figure 4. XRD pattern of Py-MCM-48

tion, the TEM micrograph of functionalized MCM-48 was recorded (Fig. 2). As it can be seen in Figure 2, the porous structure of the MCM-48 remains unchanged after functionalization. And finally the X-ray powder diffraction pattern shows that the structure of MCM-48 does not change after modification (Fig. 3). A schematic model for synthesis is shown in Fig. 4.

### 3.2. Influences of electrode composition

Since the main factor on carbon paste electrodes is the composition of the electrode, different amounts of graphite powder, paraffin oil, modified MCM-48 and MWCNTs were mixed together and the efficiency was examined (Table 1). In the first electrode composition no modified MCM-48 and MWCNTs were added, then different amounts of modified MCM-48 were added to electrode and the optimum amount was found to be 16%. By increasing the amount of modified MCM-48 to the electrode the slope decreases because MCM-48 has a silica structure, which can decrease the electrode conductivity. It was observed that by increasing the amount of MWCNTs to the electrode composition the electrode conductivity and the slope increase. The last optimum condition for the electrode was obtained as graphite powder 57%, Paraffin 22%, modified MCM-48 16%, MWCNTs 5% (W/W). Thus composition of No.8 was applied for further study.

### 3.3. Calibration curve

The calibration curve for the optimum electrode (No.8) was investigated and is shown in Fig.5. The linear range of the proposed electrode was calculated  $5.0 \times 10^{-8}$  to  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  with  $R^2 = 0.994$ . The response of the electrode can be stated by the following equation:

$$E = 28.7 \text{ Log } [\text{Hg}^{2+}] + 375.84 \quad (1)$$

Where E is the potentiometric response of the electrode (mV) and  $\text{Log } [\text{Hg}^{2+}]$  is the relative concentration of mercury ions ( $\text{mol L}^{-1}$ ).

The detection limit was determined conventionally as  $1.5 \times 10^{-8} \text{ mol L}^{-1}$  according to the intersection of the two extrapolated segments of the calibration graph [17].

### 3.4. Influences of pH

In order to investigate the influence of pH on the modified electrode, a solution containing  $5 \times 10^{-4} \text{ mol L}^{-1}$  of mercury (II) was used in the different pHs in the range of 2-9. The pH adjustment was done by adding different amounts of  $\text{HNO}_3$  or  $\text{KOH}$  to the solution. It was observed that in the pH range of 3-8 the response of the electrode is linear (Fig. 6). In acidic pHs the effect of  $\text{H}^+$  on the electrode may affect the responses and in the basic pHs hydroxospecies of mercury can be formed which decrease the response of the electrode. Since most of the real samples polluted by mercury have pHs in the range of 4-6, this electrode could be applied in

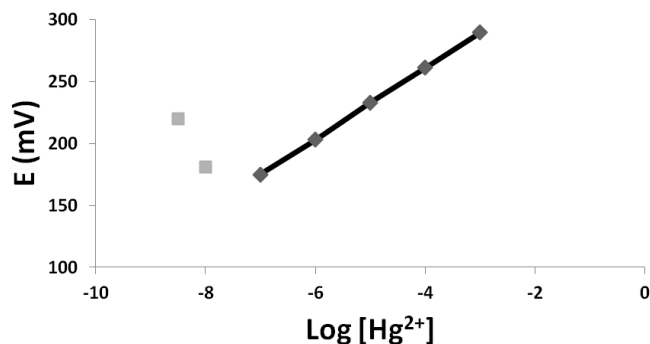


Figure 5. The calibration curve for mercury(II) ion, buffer pH = 5.5.

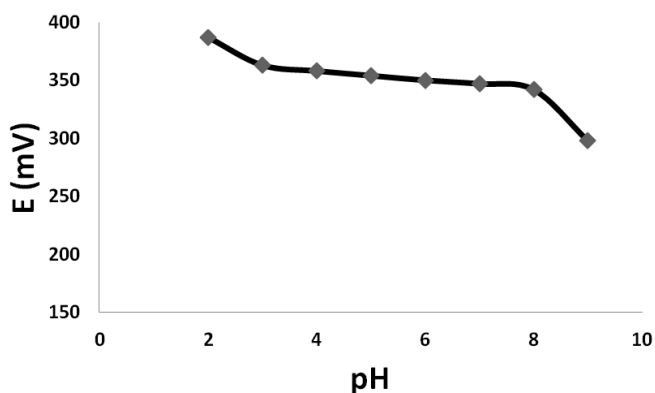


Figure 6. Influence of pH on electrode response to mercury(II).

most cases without any pH adjustment.

### 3.5. Study of Response time

Response time of ion selective electrodes is one of the most important factor in the efficiency of the electrodes. The average response time is defined as the required time for the electrodes to reach a cell potential of 90% of the final equilibrium values, after successive immersions in a series of solutions by a 10-fold concentration difference with each other. To investigate this factor on the proposed electrode concentration of mercury(II) concentration of

Table 1. optimization of the carbon paste electrode composition, acetate buffer pH = 5.5.

Electrode No.	Graphite powder (%)	Paraffin (%)	Modified MCM-48 (%)	MWCNTs (%)	Slope (mV)	Linear range ( $\text{mol L}^{-1}$ )	$R^2$
1	75	25	0	0	$7.3 \pm 2.5$	-	0.918
2	70	25	5	0	$17.4 \pm 1.5$	$1.0 \times 10^{-6}$ to $1.0 \times 10^{-2}$	0.947
3	65	25	10	0	$22.5 \pm 1.3$	$5.0 \times 10^{-7}$ to $1.0 \times 10^{-2}$	0.962
4	60	25	15	0	$26.0 \pm 1.2$	$1.0 \times 10^{-7}$ to $5.0 \times 10^{-3}$	0.978
5	60	22	18	0	$25.1 \pm 1.2$	$1.0 \times 10^{-7}$ to $5.0 \times 10^{-3}$	0.970
6	62	22	16	0	$26.9 \pm 1.1$	$1.0 \times 10^{-7}$ to $5.0 \times 10^{-3}$	0.983
7	60	22	16	2	$28.2 \pm 1.0$	$1.0 \times 10^{-7}$ to $5.0 \times 10^{-3}$	0.988
8	57	22	16	5	$29.7 \pm 1.0$	$5.0 \times 10^{-8}$ to $1.0 \times 10^{-3}$	0.994
9	54	22	16	8	$27.8 \pm 1.1$	$1.0 \times 10^{-7}$ to $5.0 \times 10^{-3}$	0.981

the test solution was increased from  $5.0 \times 10^{-8}$  to  $1.0 \times 10^{-3}$ . The response time for the electrode was calculated about 1 min.

### 3.6. Influence of interference ions

Matched Potential Method (MPM) is the suggested method for studying potentiometric selectivity coefficients [18]. The specified activity of the primary ion is added to a reference solution and the potential should be measured. In this case our reference solution was  $5.0 \times 10^{-8}$  mol L<sup>-1</sup>. Then interfering ions were successively added to an identical reference solution, until the measured potential matched that obtained before the addition of the primary ions. The matched potential method selectivity coefficient,  $k_{Hg,X}^{MPM}$  is then given by the resulting primary ion to the interfering ion activity

ratio,  $k_{Hg,X}^{MPM} = \Delta \frac{a_{Hg}}{a_X}$  [19]. The influence of Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>, Fe<sup>3+</sup>, Ag<sup>+</sup> and Zn<sup>2+</sup> were investigated and  $k_{Hg,X}^{MPM}$  values were calculated and listed in table 2. The results indicate that the electrode is selective to mercury (II) ions. On the other hand the low  $k_{Hg,X}^{MPM}$  for Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, which are the main contains of real samples, is the key role for possibility of determination of mercury (II) ions in real samples using this electrode.

### 3.7. Lifetime

In order to study the lifetime of the modified electrode, it was calibrated periodically with standard mercury solutions. Then the electrode was conditioned and gained calibrated each week. In five month the changes on the slope of calibration curve was less than 1%, so there was no changes on the efficiency of the electrode were observed during this time. Thus the lifetime of the proposed electrode was investigated about 5 mouths.

### 3.8. Sample analysis

The applicability of the electrode results was examined by studying real samples obtained from tap water Tehran Iran, and two natural water sample from sea water (Persian Golf, Iran) and from river water (Karooon River, Iran). Some soil samples have also been

Table 2. Selectivity coefficient for interfering cations.

Interfering ions (X)	$k_{Hg,X}^{MPM}$
Na <sup>+</sup>	$4.2 \times 10^{-4}$
K <sup>+</sup>	$8.9 \times 10^{-4}$
Cs <sup>+</sup>	$1.5 \times 10^{-3}$
Ca <sup>2+</sup>	$6.3 \times 10^{-4}$
Mg <sup>2+</sup>	$7.3 \times 10^{-4}$
Cd <sup>2+</sup>	$3.5 \times 10^{-3}$
Ni <sup>2+</sup>	$6.7 \times 10^{-3}$
Cu <sup>2+</sup>	$2.6 \times 10^{-3}$
Cr <sup>3+</sup>	$7.0 \times 10^{-3}$
Fe <sup>3+</sup>	$3.7 \times 10^{-3}$
Ag <sup>+</sup>	$1.4 \times 10^{-3}$
Zn <sup>2+</sup>	$6.3 \times 10^{-3}$

analyzed. For all cases some amount of mercury ions was spiked to the samples and the mercury content was calculated by direct potentiometry using calibration curve method. In all solutions the pH was adjusted to 5.5 by acetate buffer. The accuracy of the electrode was also tested by utilized the standard samples. According to Tables 3-5, good results in precision, reproducibility and recovery were observed in determination of mercury ions, confirming the acceptable performance of the electrode in real sample analysis in the pressense of interfering ions of real samples.

## 4. CONCLUSION

Using modified MCM-48 Nanoporous silica in the carbon paste electrode makes the proposed electrode a selective sensor for mercury ions. By using MWCNTs the conductivity of the electrode increases which make the electrode more sensitive to mercury ions. The long-term life time of the electrode may also be cause of using these nano structures. In short, the simplicity of preparation of the electrode, the long Lifetime and the short time of the response time make this electrode a unique sensor for fast mercury ion determination in real samples.

Table 3. Recovery of determination of mercury in certified reference materials.

Sample	Concentration ( mg kg <sup>-1</sup> )		Recovery (%)
	Certified	Found	
NBS2781	3.64	3.55	97.5
NIST SRM 1646	63.0	65.4	103.8
NRCCDORM	0.798	0.734	91.9
NIST SRM 1515	44.0	42.1	95.6

Table 4. Data of Real water samples analysis, buffer pH = 5.5.

	Found/ mg L <sup>-1</sup>	Added/ mg L <sup>-1</sup>	Found/ mg L <sup>-1</sup>	Recovery, %
tap water	ND	4	3.8	95.0
	ND	8	7.7	96.2
Persian Golf	ND	4	4.1	102.5
	ND	8	8.3	103.7
Karooon River	ND	4	4.0	100.0
	ND	8	8.1	101.2

Table 5. The concentration of mercury in soil samples with different distance with Petrochemical Company

Distance (Km)	Mean (µg Kg <sup>-1</sup> )	Minimum (µg Kg <sup>-1</sup> )	Maximum (µg Kg <sup>-1</sup> )
5	58.3	43.8	66.1
10	42.2	35.0	46.8
15	38.2	33.7	43.9
20	41.2	33.1	45.3
25	38.5	31.4	44.7

**REFERENCES**

- [1] M.H. Mashhadizadeh, I. Sheikhshoae, *Talanta*, 60, 73 (2003).
- [2] J.L. Manzoori, M.H. Sorouraddin, A.M. Haji Shabani, *J. Anal. At. Spectrom.*, 13, 305 (1998).
- [3] J.M. O'Meara, J. Börjesson, D.R. Chettle, *Appl. Radiat. Isot.*, 53, 639 (2000).
- [4] M. Tüzen, *Food Chem.*, 80, 119 (2003).
- [5] M. Ghaedi, F. Ahmadi, A. Shokrollahi, *J. Hazard. Mater.*, 142, 272 (2007).
- [6] Q. Tu, J. Qvarnström, W. Frech, *Analyst*, 125, 705 (2000).
- [7] D.W. Bryce, J.M. Fernández-Romero, M.D. Luque de Castro, *Anal. Lett.*, 27, 867 (1994).
- [8] C. Faller, N. Stojko, N. Yu., G. Henze, Kh.Z. Brainina, *Anal. Chim. Acta*, 396, 195 (1999).
- [9] R.K. Mahajan, I. Kaur, T.S. Lobana, *Talanta*, 59, 101 (2003).
- [10] K. Wu, S. Hu, J. Fei, W. Bai, *Anal. Chim. Acta*, 489, 215 (2003).
- [11] J.B. Raoof, R. Ojani, H.J. Karimi-Maleh, *J. Applied Electrochem.*, 39, 1169 (2009).
- [12] R.P. Baldwin, J.K. Christensen, L. Kryger, *Anal. Chem.*, 58, 1790 (1986).
- [13] M. Javanbakhta, F. Divsarc, A. Badieid, F. Fatollahia, Y. Khanianid, M.R. Ganjalie, P. Norouzie, M. Chaloosic, Gh.M. Ziaranif, *Electrochim. Acta*, 54, 5381 (2009).
- [14] M. Ghiacia, B. Rezaei, M. Arshadia, *Sensor Actuat B-Chem.*, 139, 494 (2009).
- [15] M.N. Abbas, G.E. Mostafa, *Anal. Chim. Acta*, 478, 329 (2003).
- [16] K. Schumacher, M. Grun, K.K. Unger, *Micropor. Mesopor. Mater.*, 27, 201 (1999).
- [17] V.K. Gupta, A.K. Singh, B.A. Gupta, *Anal. Chim. Acta*, 575, 198 (2006).
- [18] P.R. Buck, E. Lindner, *Pure Appl. Chem.* 66, 2527 (1994).
- [19] IUPAC Analytical Chemistry Division, Commission on Analytical Nomenclature. Recommendations for nomenclature of ion-selective electrodes. *Pure Appl. Chem.* 48, 127 (1976).