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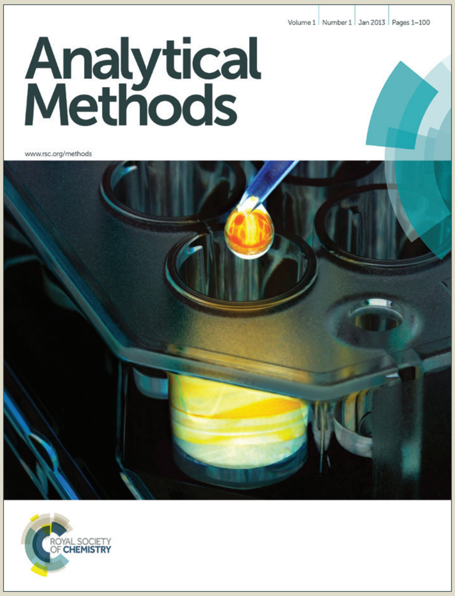

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Multi-walled carbon nanotube and nanosilica chemically modified carbon paste electrodes for determination of mercury(II) ion in polluted water samples

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Abstract

Novel carbon paste ion selective electrodes based on 1,4-bis(6-bromohexyloxy)benzene (BHOB) ionophore were constructed in order to determine Hg(II) ion concentration. Multi-walled carbon nanotubes (MWCNTs) and nanosilica modifiers were used for improving the response characteristics of a mercury carbon paste sensors. MWCNTs have good conductivity which helps the transduction of the signal in carbon paste electrode. These potentiometric sensors respond to Hg(II) ions in the wide linear concentration range of 1×10^{-1} - 1.0×10^{-7} and 1.0×10^{-1} – 1.8×10^{-8} mol L^{-1} with Nernstian slopes of 28.75±0.46 and 29.92±0.15 mV $decade^{-1}$ of Hg(II) ion and detection limit of 1×10^{-7} and 1.8×10^{-8} mol L^{-1} for MWCNTs-CPE (electrode V) and MWCNTs/nanosilica-CPE (electrode VII), respectively. The electrodes were pH independent within the range of 3.0-7.5 and 2.5-8.5, with a fast response time of about 7 and 4 s, and can be used for at least 110 and 145 days without any considerable divergences in the potentials for electrode (V) and electrode (VII), respectively. The proposed sensors thus allowed sensitive, selective, simple, low-cost, and stable electrochemical response to Hg(II) ions in the presence of a large number of alkali, alkaline earth, transition and heavy metal ions. Such abilities promote new opportunities for determining Hg(II) ions in a wide range of real samples. The results obtained were compared well with those obtained using inductively coupled plasma atomic emission spectrometry (ICP-AES).

Keywords: Potentiometric Sensors; Mercury determination; Multi-walled carbon nanotube (MWCNTs); Nanosilica; Water samples

1. Introduction

Mercury is considered a hazardous environmental pollutant which is being released into water bodies through natural and anthropogenic sources [1, 2]. It is non-biodegradable and accumulates in our body through food and water supplements causing health hazards to the human beings and all other microorganisms [2, 3]. Mercury exists in three forms as elemental mercury, inorganic salts and organic compounds and obviously all forms are poisonous. Mercury poisoning is also known as hydrargyria or mercurialism and most commonly affecting the neurologic, gastrointestinal and renal organ systems [4, 5]. In the present scenario of industrialization and mining, there is the scarcity of fresh environment due to requirement of need based industrial activities on one side and on the other side silent mode or less attention of various environment protection agencies towards the formulation of strict guidelines for the release of mercury into the environment. Thus, the pollution of mercury is on the rise and consequently causing serious health hazards to humans. Due to its toxicity and serious hazards towards the human health, there is a strong need to develop the methods to determine the mercury in aqueous environmental samples [6, 7].

Different instrumental techniques, including X-ray fluorescence [8], inductively coupled plasma optical emission spectrometry (ICP-OES) [9, 10], spectrophotometry [11] and neutron activation analysis (NAA) [12], have been applied to the determination of mercury. However, these instrumental techniques are too expensive and not available in most analytical laboratories with their need for more time. Most of the mentioned methods are time consuming, too costly, and not capable of on-site mercury in most analytical laboratories. Also, their monitoring involved multiple sample manipulations. However, electrochemical detection offered several advantages over these methods, such as ease of use, low cost, direct detection, miniaturization, and fast response times [13]. The development and application of ion-selective electrodes for responding to metal cations [14-16] and anionic species [17-19] continues to be an interesting area of analytical research as they provide accurate, rapid, non-destructive and low cost methods of analysis. Nowadays, conventional potentiometric carbon paste ion-selective electrodes are highly selective, highly sensitive, and of low detection limit. Over the past five decades, carbon paste, i.e., a mixture of carbon (graphite) powder and a binder (pasting liquid), has become one of the most popular electrode materials used for the laboratory preparation of various electrodes, sensors, and detectors. The operation mechanism of such chemically modified carbon paste electrodes (CMCPEs) depends on the properties of the modifier materials used to import selectivity and sensitivity towards the target species [20-25].

Recently, carbon nanotubes (CNTs) have been used in carbon paste electrodes [26, 27] for fabricating electrochemical sensors and biosensors due to their special physicochemical properties, such as ordered structure with high surface-to-volume ratio, ultra-light weight, excellent mechanical strength, high electrical conductivity, high thermal conductivity and chemical performance. The combinations of these characteristics make CNTs unique materials with the potential for diverse applications. However, upto date their derivates have been tested in ISEs in potentiometric analysis. The presence of CNTs in the composition of the carbon paste could improve conductivity and transduction of chemical signal to electrical signal but CNTs haven't ion selectivity. Using MWCNTs in the carbon paste improves the conductivity of the electrode and, therefore, conversion of the chemical signal to an electrical signal is better occurred. Carbon nano-tubes especially multi-walled ones have many properties that make them ideal as components in electrical circuits, including their unique dimensions and their unusual current conduction mechanism [28].

Silica-based materials are of interest for a number of reasons. They are robust inorganic solids displaying both high specific surface area (200–1500 m^2 g^{-1}) and a three-dimensional structure made of highly open spaces interconnected to each other. This would impart high diffusion rates of selected target analytes to a large number of accessible binding sites, which constitutes definite key factor in designing sensor devices with high sensitivity. On the other hand, large varieties of organic moieties or inorganic layers of defined reactivity can modify the silica surface. When applied in connection to electrochemistry, these properties could be advantageously exploited in electroanalysis by inducing high selectivity (either by specific binding or by preferential recognition), or enabling electrocatalysis at the modified electrode [29-31].

In this study, Hg(II) carbon paste electrode based on 1,4-bis(6-bromohexyloxy)benzene (BHOB) ionophore was constructed in order to determine Hg(II) ion concentration. Unfortunately, this electrode showed low response to the Hg(II) ion. Therefore, the electrode was modified by MWCNTs alone or MWCNTs and nanosilica to achieve the better electrode response. The modified electrodes showed high response to Hg(II) ion over the other interfering ions. The modified electrodes were used in determination of mercury content in real spiked water samples.

2. Experimental

2.1. Reagents

All the reagents were of the analytical grade and deionized water was used throughout the experiments. Mercury chloride [$HgCl_2$] was supplied from Sigma-Aldrich. While 1,4-bis(6-bromo-hexyloxy)benzene (BHOB) was newly prepared by the authors [32]. Multi-walled carbon nano tube (MWCNT) with the highest purity (diameter within 10–20 nm) was purchased from Merck. Nanosilica (Sigma-Aldrich), paraffin oil (Merck) and Graphite powder (synthetic 1–2 μm) (Aldrich) were of high purity and used for the fabrication of different electrodes. Chloride salts of zinc, magnesium, cadmium, chromium, strontium, nickel, calcium, potassium, manganese, lead, barium, cobalt, sodium, ferrous and aluminum are used as interfering ions.

2.1.1. Samples

Water samples included wastewater (Sample 1 was supplied from Egyptian Petroleum Research Institute, Nasr City, Cairo), cooling tower waters (Egyptian Petrochemical Company (sample 2) and Sidpec Petrochemical Company (sample 3), Amryia, Alexandria, Egypt), tap water (sample 4 was supplied from Egyptian Petroleum Research Institute, Nasr City, Cairo), formation water (Meleiha, Western Desert, Agiba Petroleum Company (sample 5), Karama, Al-Wahhat-Al-Bahhriyah, Qarun Petroleum Company (sample 6), Egypt) and drinking water sample (sample 7, our laboratory, Faculty of Science, Cairo University).

2.2. Apparatus

Laboratory potential measurements were performed using Jenway 3505 pH-meter. Silver-silver chloride double-junction reference electrode (Metrohm 6.0726.100) in conjugation with different ion selective electrodes was used. pH measurements were done using Thermo-Orion, model Orion 3 stars, USA. Prior to analysis, all glassware used were washed carefully with distilled water and dried in the oven before use.

2.3. Procedures

2.3.1. Synthesis of 1,4-bis(*6-bromohexyloxy*)benzene

Synthesis of 1,4-bis(6-bromohexyloxy)benzene was carried out in two steps [32]. It was prepared by the reaction of one mole of 1,4-dihydroxybenzene (hydroquinone) with two moles of 1,8-dibromopentane in the presence of sodium ethoxide under nitrogen flow to prevent oxidation of hydroquinone [32].

2.3.2. Preparation of modified carbon paste electrodes

Different amounts of the BHOB ionophore along with appropriate amount of graphite powder, paraffin oil, MWCNTs and with (without) nanosilica were thoroughly mixed. This matrix was thoroughly mixed in the mortar and the resulted paste was used to fill the electrode body [21-23, 25, [33-35]. The sensors were used directly for potentiometric measurements without preconditioning. A fresh surface of the paste was obtained by squeezing more out. The surplus paste was wiped out and the freshly exposed surface was polished on a paper until the surface showed shiny appearance.

2.3.3. Electrodes system and emf measurements

All the emf observations were made relative to Ag/AgCl electrode with a pH/mV meter. The emf measurements were carried out with the following cell assembly:

Ag/AgCl | sample solution | modified CPEs

The performance of the electrodes was investigated by measuring the emfs of mercury chloride solution which is prepared with a concentration range of $1x10^{-1}$–$1.8x10^{-8}$ mol L^{-1} by serial dilution. Each solution was stirred and the potential was recorded when it became stable, and then plotted as a logarithmic function of Hg(II) activity.

2.3.4. The response time

The method of determining response time in the present work is being outlined as follows. The electrode was dipped in a 0.01 mol L^{-1} solution of the ion concerned and immediately the concentration is changed by serial dilution (10 fold lower in concentration), and the solutions were continuously stirred. The potential of the solution was read at zero second, just after dipping of the electrode in the second solution and subsequently recorded after different time intervals. The potentials were then plotted versus the time. The time during which the potentials attained constant value represented the response time of the electrode.

2.3.5. Preparation of sample solution

5 mL aliquots of 10^{-1}- 10^{-8} mol L^{-1} Hg(II) solution were transferred into 25 ml beaker at 25 ºC. The pH of each solution was adjusted to 4 using acetate buffer, followed by immersing the electrode (V) and electrode (VII) in conjugation with Ag/AgCl reference electrode in the solution.

The potential change was plotted against the logarithm of Hg(II) concentration from which the calibration curves were constructed.

2.3.6. Determination of Hg(II) in real spiked water samples

About 5 ml water samples were transferred to a 25 ml beaker, spiked with certain concentration of Hg(II) ion and adjusted to pH 4 with acetate buffer, then content was estimated via potentiometric calibration using modified CPEs as sensing electrodes. The method was repeated several times to check the accuracy and reproducibility of the proposed method.

3. Results and discussion

3.1. Electrode composition and modification

Different carbon paste compositions, as shown in Table 1, were prepared. As it can be seen, three kinds of carbon paste electrodes were prepared (unmodified and modified CPEs). The first modified CPE, with optimized composition (BHOB-CPE) (electrode. II), does not show Nernstian response as it gives slope about 19.36 mV decade^{-1}. Using MWCNT in the composition of the second carbon paste not only improves the conductivity of the sensor, but also increases the transduction of the chemical signal to electrical signal. By increasing the conductivity, the dynamic working range and response time of the sensor were improved. If the transduction property of the sensor increases, the potential response of the sensor improved to Nernstian values. This is clearly seen from Table 1 where MWCNT-CPE (electrode V) satisfy this fact. Using nanosilica in the composition of the third carbon paste can also improve the response of the electrode. Nanosilica is a filler compound which has high specific surface area. It has a hydrophobic property that helps extraction of the ions into the surface of the CPE. Also, it enhances the mechanical properties of the electrode [28]. It is clearly seen from Table 1, MWCNT/ nanosilica-CPE (electrode VII) has the highest slope value. Using the optimized paste composition described in Table 1, the potentiometric response of the sensors was studied for Hg(II) within the concentration range of 1×10^{-1} to 1.0×10^{-7} and 1.0×10^{-1} – 1.8×10^{-8} mol L^{-1} at 25 °C for MWCNTs-CPE (electrode V) and MWCNTs/nanosilica-CPE (electrode VII), respectively, and the data obtained were represented graphically in Fig. 1. The results showed that the sensors have Nernstian response of 28.75±0.46 and 29.92±0.15 mV decade^{-1} and linear concentration range from 1×10^{-1} to 1×10^{-7} and from 1.0×10^{-1} to 1.8×10^{-8} mol L^{-1} for electrode (V) and electrode (VII), respectively. Experiments were repeated several times to check the reproducibility of the results. EMFs were plotted against log concentration of mercury ions and calibration curves were drawn for five sets of experiments and a standard deviation of ±0.12-0.23 mV was observed. The detection limit of the sensors was determined according to IUPAC recommendations [36] from the intersection of two extrapolated linear portions of the curve [21-25, 33-35, 37-40] and was found to be 1.0×10^{-7} and 1.8×10^{-8} mol L^{-1} for electrode (V) and electrode (VII), respectively (Table 2).

3.2. Response time

The response time of an ion-selective electrode is an important factor when applying potentiometric technique. The required time for the electrodes to reach a cell potential of 90% of the final equilibrium values is defined as the average response time for any electrode. The potential values were recorded after successive immersions of the electrodes in a series of solutions, each having a 10-fold concentration difference [21-25, 33-35, 37-41]. The practical response time was recorded by changing the Hg(II) ion concentration in solution, over a concentration range from 1.0×10^{-2} to 1.0×10^{-7} mol L^{-1}. The actual potential versus time traces is shown in Fig. 2. These potential–time plots for these concentrations clearly indicate that the potentiometric response time is found to be 7 and 4 s for Hg(II) using electrode V and electrode (VII), respectively. These fast response times can be explained by the fact that these electrodes contain carbon particles surrounded by a very thin film of paraffin oil and acting as a conductor and the absence of the internal reference solution.

3.3. Lifetime

The lifetime of the electrodes was determined by recording its potential at an optimum pH value and plotting its calibration curve each day. The lifetime of the proposed modified Hg(II) sensors was evaluated by periodically recalibrating the potentiometric response to Hg(II) ion in a series of standard mercury chloride solutions. After conditioning step, the sensors repeatedly calibrated five times during a period of 110 and 145 days for electrode V and electrode VII, respectively, and their responses are depicted in Fig. 3. The sensors were gently washed with distilled water, dried and stored at room temperature when not in use. As it can be seen from Fig. 3, before 110 and 145 days for electrode V and electrode VII, respectively, no significant change in the performance of the sensor was observed (there is a slight gradual decrease in the slopes from 28.75 to 27.01 and 29.92 to 28.15 mV decade^{-1} and an increase in the detection limit from 1×10^{-7} to 1×10^{-6} and 1.8×10^{-8} to 1×10^{-7} mol L^{-1} for electrode V and electrode VII, respectively.

3.4. Effect of pH

The influence of pH on the potentiometric response of these new proposed electrodes in the pH range from 1.0 to 10.0 at 1.0×10^{-3} and 1.0×10^{-5} mol L^{-1} of Hg(II) ion solutions was investigated and the results obtained are shown in Fig. 4. The operational range was studied by changing the pH of the test solution with dilute HCl and/or NaOH. As it can be seen, the potentials remain constant in the pH range of 3-7.5 and 2.5-8.5 as the working pH range for electrode V and electrode VII, respectively. It seems, at higher pH values, a drift in response was achieved which can be attributed to simultaneous formation of hyrdoxo complexes or hydroxide precipitate or because of probable change in stoichiometry of metal chelate species. At low pH values, the response performance of the electrodes significantly decreased by protonation of proposed carrier and various functional group of graphite powder or activated MWCNT. Therefore, the previously mentioned pH ranges were selected as working range. Acetate buffer of the suitable pH (4) was prepared and used for the subsequent study.

3.5. Effect of temperature on the test solution

Calibration graphs (electrode potential (E_{elec}) versus p[$Hg_{(II)}$] were constructed at different test solution temperatures (10- 70 ºC). For the determination of the isothermal coefficient (dEº/dt) of the electrodes, the standard electrode potentials (Eº) against the normal hydrogen electrode at different temperatures were obtained from calibration graphs as the intercepts at p[Hg(II)] = 0 (after subtracting the values of the standard electrode potential of the Ag/AgCl electrode at these temperatures) and were plotted versus (t−25), where t was the temperature of the test solution in ºC. A straight line plot is obtained according to Antropov's equation [21, 22, 24, 25, 33-35, 37-40, 42]:

$$\mathbf{E^{o} = E^{o}_{(25)} + (dE^{o}/dt)(t\text{-}25)}$$

Where $E^{o}_{(25)}$ is the standard electrode potential at 25 ºC, T is the temperature in unit cellulous, the slope of the straight-line obtained represents the isothermal coefficient of the electrode and found to be 0.000456 and 0.000365 V/ºC for electrode (V) and electrode (VII), respectively (Fig 5). The values of the obtained isothermal coefficients of the electrodes indicate their high thermal stability within the investigated temperature range and they can be used up to 50 ºC without noticeable deviation from the Nernstian behaviour.

3.6. Potentiometric selectivity

The selectivity coefficients of the electrodes towards different cationic species (M^{n+}) were evaluated by using both the matched potential (MPM) [22, 33, 37, 38] and the mixed solution (MSM) [21, 37] methods, which are recommended by IUPAC [22, 33, 36-38]. According to the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion (A) and the interfering ion (B) that gives the same potential change in a reference solution. The selectivity coefficient, K^{MPM}, is determined as

$$K^{\mathrm{MPM}}_{\mathrm{Hg,\,B}} = \Delta A / a_{\mathrm{B}} \;, \qquad \text{Eq. (1)}$$

where, ΔA = $a'_{A} - a_{A}$, a_{A} is the initial primary ion activity and a'_{A} the activity of A in the presence of the interfering ion, a_B. The concentration of Hg(II) used as primary ion in this study was 1.0×10^{-3} mol L^{-1}. In the mixed solution method, the selectivity coefficient, K^{MSM}, was evaluated graphically from potential measurements on solutions containing a fixed concentration of Hg(II) ion (1.0×10^{-3} mol L^{-1}) and varying amounts of interfering ions (M^{n+}) according to the equation

$$K^{\mathrm{MSM}}_{\mathrm{Hg,\,M}} \; a^{2/n}_{\mathrm{M}} = a_{\mathrm{Hg}}\{\exp\,(\mathrm{E}_2 - \mathrm{E}_1)\,2\mathrm{F}/\mathrm{RT}\} - a_{\mathrm{Hg}} \qquad \text{Eq. (2)}$$

Where E_1 and E_2 are the electrode potentials for the solution of Hg(II) ions alone and for the solution containing interfering ions and mercury ions, respectively, and n is the charge of the interfering ion. According to Eq. (2), the K^{MSM} values for diverse cations can be evaluated from the slope of the linear graph of $a_{\mathrm{Hg}}\{\exp((2((\mathrm{E}_2\text{-}\mathrm{E}_1)\mathrm{F})/\mathrm{RT})\}-a_{\mathrm{Hg}}$ versus $a_{\mathrm{M}}^{2/n}$ [34]. The resulting values of the selectivity coefficients are summarized and compared in Table 3.

The selectivity coefficients obtained by both methods are usually rather similar for the mono-, bi- and trivalent interfering ions. Nevertheless, in case of univalent interferences, the values obtained by the MSM are significantly larger than those by the MPM. Such larger coefficients arise from the term $a^{2/n}$ in Eq.(2); the smaller the charge of the interfering ion, n, the larger the selectivity coefficient. The selectivity coefficients are in the order of 10^{-2} to 10^{-5} for most of the interfering ions studied, which indicates that the disturbance produced by these metal ions in the operation of the Hg(II) ion-selective electrode is negligible. Among the studied interfering ions, Fe(III) has the highest selectivity coefficients, in the range $(1.53–2.73)\times10^{-2}$, which may be connected with the higher charge and affinity of MWCNT and nanosilica to this ion. The above results also clearly demonstrate that the electrode shows the best selectivity for the Hg(II) ion.

3.7. Analytical applications

The proposed sensors were found to work well under laboratory conditions. It is clear that the amount of Hg(II) ions can be accurately determined using the proposed sensors. To assess the applicability of the proposed sensor to real samples, Hg(II) was measured in different samples (formation water, tap water, cooling tower and waste water samples) by direct potentiometry using the calibration graph and inductively coupled plasma atomic emission spectrometry (ICP-AES). The results obtained by potentiometric calibration are presented in Table (4), and were compared with those obtained by inductively coupled plasma atomic emission spectrometry (ICP-AES) which showed good agreement between them.

This validates the applicability of the MWCNTs-CPEs (electrode V) and MWCNTs/nanosilica-CPE (electrode VII) for the selective determination of Hg(II) ions in the analyzed environmental samples.

3.8. Method validation

The method was validated with respect to linearity, lower limit of detection, accuracy, precision, repeatability, robustness and ruggedness accordance to ICH guidelines [22, 35, 37, 42].

3.8.1. Linearity and lower limit of detection

Under optimal experimental conditions, the linearity of the proposed method was investigated. It has been shown that the fabricated sensors exhibit Nernstian response over the concentration ranges of 1.0×10^{-1} – 1.0×10^{-7} and 1.0×10^{-1}-1.8×10^{-8} mol L^{-1} with lower limits of detection of 1.0×10^{-7} and 1.8×10^{-8} mol L^{-1} for electrode (V) and electrode (VII), respectively (Table

2). It is obvious that the use of MWCNTs/nanosilica-CPE improve the sensitivity for detection of very small concentration of Hg(II) ion.

3.8.2. Accuracy

The accuracy of the proposed MWCNTs-CPE (electrode V) and MWCNTs/nanosilica-CPE (electrode VII) sensors was investigated by the analysis of Hg(II) ion in its spiked real water samples using standard addition method. The results obtained in Table 2 showed mean percentage recoveries of 99.19±0.37 and 99.95±0.09 for electrode (V) and electrode (VII), respectively, revealing good accuracy for the determination of cerium in its different samples.

3.8.3. Precision

The precision of the proposed potentiometric method was determined for two different concentrations of pure Hg(II) solution, different water samples. Table (5) gives a statistical summary of each of the titration series using electrode (V) and electrode (VII). RSD(%) and SD values were obtained within the same day to evaluate repeatability (intra-day precision) and over six days to evaluate intermediate precision (inter-day precision). The low values of the relative standard deviation (RSD%) and standard deviation (SD) also indicate the high precision and the good accuracy of the proposed method.

3.8.4. Robustness and Ruggedness

The robustness of this proposed method was done by investigating to what extent the capacity of the method remains unaffected by a small but a deliberate variation in method parameters and hence provides an indication of its reliability during normal usage [37, 38, 42]. The ruggedness of the proposed method was done by investigating the reproducibility of the results obtained by the analysis of the same samples under different conditions such as different instruments, laboratories and analysts. The results obtained using another model of pH-meter (HANNA 211, Romania) was compared with those obtained using Jenway 3505 pH-meter. The results obtained are close and also reveal validity of the method (Table 2).

3.9. Comparative study

For comparative purposes, Table 6 lists the linear range, detection limit, slope, pH range and response time of recently published Hg(II)-selective electrodes [43-49] against the proposed electrode. From the results in these tables, it can be concluded that, in many cases, the performances of the proposed electrodes show superior behavior if compared with the previously reported electrodes.

4. Conclusion

The results of this study show that the potentiometric method using MWCNTs-CPE and MWCNTs/nanosilica-CPE provides an attractive alternative for the determination of Hg(II) ion. The electrodes exhibited linear response over a wide concentration range with a Nernstian slope, fast response time, selective to mercury ion, and is easy to prepare. Another unique feature of the present sensors for mercury is their good long term stability (more than 110 and 145 days). The proposed electrodes can be successfully applied for determination of trace amount of Hg(II) ions in polluted water samples.

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Tables Caption

Table 1: Optimization of the carbon paste ingredients.

Table 2: Response characteristics of electrode (V) and electrode (VII) potentiometric sensors.

Table 3: Selectivity coefficients of various ions using electrode (V) and electrode (VII).

Table 4: Determination of Hg(II) ions in spiked water samples using electrode (V) and electrode (VII).

Table 5: Evaluation of intra- and inter-days precision and accuracy of CPEs (electrodes V and VII) in water samples.

Table 6: Comparing some of the Hg(II)-MWCNTs/Nanosilica-CPE (electrode VII) and MWCNTs-CPE (electrode V) (characteristics with some of the previously reported Hg(II)-ISEs.

Figure Caption

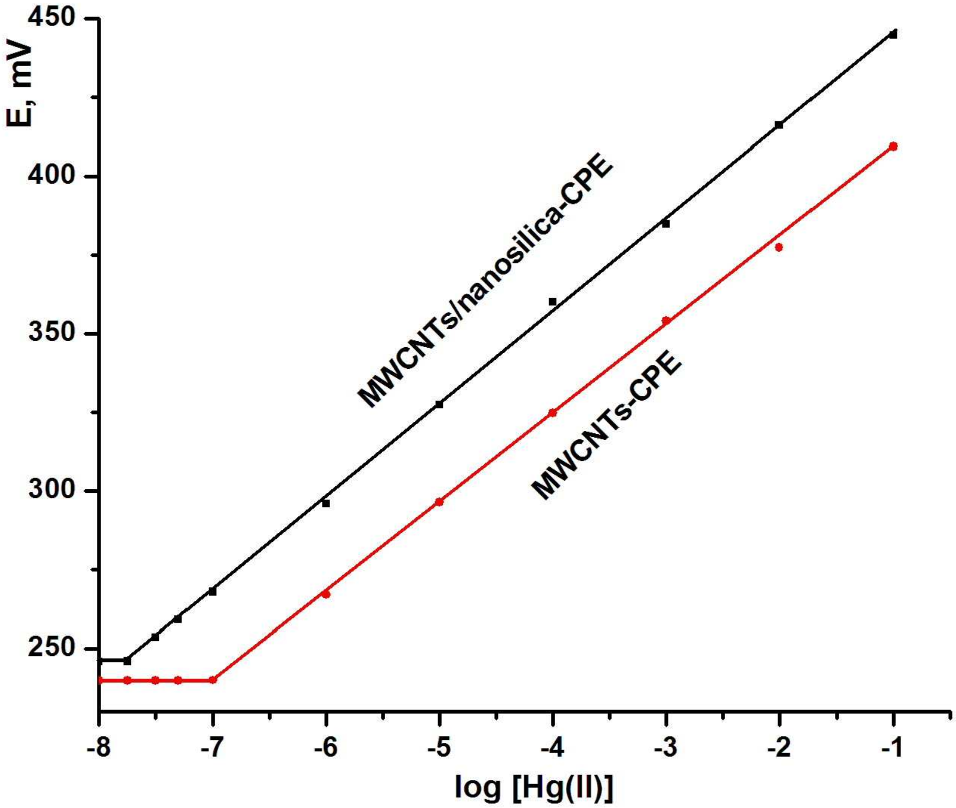
Fig. 1: Calibration curve for Hg(II)-chemically modified carbon paste based on MWCNTs-CPE (electrode V) and MWCNTs/nanosilica-CPE (electrode VII).

Fig. 2: Dynamic response of (a) electrode (V) and (b) electrode (VII) obtained by successive increase of Hg(II) ion concentration.

Fig. 3: Life time of Hg(II)- MWCNTs-CPE (electrode V) and MWCNTs/nanosilica-CPE (electrode VII).

Fig. 4: Effect of pH of test solutions on the response of (a) electrode (V) and (b) electrode (VII).

Fig. 5: Effect of temperature on the performance of (a) electrode (V) and (b) electrode (VII).



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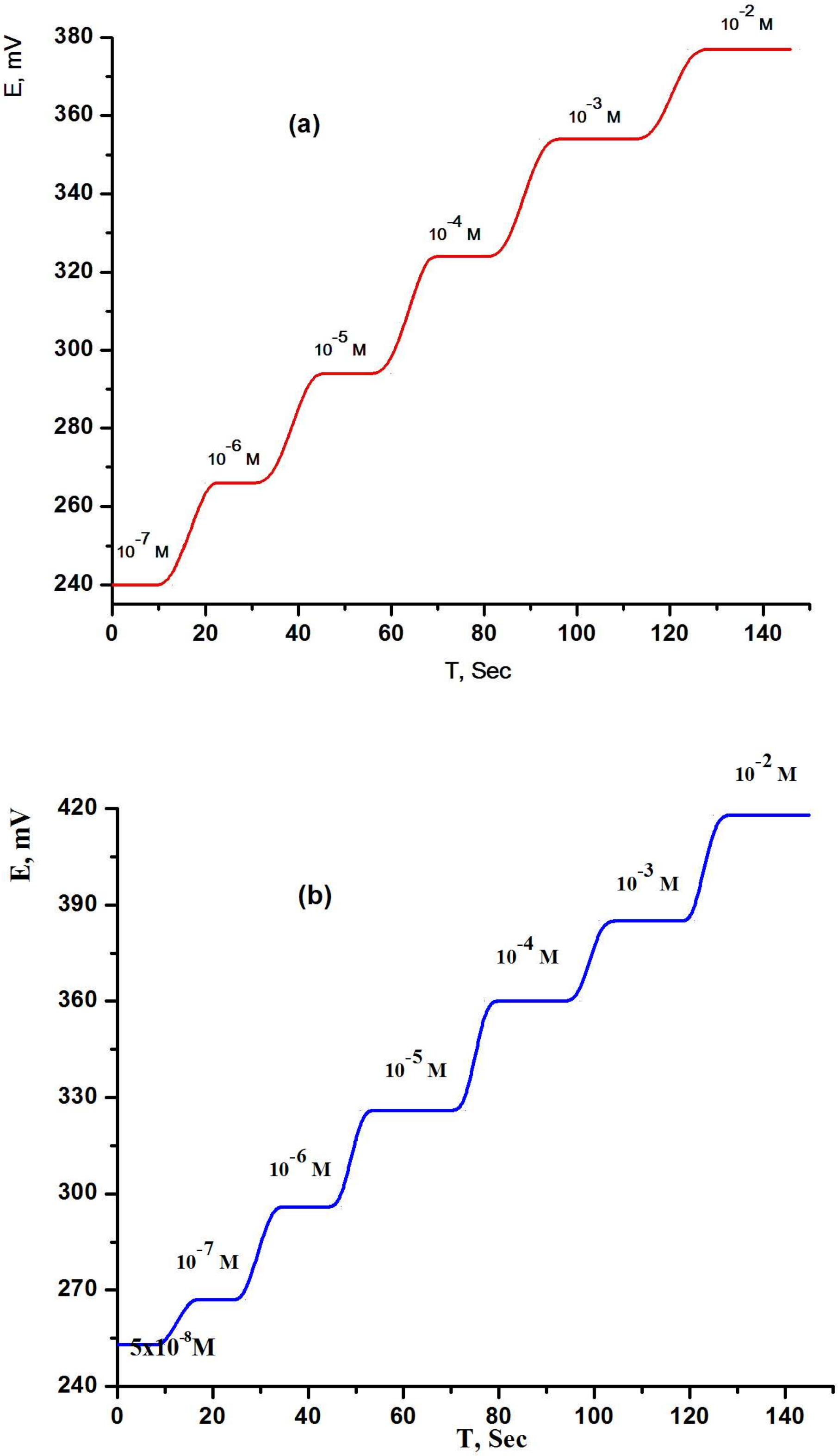

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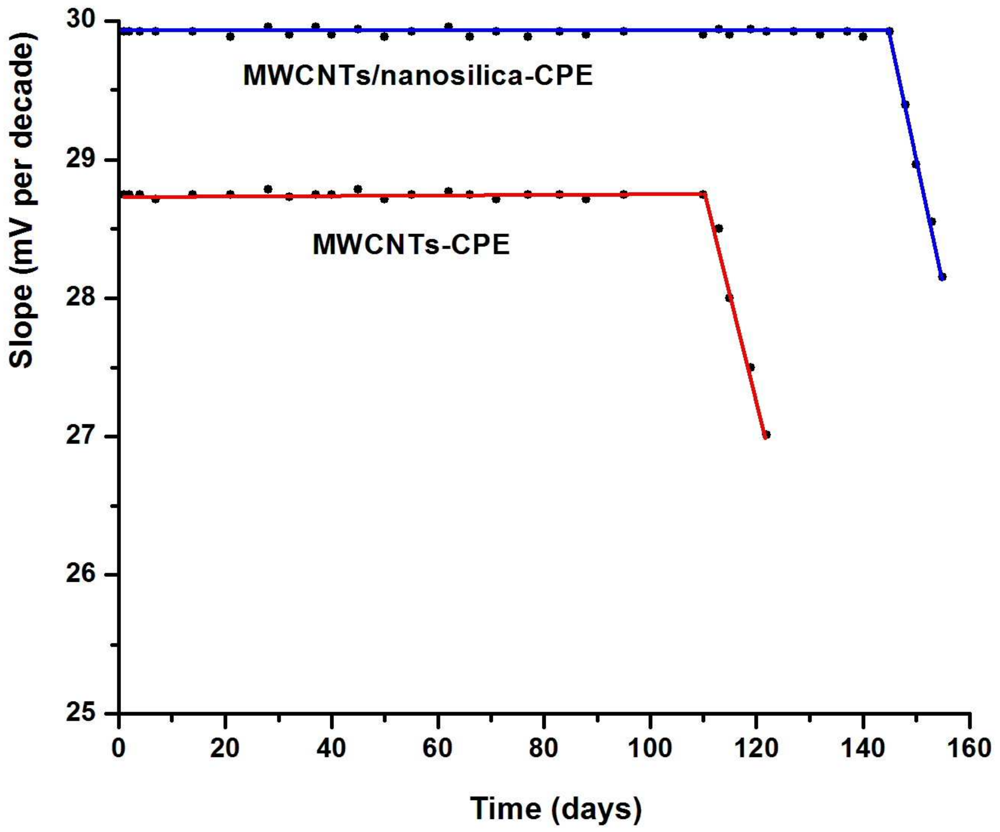

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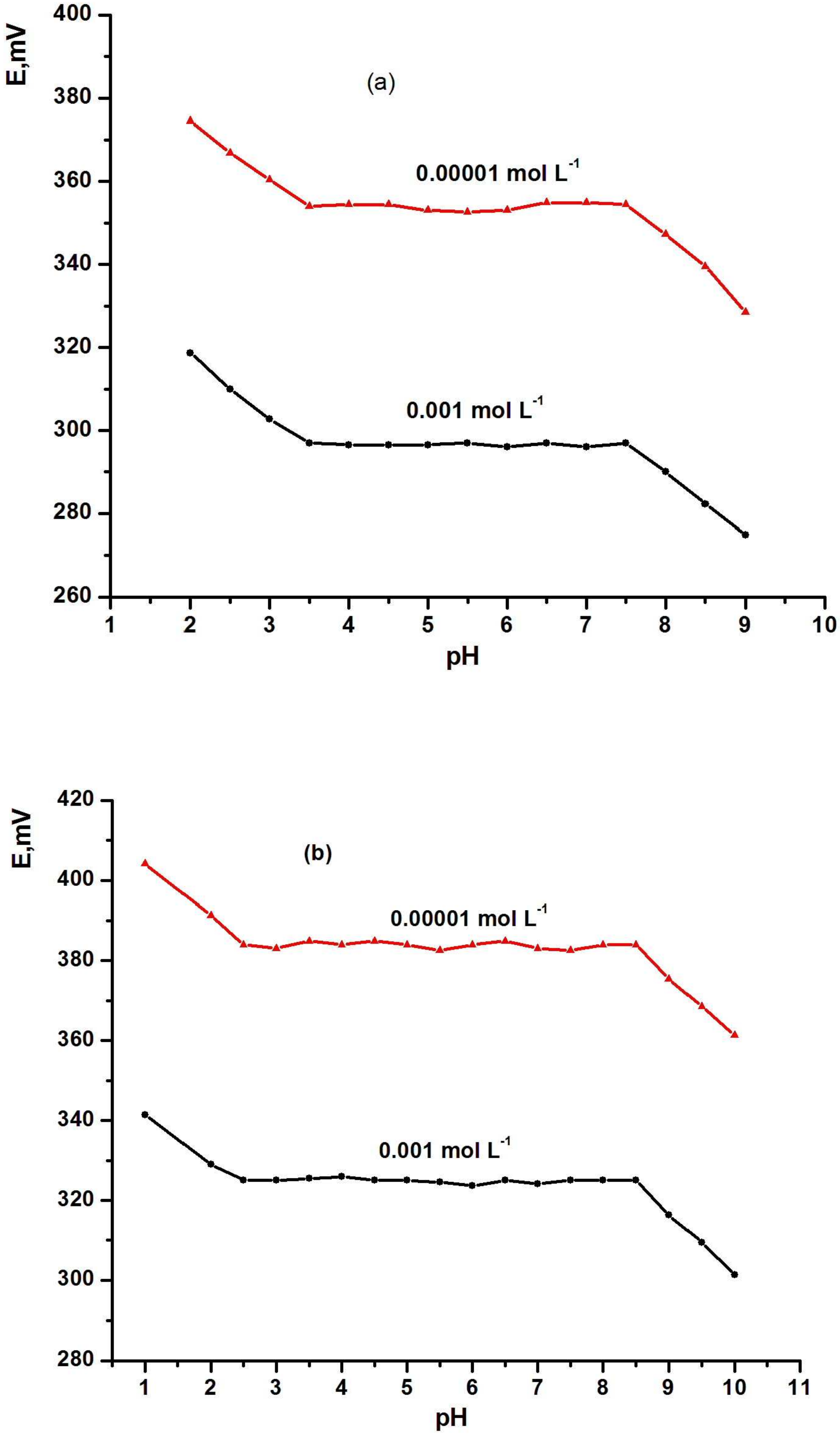

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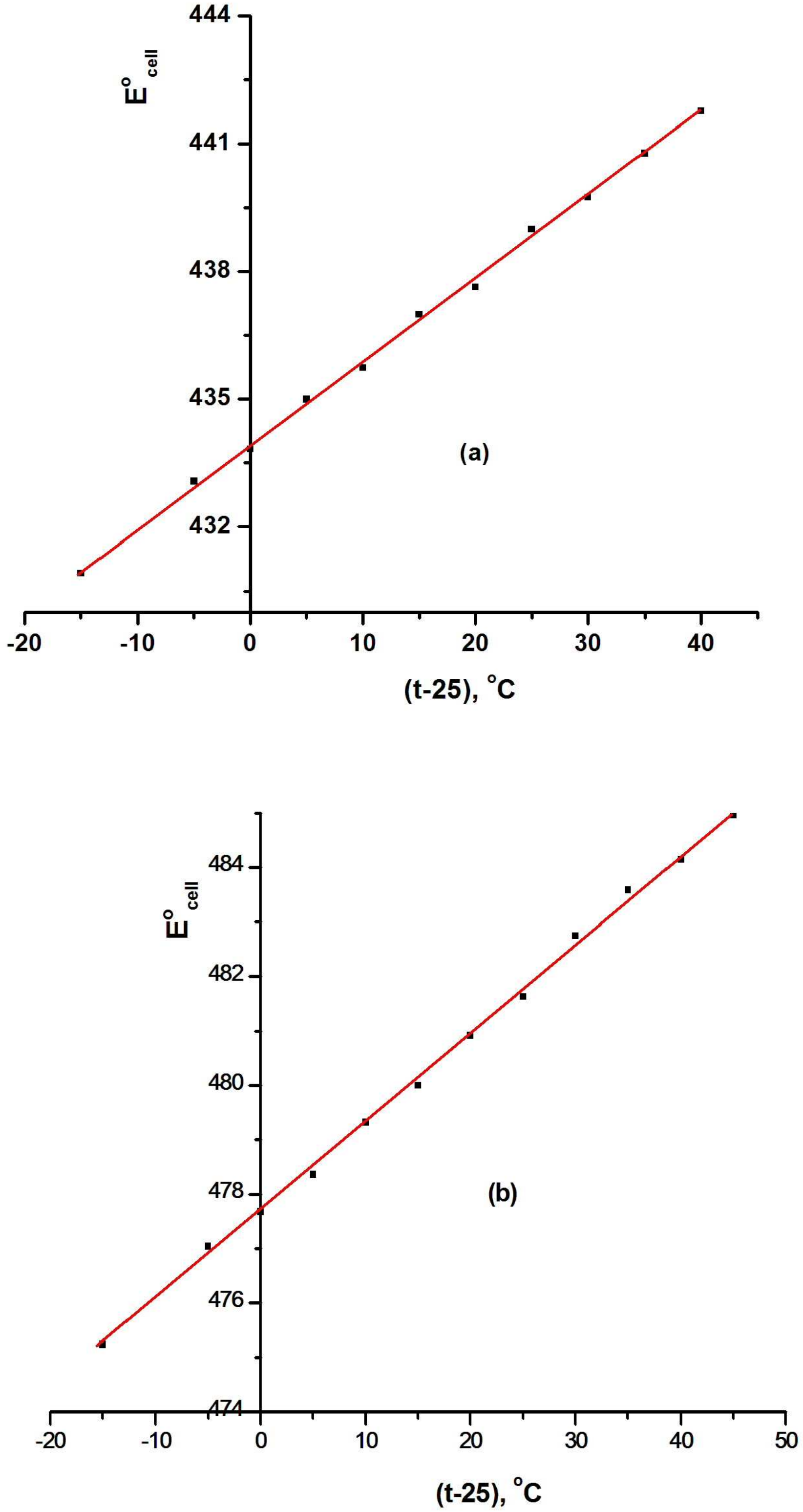

Fig. 5: Effect of temperature on the performance of (a) electrode (V) and (b) electrode (VII).

Table 1: Optimization of the carbon paste ingredients

No.	Ionophore (%)	Paraffin (%)	Graphite powder (%)	MWCNTs (%)	Nanosilica (%)	Slope (mV decade^{-1})	Linear range (mol L^{-1})	R^2
I	0	30	70	0	0	14.64	1×10^{-5}-1×10^{-2}	0.963
II	6	28	66	0	0	19.36	4.5×10^{-6}-1×10^{-2}	0.978
III	10	25	61	4	0	23.35	1×10^{-6}-1×10^{-1}	0.981
IV	13	22	60	5	0	26.97	5×10^{-6}-1×10^{-1}	0.991
V	16	21	58	5	0	28.75	1×10^{-7}-1×10^{-1}	0.993
VI	16	21	56	5	2	29.02	5.5×10^{-8}-1×10^{-1}	0.997
VII	16	21	54	5	4	29.92	1.8×10^{-8}-1×10^{-1}	0.999
VIII	16	21	53	5	5	28.95	1×10^{-7}-1×10^{-1}	0.993
IX	16	21	59	0	4	25.86	9×10^{-7}-1×10^{-1}	0.989

Table 2: Response characteristics of electrode (V) and electrode (VII) potentiometric sensors.

Parameter	**MWCNT-CPE** **Electrode V**	**MWCNT /Nanosilica-CPE** **Electrode VII**
Slope (mV decade^{-1})	28.75±0.46	29.92±0.15
Correlation coefficient, r	0.993	0.999
Lower detection limit (mol L^{-1})	1×10^{-7}	1.8×10^{-8}
Response time (s)	7	4
Working pH range	3 – 7.5	2.5 – 8.5
Usable range (mol L^{-1})	1×10^{-7} - 1.0×10^{-1}	1.8×10^{-8} - 1×10^{-1}
SD of slope (mV decade^{-1})	0.379	0.062
Intercept (mV)	438.25 ± 1.03	477.64 ± 0.61
Life time (days)	110	145
Accuracy (%)	99.19	99.95
Precision (%)	0.285	0.094

Table 3: Selectivity coefficients of various ions using electrode (V) and electrode (VII).

Interfering ions	$K^{\mathrm{MSM}}_{\mathrm{Hg,\,M}}$ electrode (V)	$K^{\mathrm{MSM}}_{\mathrm{Hg,\,M}}$ electrode (VII)	$K^{\mathrm{MPM}}_{\mathrm{Hg,\,B}}$ electrode (V)	$K^{\mathrm{MPM}}_{\mathrm{Hg,\,B}}$ electrode (VII)
Cu^{2+}	8.37×10^{-3}	5.23×10^{-3}	7.85×10^{-3}	6.17×10^{-3}
Co^{2+}	6.97×10^{-4}	4.03×10^{-4}	5.14×10^{-4}	4.18×10^{-4}
Cd^{2+}	3.32×10^{-4}	2.21×10^{-4}	3.01×10^{-4}	2.48×10^{-4}
Zn^{2+}	4.42×10^{-4}	2.57×10^{-4}	3.99×10^{-4}	2.75×10^{-4}
Mg^{2+}	6.42×10^{-4}	4.86×10^{-5}	5.89×10^{-4}	5.06×10^{-5}
Mn^{2+}	7.06×10^{-5}	5.35×10^{-5}	6.87×10^{-5}	5.77×10^{-5}
Ca^{2+}	2.94×10^{-4}	2.06×10^{-4}	3.05×10^{-4}	2.11×10^{-4}
Fe^{3+}	2.73×10^{-2}	1.53×10^{-2}	2.42×10^{-2}	2.03×10^{-2}
Cr^{3+}	4.42×10^{-3}	2.98×10^{-3}	6.21×10^{-3}	3.56×10^{-3}
Al^{3+}	7.58×10^{-5}	5.96×10^{-5}	6.91×10^{-5}	5.43×10^{-5}
Na^{+}	2.26×10^{-4}	3.09×10^{-4}	4.12×10^{-5}	2.96×10^{-4}
K^{+}	3.39×10^{-5}	4.03×10^{-5}	3.95×10^{-5}	4.38×10^{-5}
Sr^{2+}	4.60×10^{-3}	3.73×10^{-3}	2.94×10^{-3}	3.65×10^{-3}
Ba^{2+}	4.66×10^{-3}	2.91×10^{-3}	3.18×10^{-3}	4.17×10^{-3}
Ni^{2+}	4.32×10^{-3}	4.66×10^{-4}	4.46×10^{-4}	5.26×10^{-4}
Bi^{3+}	5.53×10^{-5}	3.22×10^{-5}	5.06×10^{-4}	4.66×10^{-4}
Sb^{3+}	6.16×10^{-5}	4.22×10^{-5}	5.12×10^{-5}	4.61×10^{-5}
Ag^{+}	3.98×10^{-5}	3.50×10^{-5}	1.21×10^{-6}	3.82×10^{-5}

Table 4: Determination of Hg(II) ions in spiked water samples using electrode (V) and electrode (VII).

Samples	[Hg(II)] (µg L^{-1})									
	MWCNTs -CPE (Electrode V)				MWCNT /Nanosilica-CPE (Electrode VII)			ICP-AES		
	Added	Found	R.S.D (%)	Recovery (%)	Found	R.S.D (%)	Recovery (%)	Found	R.S.D (%)	Recovery (%)
1	1.50	1.481	0.452	98.73	1.490	0.125	99.33	1.462	0.735	97.47
	3.50	3.483	0.536	99.51	3.492	0.201	99.77	3.47	0.366	99.14
2	2.00	1.972	0.373	98.60	1.983	0.097	99.15	1.919	0.607	95.95
	2.50	2.486	0.635	99.44	2.497	0.075	99.88	2.457	0.947	98.28
3	2.50	2.469	0.164	98.76	2.495	0.045	99.80	2.458	0.274	98.32
	3.00	2.972	0.201	99.07	2.996	0.021	99.87	2.951	0.253	98.37
4	1.50	1.498	0.049	99.87	1.510	0.089	100.7	1.490	0.107	99.33
	2.50	2.497	0.008	99.88	2.521	0.241	100.8	2.489	0.115	99.56
5	4.00	3.977	0.483	99.43	3.997	0.073	99.93	3.969	1.014	99.23
	6.50	6.483	0.282	99.74	6.499	0.049	99.98	6.479	0.673	99.68
6	4.00	3.979	0.078	99.48	3.996	0.014	99.90	3.969	0.106	99.23
	6.50	6.489	0.062	99.83	6.497	0.009	99.95	6.486	0.121	99.78

Sample 1:, sample 2, sample 3, sample 4, sample 5 and sample 6.

Table 5. Evaluation of intra- and inter-days precision and accuracy of CPEs (electrodes V and VII) in water samples

Electrode type	Sample No.	[Hg(II)] Taken, (mg mL^{-1})	Intra day				Inter day			
			[Hg(II)] Found, (mg mL^{-1})	Recovery (%)	SD	RSD%	[Hg(II)] Found, (mg mL^{-1})	Recovery (%)	SD	RSD%
MWCNT-CPE electrode (V)	Pure [Hg(II)]	1.00	0.997	99.70	0.004	0.011	0.998	99.80	0.007	0.213
		1.50	1.497	99.80	0.002	0.018	1.494	99.60	0.009	0.416
	Sample 1	1.00	0.989	98.90	0.105	1.017	0.984	98.40	0.121	1.031
		1.50	1.489	99.27	0.084	1.025	1.485	99.00	0.150	1.003
	Sample 3	1.00	0.992	99.20	0.069	0.463	0.991	99.10	0.152	1.046
		1.50	1.491	99.40	0.047	0.637	1.489	99.27	0.174	1.017
	Sample 6	1.00	0.988	98.80	0.108	1.005	0.983	98.30	0.094	1.002
		1.50	1.484	98.93	0.101	1.011	1.491	99.40	0.074	1.016
MWCNT /Nanosilica-CPE electrode (VII)	Pure [Hg(II)]	0.75	0.751	100.1	0.002	0.358	0.749	99.87	0.004	0.563
		2.00	2.010	100.5	0.004	0.531	1.997	99.85	0.007	0.472
	Sample 1	0.75	0.748	99.73	0.086	0.853	0.746	99.47	0.004	0.372
		2.00	1.983	99.15	0.046	0.789	1.969	98.45	0.011	0.984
	Sample 3	0.75	0.749	99.87	0.005	0.465	0.747	99.60	0.013	1.092
		2.00	1.992	99.60	0.089	0.657	1.984	99.20	0.003	0.992
	Sample 6	0.75	0.748	99.73	0.077	0.251	0.749	99.87	0.002	0.999
		2.00	1.996	99.80	0.036	0.302	1.989	99.45	0.013	1.006

Table 6: Comparing some of the Hg(II)- MWCNTs/Nanosilica-CPE (electrode VII) and MWCNTs-CPE (electrode V) (characteristics with some of the previously reported Hg(II)-ISEs.

References	Slope (mV decade^{-1})	Response time (s)	pH	Life time (months)	Linear range (mol L^{-1})	DL (mol L^{-1})
Proposed electrode (electrode VII)	29.92	4	2.5-8.5	<5	$1.8\times10^{-8} – 1.0 \times 10^{-1}$	1.8×10^{-8}
Proposed electrode (electrode V)	28.75	7	3.0-7.5	<4	$1.0 \times 10^{-7} – 1.0 \times 10^{-1}$	1.0×10^{-7}
43	29.35	< 20	1.0 - 4.0	3	1.0×10^{-6} - 1.0×10^{-1}	6.3×10^{-6}
44	29.0	< 10	1.0 – 4.0	3	$2.0 \times 10^{-7} – 3.0 \times 10^{-2}$	5.0×10^{-8}
45	32.1	<20	2.7–5.0	<2	$2.51 \times 10^{-5} – 1.0 \times 10^{-1}$	2.51×10^{-5}
46	29.3	5	2.0 - 4.3	<2	$5.0 \times 10^{-9}– 1.0 \times 10^{-4}$	2.5×10^{-9}
47	25.0	10	6.6 - 9.3	4	$1.2 \times 10^{-5} – 1.0 \times 10^{-1}$	8.9×10^{-6}
48	29.0	45	2.0 - 5.0	3	$4.0 \times 10^{-6} – 1.0 \times 10^{-3}$	1.3×10^{-6}
49	29.06	10	3.5–6.5	<3	1.0×10^{-6} - 1.0×10^{-2}	6.0×10^{-7}